Growth of Single Crystals

Naica Cave, Mexico
0.5 My, 50 °C

$CaSO_4 \cdot 2H_2O$ - gypsum

1.2 × 15 m

Growth of Single Crystals

Single crystals

- Single-crystal X-ray diffraction analysis of crystal structure

- Vital for meaningful property measurements of materials

- Measurements of anisotropic phenomena (electrical, optical, magnetic, mechanical, thermal) in anisotropic crystals (symmetry lower than cubic)

- Fabrication of devices

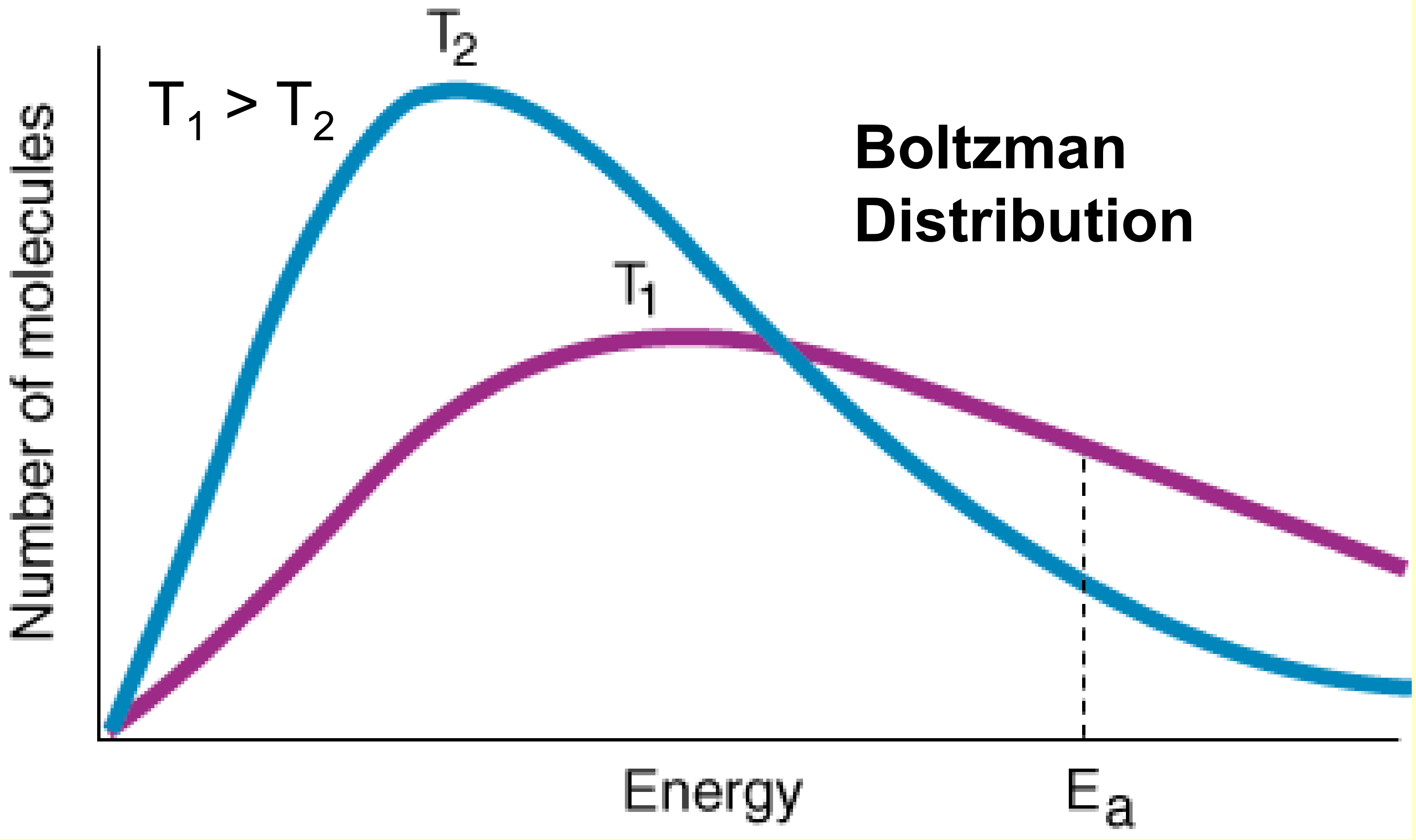
$Y_3Al_5O_{12}$ (YAG = yttrium aluminum garnet) and beta-beryllium borate (BBO) for doubling and tripling the frequency of CW or pulsed laser light

SiO_2 (quartz) crystal oscillators for RF generators and mass monitors

Lithium niobate for photorefractive applications

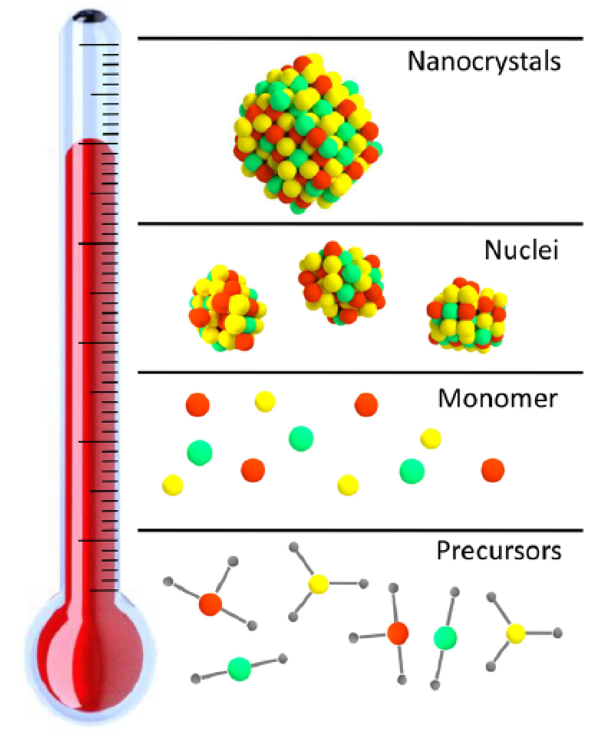
Thermodynamics and Kinetics of Crystallization

As a material cools off the average kinetic energy drops



Stages of Crystallization

- **Nucleation – formation of nuclei of critical size, depositon vs. dissolution**
- **Growth – diffusion of material toward the critical nuclei, crystal growth**

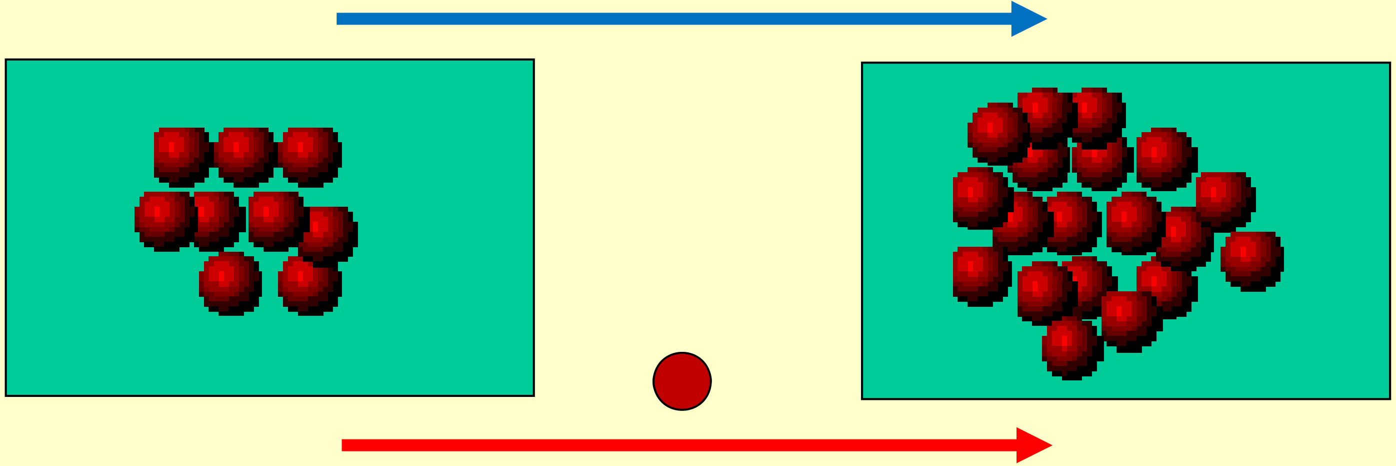


Formation of Nuclei

Molecules are always bumping into each other – random collisions - sometimes they stick – with low kinetic energy

At lower kinetic energies more molecules stick together

= form nuclei



Cooling = lower kinetic energy

Addition of monomer

Transformation from Liquid to Solid

VOLUME

The energy of a crystalline phase is less than that of a liquid

The difference = the volume free energy ΔG_v (a negative value)

As the solid grows in size, the magnitude of the total volume free energy increases

The volume free energy ΔG_v drives crystallization

SURFACE

When solids form in a liquid there is an interface created

The surface free energy, γ_{SL} = the solid/liquid interfacial energy associated with this interface (changed in different solvents)

As the solid grows, the total surface free energy increases (a positive value)

The surface free energy hinders crystallization

Volume Free Energy

$$\Delta G_V = -\frac{RT \ln S}{V_m}$$

ΔG_V – the free energy change between the ‘monomer’ in liquid/solution and in a unit volume of bulk crystal

S – supersaturation = the quotient of the actual concentration [M] and the concentration of the respective species at equilibrium with the flat crystal surface $[M_\propto]$ (solubility), indicates how far away from equilibrium the system is:

$$S = \frac{[M]}{[M_\infty]}$$

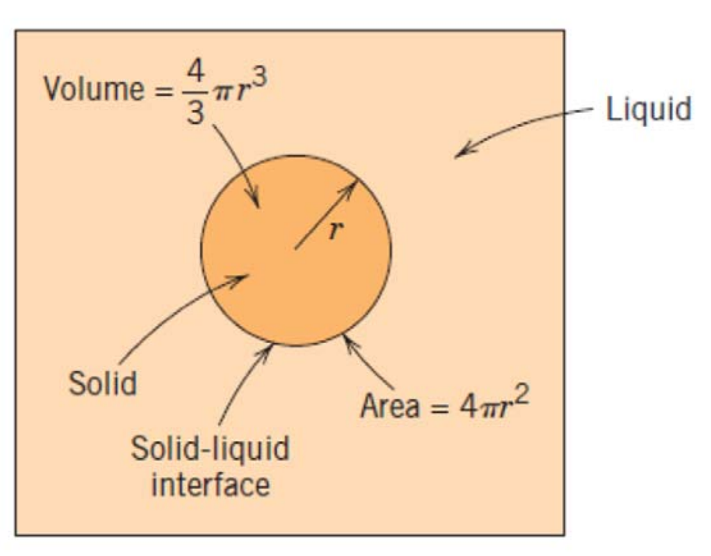
V_m – molar volume of the monomer composing the bulk crystal

Thermodynamics of Nucleation

The driving force = the supersaturated solution is not stable in energy

The total change in free energy for the nucleating system is the sum of the two factors

For spherical nuclei



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

The volume free energy goes up with the cube of the radius

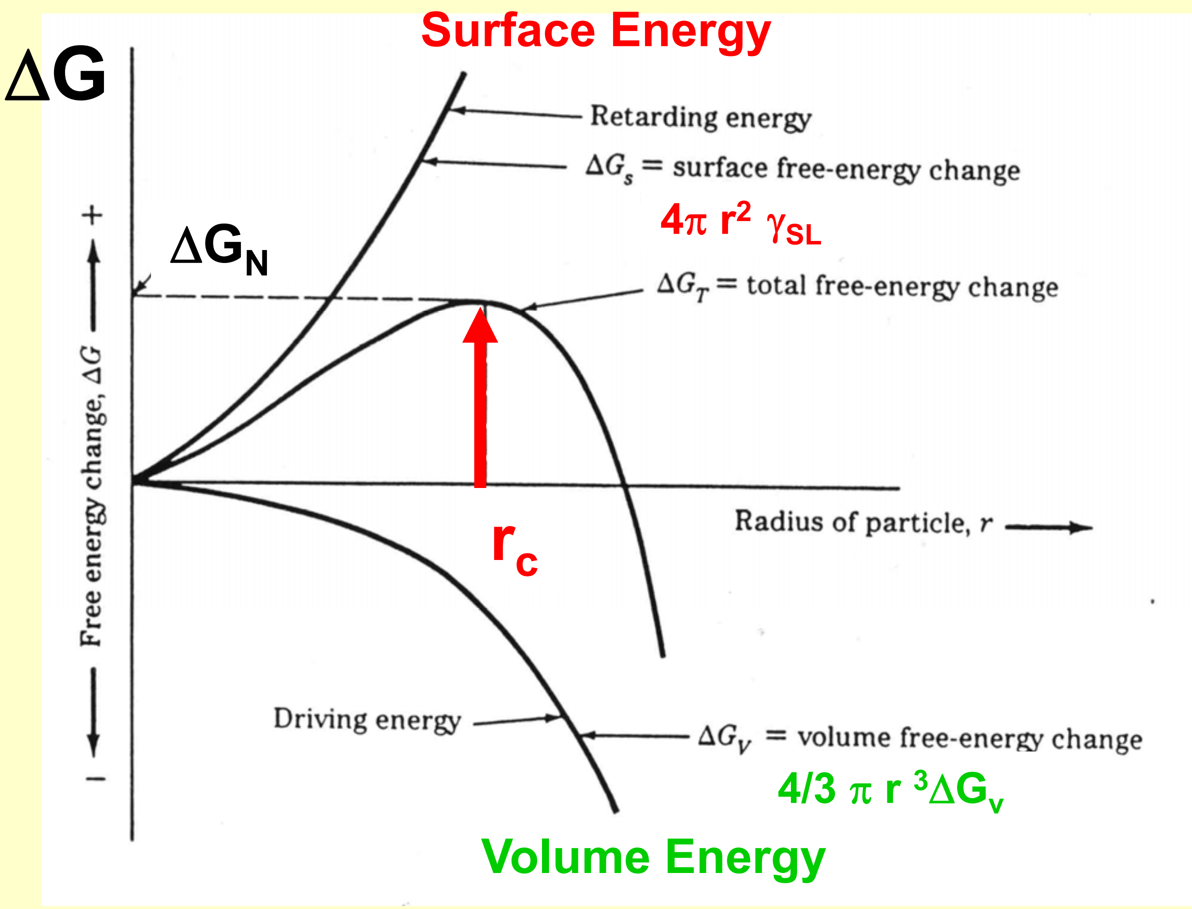
The surface free energy goes up with the square of the radius

ΔG_T has a maximum at a critical radius – critical free energy ΔG_N

If just a few molecules stick together, they will redissolve

If enough molecules stick together, the embryo will grow

Nucleation



r: radius of spherical nuclei

r_c: critical radius

ΔG_T: total free energy change

ΔG_s: surface free energy change

ΔG_v: volume free energy change

ΔG_N: critical free energy change

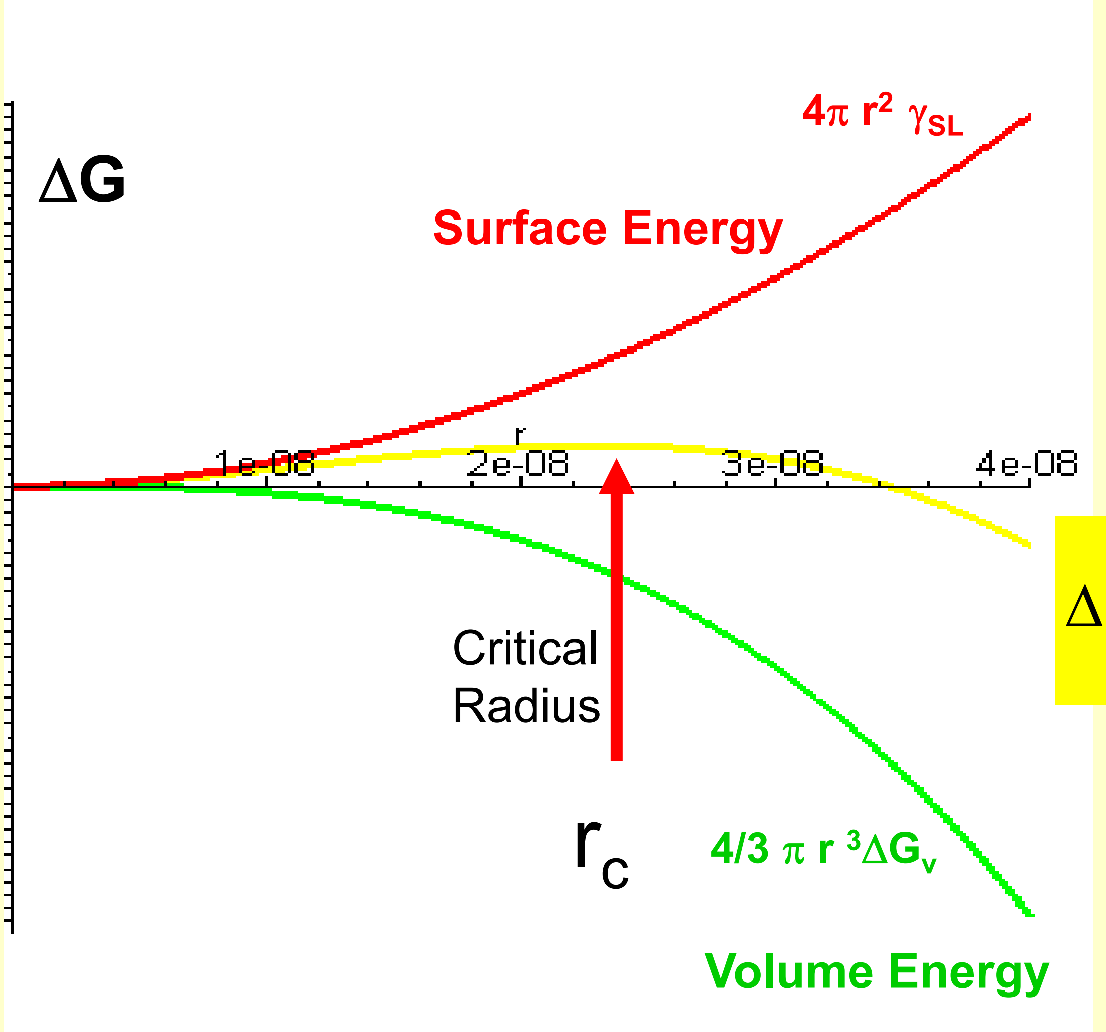
(activation energy to nucleation)

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

$r < r_c$
a nucleus dissolves

$r > r_c$
a nucleus grows by itself

Total Free Energy of Nucleation



$$\Delta G_T = -\frac{4\pi r^3 RT \ln S}{3V_m} + 4\pi r^2 \gamma$$

Nucleation - Critical Radius r_c

$$\Delta G_T = -\frac{4\pi r^3 RT \ln S}{3V_m} + 4\pi r^2 \gamma \longrightarrow \frac{d(\Delta G_T)}{dr} = 0$$

r_c critical nuclei radius is:

$$r_c = -\frac{2\gamma_{SL}}{\Delta G_V} = \frac{2\gamma_{SL} V_m}{RT \ln S}$$

S = supersaturation

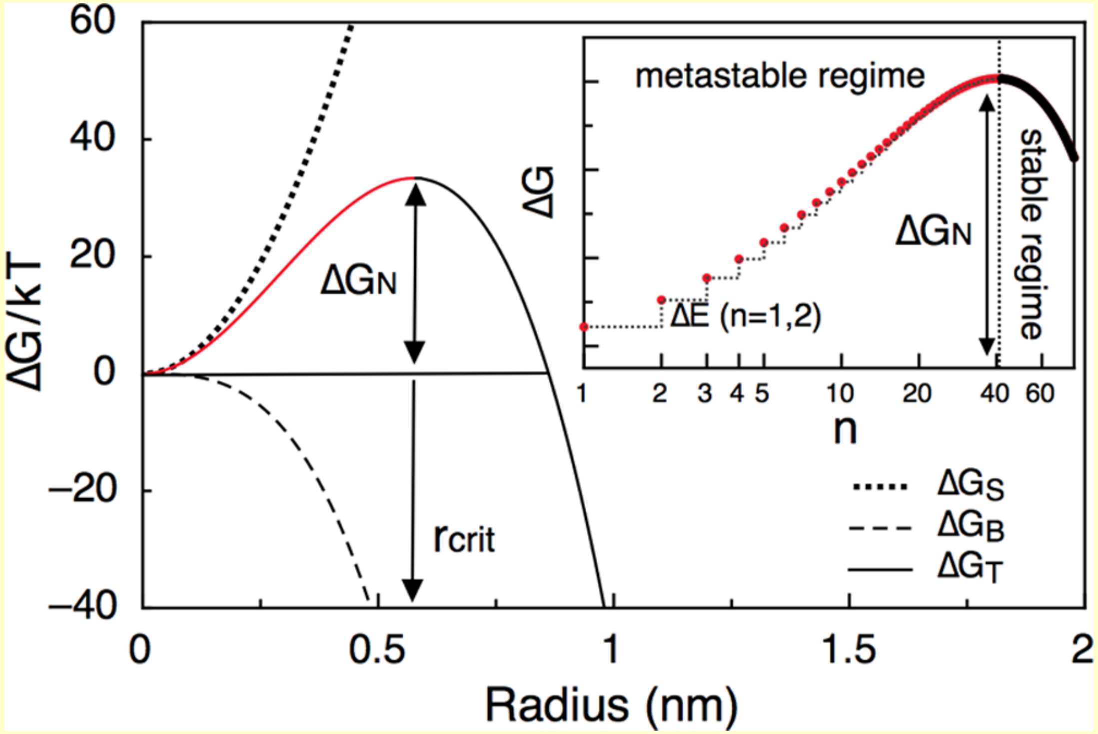
r_c = the minimum size at which a particle can survive in solution without being redissolved

At larger supersaturation S, the critical radius of nuclei is smaller

Nucleation - Critical Free Energy ΔG_N

$$\Delta G_N = \frac{16\pi\gamma_{SL}^3 V_m^2}{3(RT\ln S)^2}$$

The free energy necessary to form stable nuclei
Thermodynamic barrier to nucleation



Rate of Nucleation

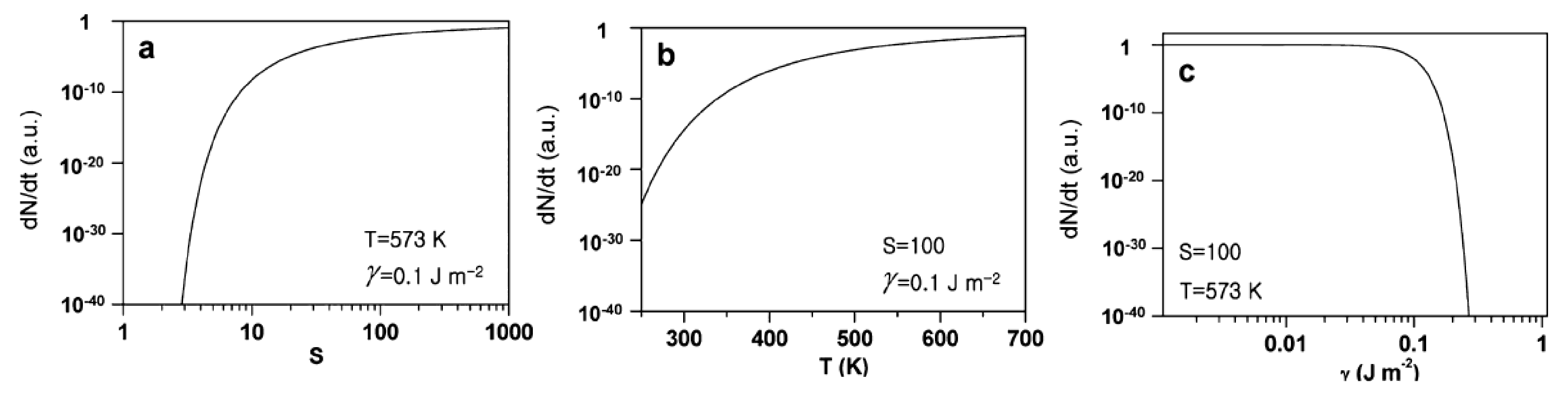
ΔG_N – the free energy barrier to nucleation
S – supersaturation
V_m – molar volume of the bulk crystal
[N] – concentration of nuclei

Arrhenius equation

The number of nuclei formed per unit time per unit volume

$$\frac{d[N]}{dt} = A\exp\left(-\frac{\Delta G_N}{kT}\right) = A\exp\left(-\frac{16\pi\gamma_{SL}^3 V_m^2}{3k^3T^3N_A^2(\ln S)^2}\right)$$

Nucleation Rate



$$\frac{d[N]}{dt} = A\exp\left(-\frac{\Delta G_N}{kT}\right) = A\exp\left(-\frac{16\pi\gamma_{SL}^3 V_m^2}{3k^3T^3N_A^2(\ln S)^2}\right)$$

V_m = 3.29 × 10^{-5} m^3 mol^{-1} (the value for CdSe)

Homogeneous Nucleation

The process of solid formation from liquid phase = homogeneous nucleation

– random collisions of monomers and formation of nuclei

It only occurs if the material is very pure

The size of the critical radius is:

$$r_c = -\frac{2\gamma_{SL}}{\Delta G_V} = \frac{2\gamma_{SL} V_m}{RT \ln S}$$

Metal crystallization from melts

ΔT = the undercooling
T_m = melting point
ΔH_f = the heat of fusion

$$r_c = \frac{2\gamma_{SL} T_m}{\Delta H_f \Delta T}$$

Metals often experience undercooling of 50 to 500 ºC

Heterogeneous Nucleation

Homogeneous nucleation usually only occurs under very clean conditions

Impurities and inhomogeneities provide a “seed” for nucleation

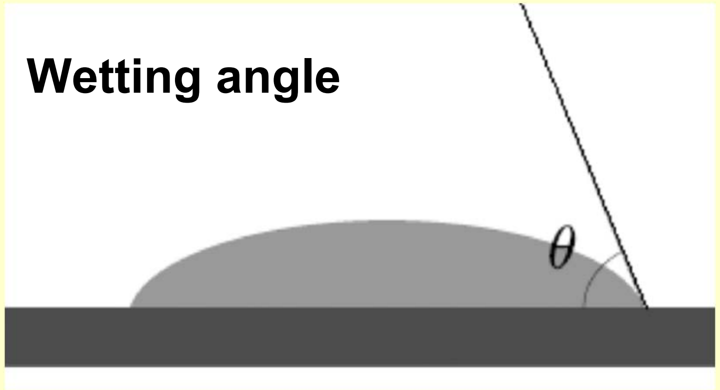
Solidification can start on a wall

It is like cloud seeding, or water condensing on the side of a glass

Adding impurities on purpose = inoculation

$$\Delta G_N^{\text{hetero}} = \phi \, \Delta G_N^{\text{homo}}$$

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



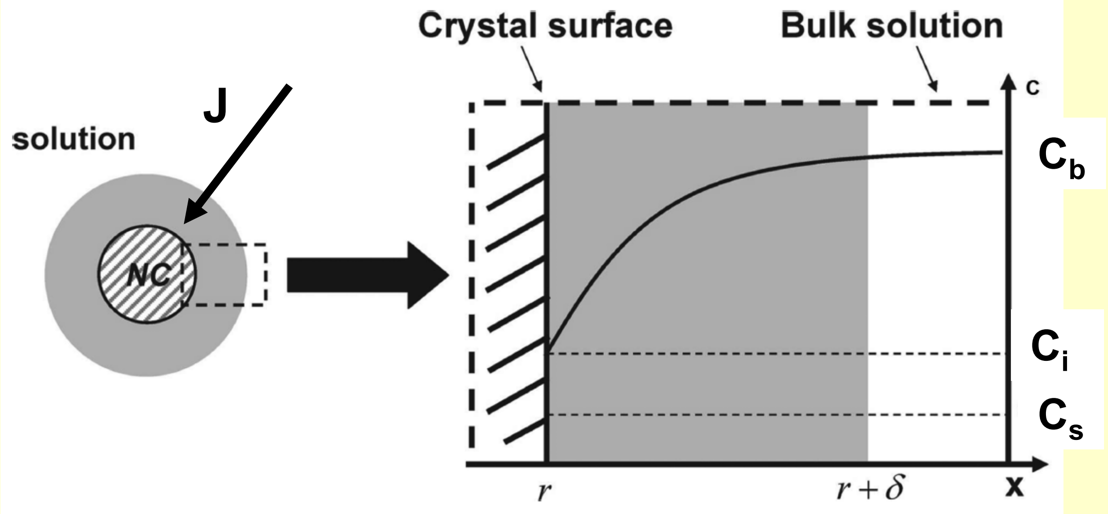
The free energy barrier to heterogeneous nucleation is always smaller than to homogeneous nucleation

Growth

Growth of particle = monomer diffusion + surface reaction

The growth rate of spherical particles (dr/dt) depends on:

- **the flux of the monomers to the particles (J)**
- **the rate of surface reaction (k)**



Fick: the flux J of monomers passing through a spherical plane with radius x

$$J = 4\pi x^2 D \frac{dC}{dx}$$

$$J = 4\pi D r \left(C_b - C_i\right)$$

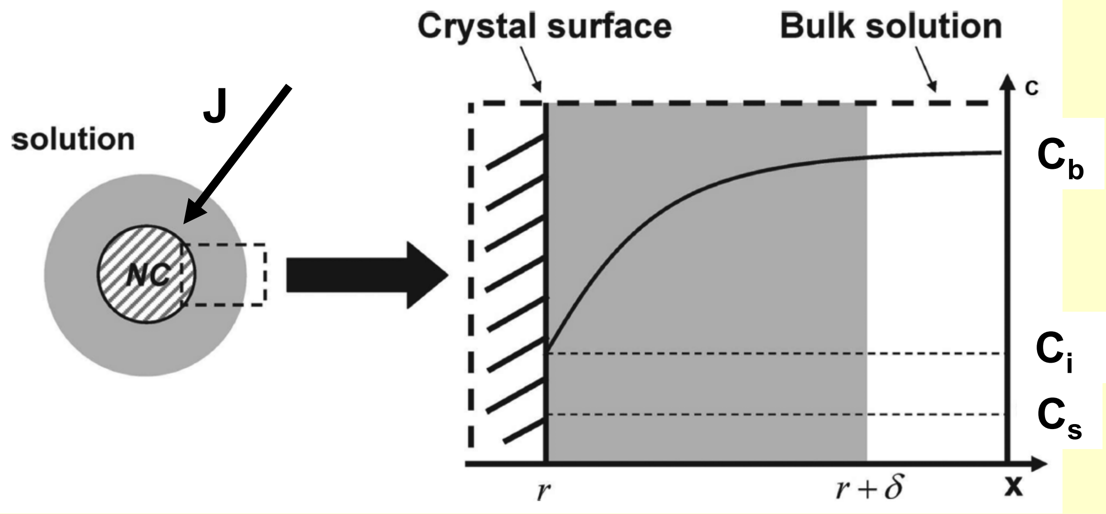
The rate of surface reaction

$$J = 4\pi r^2 k \left(C_i - C_s\right)$$

C_b = the bulk concentration of monomers within the solution
C_i = the concentration of monomers at the solid/liquid interface
C_s = the solubility of the particle

Growth

Growth (dr/dt) = monomer diffusion (J) + surface reaction (k)



If diffusion is the rate limiting factor

$$\frac{dr}{dt} = \frac{DV_m}{r}\left(C_b - C_s\right)$$

the growth rate of a particle decreases as *r* increases

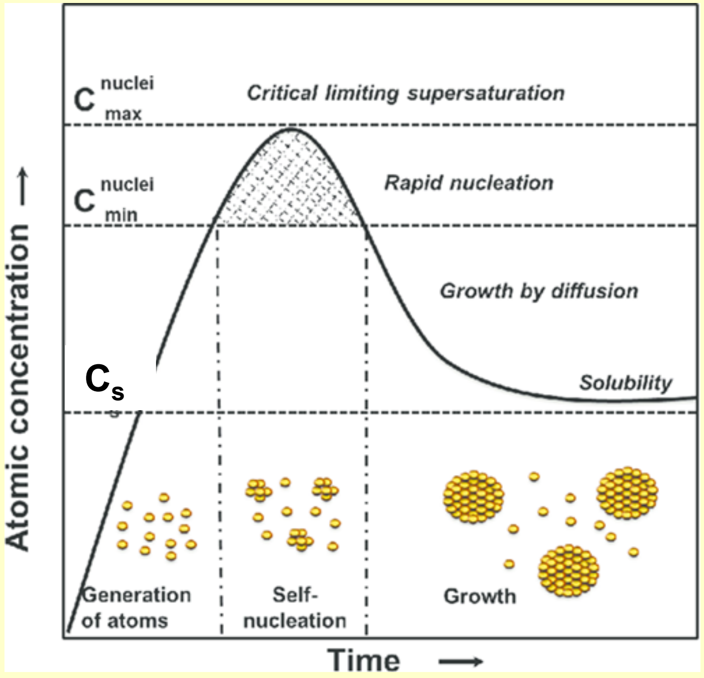
The growth rate

$$\frac{dr}{dt} = \frac{DV_m\left(C_b - C_s\right)}{r + \frac{D}{k}}$$

If the surface reaction is the rate limiting factor

$$\frac{dr}{dt} = kV_m\left(C_b - C_s\right)$$

La Mer Mechanism



3 Separate stages:

- **Monomer formation**
- **Burst nucleation**
- **Growth by diffusion**

Monomer formation - concentration of monomer increases to a critical value c_{min}

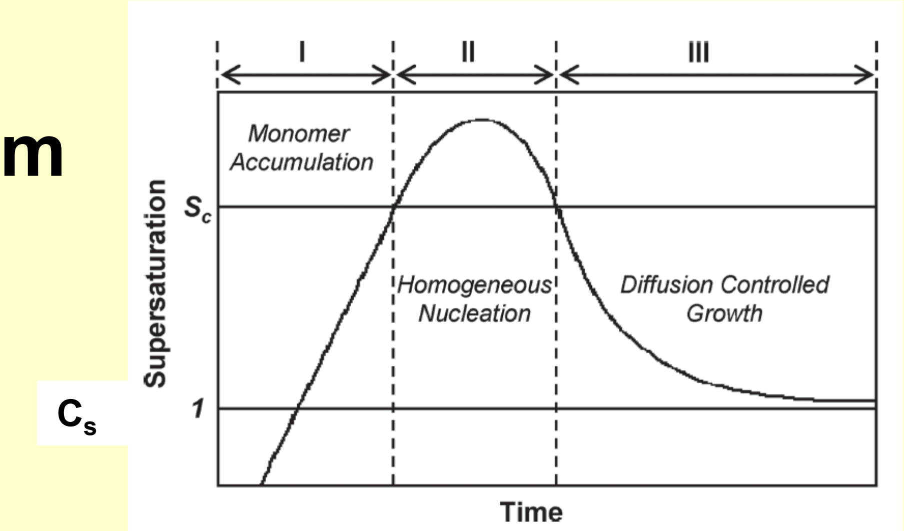
Burst nucleation - many nuclei are generated at the same time, monomer is consumed and its concentration drops below c_{min}

Growth - the nuclei grow without additional nucleation, all of the particles nucleate simultaneously, their growth histories are the same

Control of the size distribution of the ensemble of particles during growth - synthesis of monodisperse nanocrystals

La Mer Mechanism

$$S = \frac{[M]}{[M_{\infty}]} = \frac{c}{c_s}$$



Stage I - The concentration of "monomer", (the minimum subunit of bulk crystal) constantly increases with time, precipitation does not occur even under supersaturated conditions (S > 1) as the energy barrier for spontaneous homogeneous nucleation is too high

Stage II - Nucleation occurs, the critical supersaturation (S_c) is high enough to overcome the energy barrier for nucleation, the formation and accumulation of stable nuclei
The rate of monomer consumption exceeds the rate of monomer supply, the monomer concentration decreases until it reaches the level at which the nucleation rate drops to zero

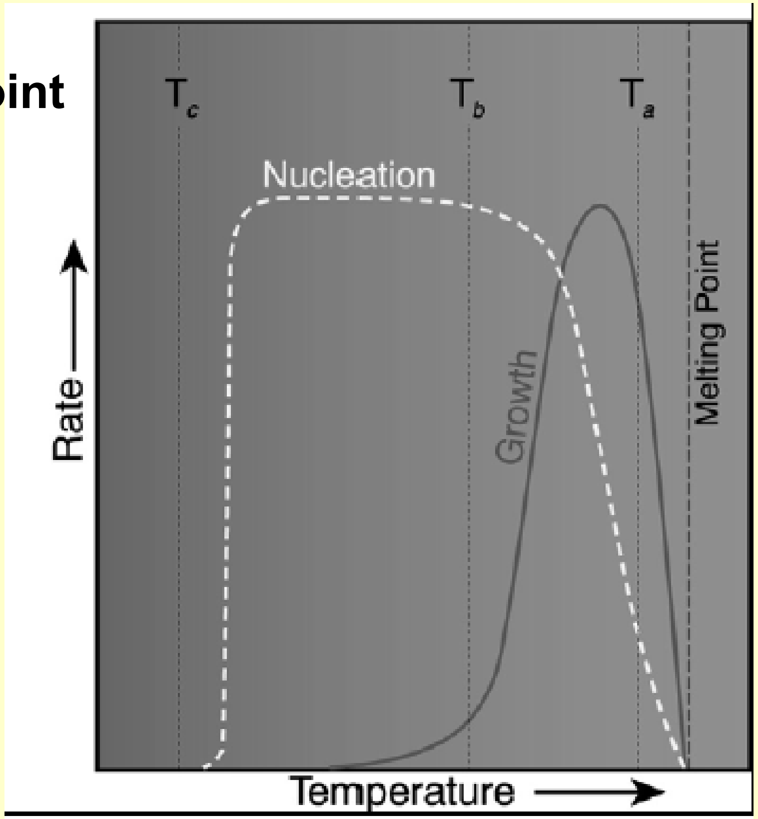
Stage III - The growth stage, nucleation stopped, the particles keep growing as long as the solution is supersaturated by diffusion of monomer towards crystals

Nucleation vs. Crystal Growth

Rate of nucleation vs. Rate of growth

Undercooling = cooling below the melting point

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



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

Growth of Single Crystals

Crystallization techniques: vapor, liquid, solid phase

High temperature methods
- **Czochralski**
- **Stockbarger and Bridgman**
- **Verneuil**
- **Zone melting**

Medium temperature methods
- **Fluxes, Ionic Liquids**
- **Electrochemical from melts**
- **Hydrothermal**
- **Vapor phase transfer**
- **Sublimation**

Low temperature methods
- **Solution**
- **Gel**

Czochralski Method

1917

Crystal pulling technique

Single crystal growth from the melt precursor(s)

Crystal seed placed in contact with surface of melt

Temperature of melt held just above melting point = highest viscosity, lowest vapor pressure

Seed gradually pulled out of the melt, 1 mm per hour

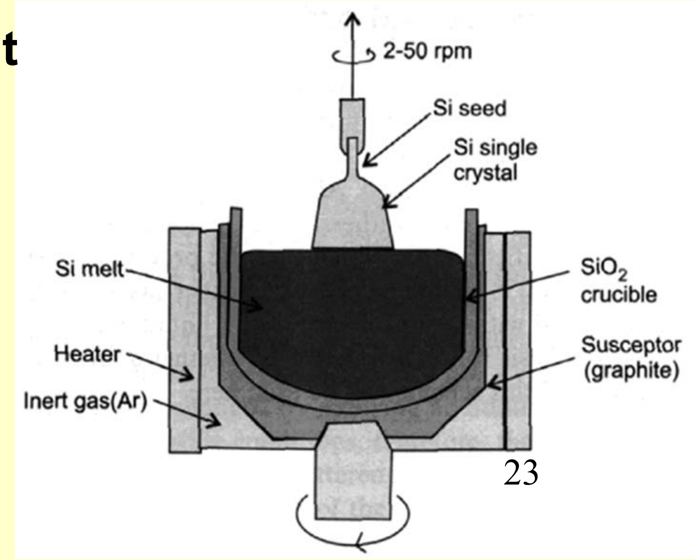
Melt solidifies on surface of seed

Melt and seed usually rotated counterclockwise with respect to each other to maintain constant temperature and to facilitate uniformity of the melt during crystal growth, 10 rpm

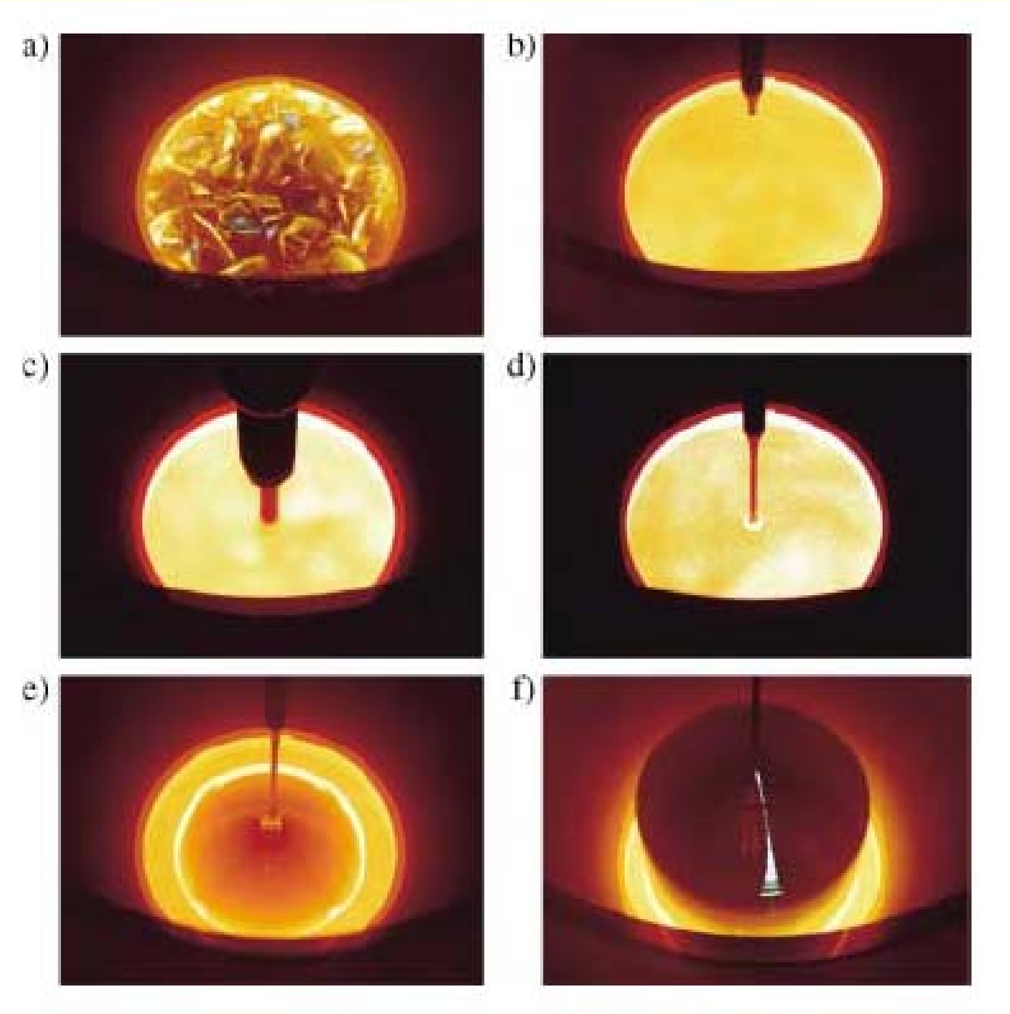
Produces higher quality crystals, less defects

Inert atmosphere, often under pressure around growing crystal and melt to prevent any materials loss

Jan Czochralski
(1885 – 1953)



Czochralski Method



Six steps in the growth of a silicon single crystal:

a) Evacuation and heating of the polycrystalline silicon ("pumping")

b) Setting the temperature of the Si melt just above 1414 ºC ("melting")

c) Dipping the thin Si seed crystal into the homogeneous Si melt ("dipping")

d) Initiating crystallization at the neck of the thin Si seed ("necking")

e) Adjustment of the shoulder of the desired single crystal diameter ("shoulder"; four positions which portray the fourfold drawing axis [100] are visible at the hot, light marginal zone of the single crystal)

f) Growing phase of the single crystal with constant diameter ("body")

Czochralski Method

Silicon

Diam 300 mm
Length 2 m
Weight 265 kg

Czochralski Method

The Czochralski crystal pulling technique for growing large single crystals in the form of a rod
Subsequently cut and polished for various applications

Si Ge GaAs $LiNbO_3$ $SrTiO_3$ $NdCa(NbO_3)_2$

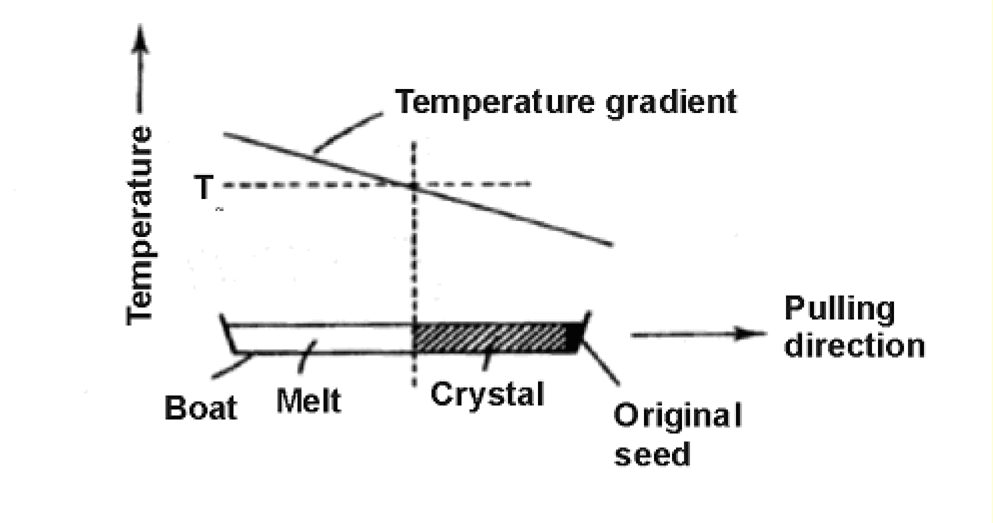
Growing bimetallic crystals like GaAs

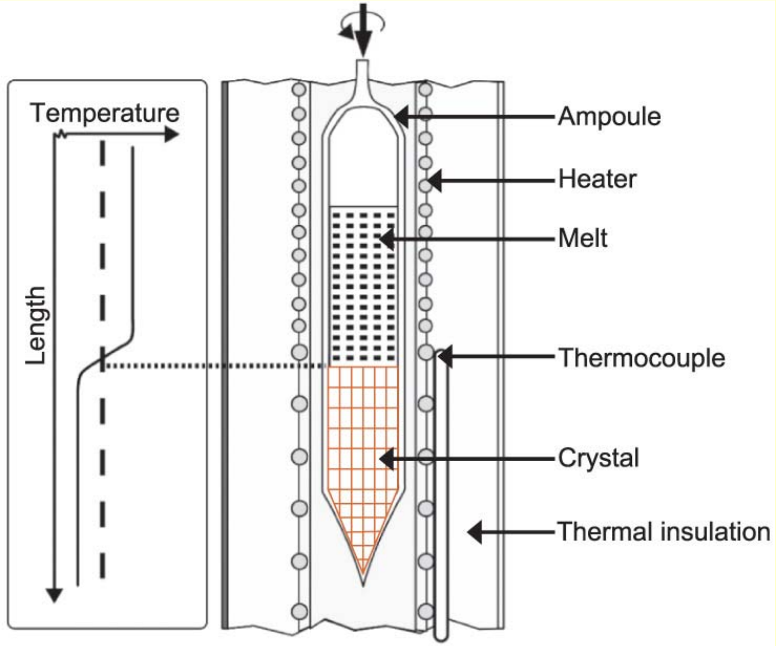
Layer of molten inert oxide like B_2O_3 spread on to the molten feed material to prevent preferential volatilization of the more volatile component of the bimetal

Critical for maintaining precise stoichiometry for example $Ga_{1+x}As$ and $GaAs_{1+x}$ which are respectively rich in Ga and As, become p-doped and n-doped

Bridgman/Stockbarger Method

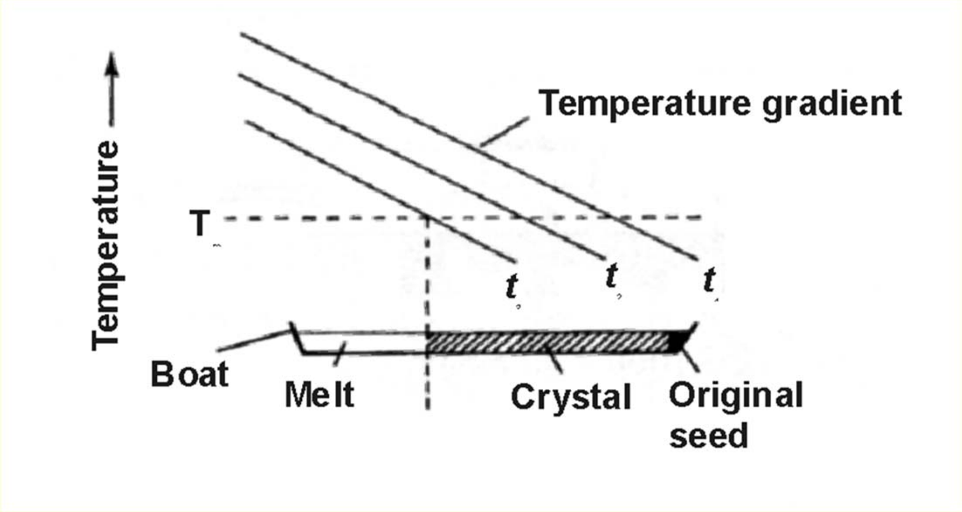
Bridgman/Stockbarger method is based on a crystal growing from the melt, involves the relative displacement of melt and a temperature gradient furnace, fixed gradient and a moving melt/crystal

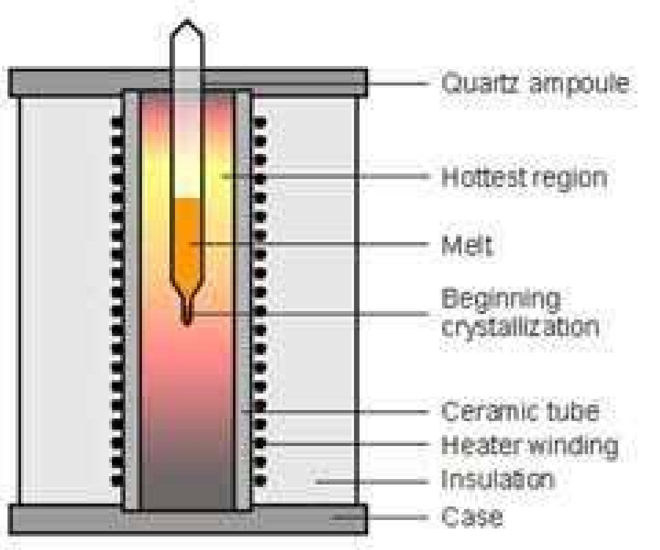




Bridgman/Stockbarger Method

Gradient Bridgman/Stockbarger method is again based on crystal growth from a melt, but now a temperature gradient furnace is gradually cooled and crystallization begins at the cooler end, fixed crystal and changing temperature gradient





Stockbarger and Bridgman Methods

Both methods are founded on the controlled solidification of a stoichiometric melt of the material to be crystallized

Enables oriented solidification

Melt passes through a temperature gradient

Crystallization occurs at the cooler end

Both methods benefit from seed crystals and controlled atmospheres (sealed containers)

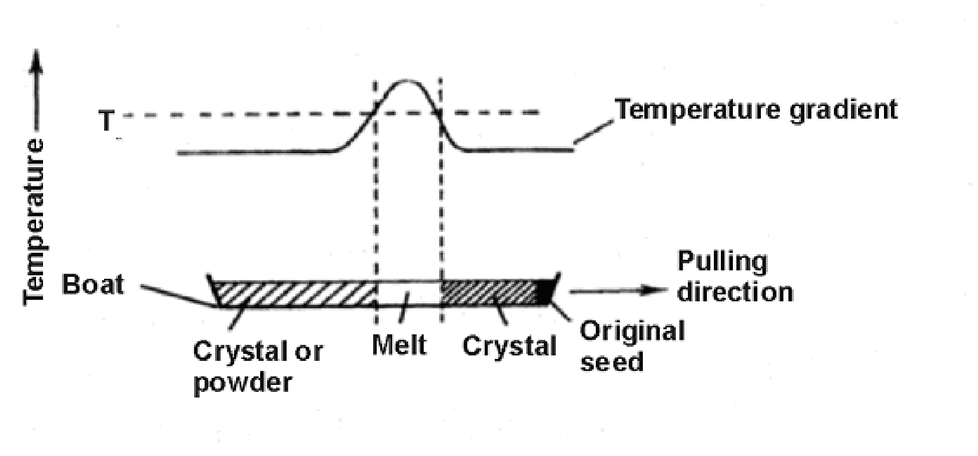
Crystal	mp (^oC)	Velocity of grad. mm h^{-1}	Container material
Al_2O_3	2037	2-8	Mo
$FeAl_2O_4$	1790	5-10	Ir
Cu	1083	6-60	Graphite
AgBr	434	1-5	Pyrex
Ar (!)	-189	0.5-1.5	Mylar

Zone Melting

- Crystal growth
- Purification of solids

Thermal profile furnace, RF, arc, electron beam heating
Material contained in a boat (must be inert to the melt)

Only a small region of the charge is melted at any one time
Initially part of the melt is in contact with the seed
Boat containing sample pulled at a controlled velocity through the thermal profile furnace - zone of material melted
Oriented solidification of crystal occurs on the seed



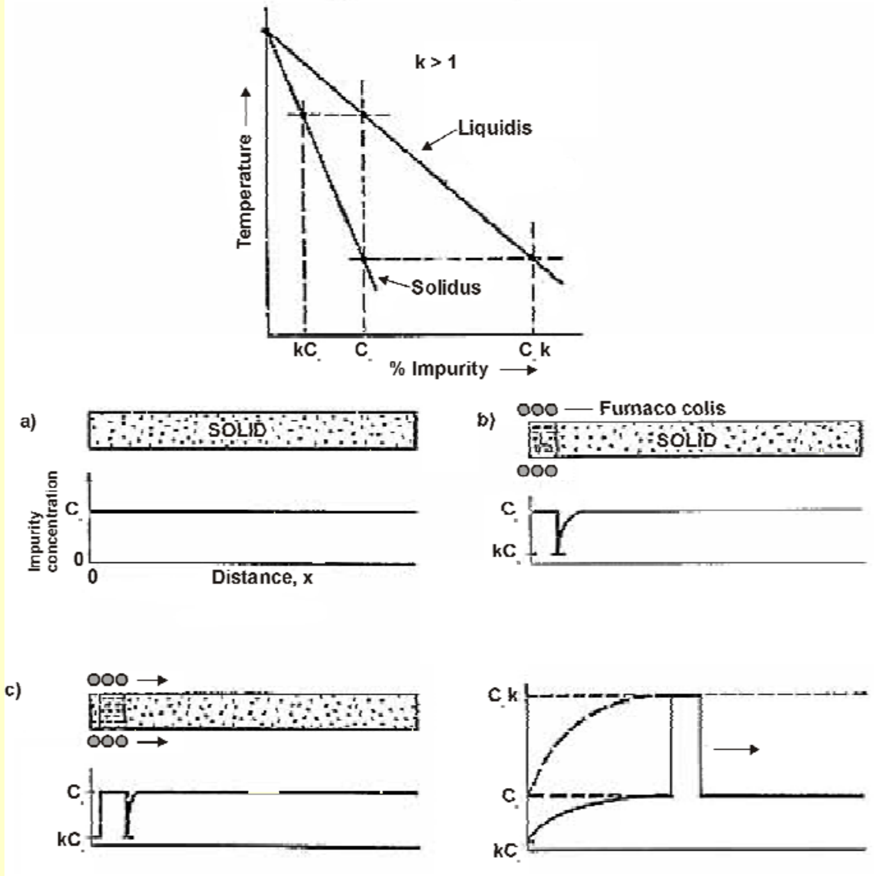
Zone Melting

- Crystal growth
- Purification of solids

Zone refining methods for purifying solids
Partitioning of impurities occurs between melt and the crystal

Impurities concentrate in liquid more than the solid phase, swept out of crystal by moving the liquid zone

Used for purifying materials like W, Si, Ge to ppb level of impurities, often required for device applications



Zone Melting

A small slice of the sample is molten and moved continuously along the sample

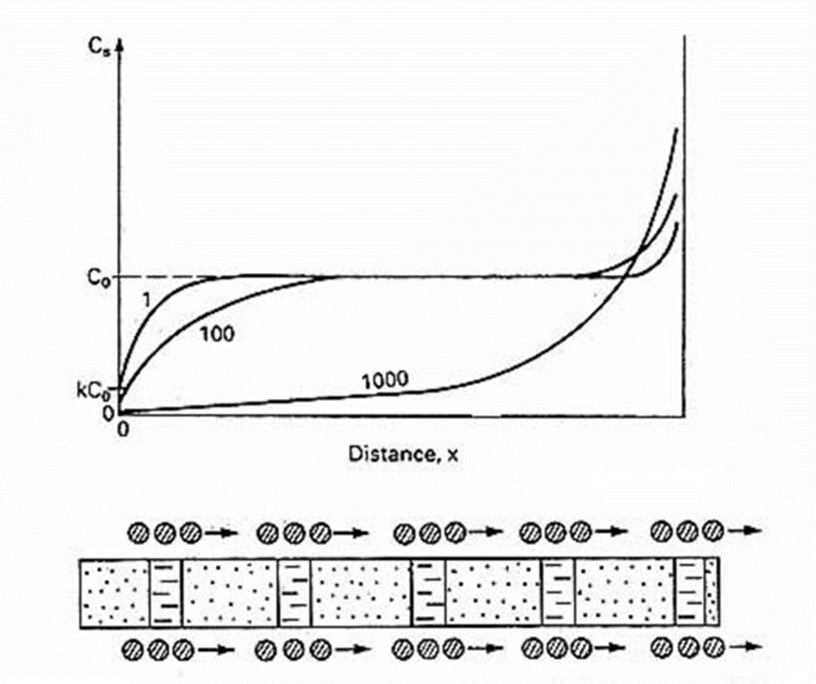
Impurities normally dissolve preferably in the melt

Segregation coefficient k:

$k = c_{solid}/c_{liquid}$

(c: concentration of an impurity)

Only impurities with k < 1 can be removed by zone melting !!



A multi-heater arrangement gives much faster zone refining

Verneuil Fusion Flame Method

1902 - French chemist Auguste Verneuil

The first commercially successful method of manufacturing synthetic gemstones - ruby, sapphire, diamond simulants rutile and strontium titanate

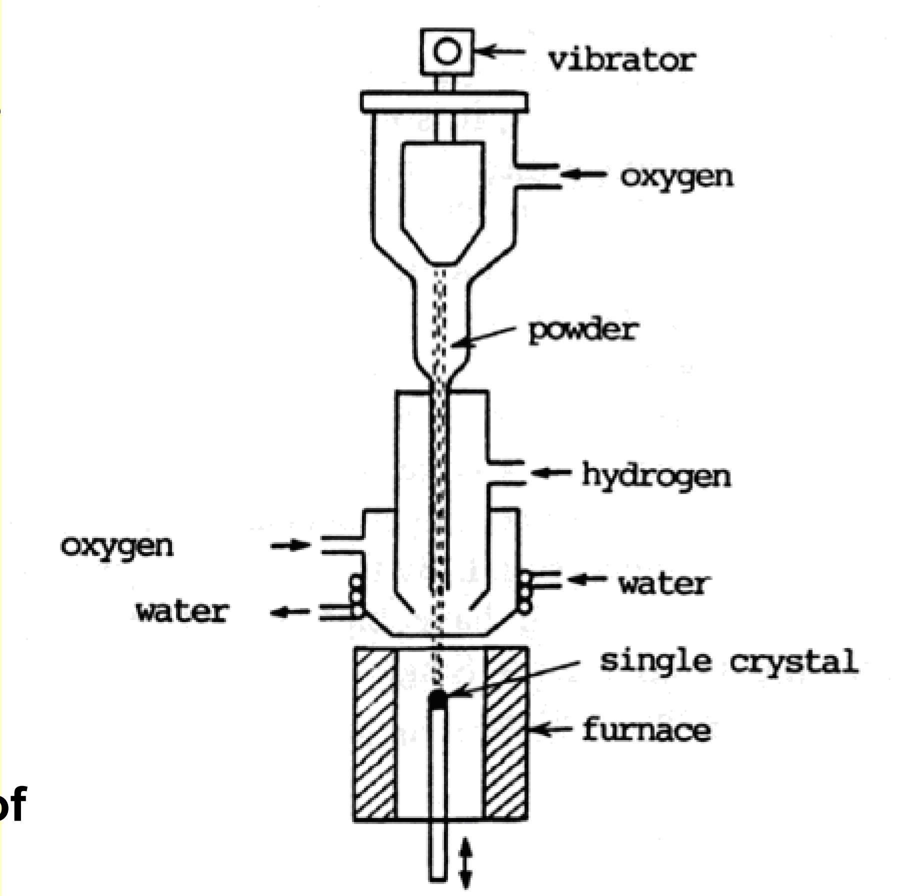
Verneuil Fusion Flame Method

Useful for growing crystals
of extremely high melting metal oxides

Examples include:

- Ruby from Cr^{3+}/Al_2O_3 powder
- Sapphire from Cr_2^{6+}/Al_2O_3 powder
- Spinel, CoO, ferrites

Starting material fine powder
Passed through O_2/H_2 flame
or plasma torch
Melting of the powder occurs in the flame
Molten droplets fall onto the surface of a seed or growing crystal
Controlled crystal growth



Lowered 10 mm/hour

Flux Method

Material dissolved in a suitable flux = solvent (metals, fluorides, oxides), lower melting point than the pure solute

Single crystals grown from supersaturated solution

Suitable method for materials which:

- vaporize or dissociate at temperatures above their mp

- there are no suitable containers at elevated temperatures

Material	Flux
As	Ga
B	Pt
Si, Ge	Pb, Zn, Sn
GaAs, GaP	Pb, Zn, Sn
$BaTiO_3$	KF
ZnO	PbF_2
ZnS	SnF_2
$MgFe_2O_4$	NaF
Co_3O_4	B_2O_3 – PbO
Fe_2O_3	$Na_2B_4O_7$
TiO_2	$Na_2B_4O_7$ – B_2O_3

AlF_3

2.0 g of AlF_3, 25.0 g of $PbCl_2$, 2.5 g PbF_2

24 h at 1200 K, cooled at 4 deg h^{-1}

down to 723 K

Thick platelets and small cubes

Solution Methods

Suitable for materials with a reasonable solubility in the selected solvent:
water, organic solvents, $NH_3(l)$, HF, $SO_2(l)$

Nucleation – homogeneous – heterogeneous
Dilute solution, solvent with low solubility for given solute
Supersaturated solution, seed crystals
Single crystals grown at constant supersaturation

Techniques:

- **slow evaporation**
- **slow cooling**
- **vapor diffusion**
- **antisolvent diffusion**
- **reactant diffusion**
- **recirculation, thermal differential, convection**
- **cocrystallants ($OPPh_3$ for organic proton donors)**
- **counterion, similar size of cation and anion least soluble**
- **ionization of neutral compounds, protonation/deprotonation, H-bonding**

KDP crystals (KH_2PO_4)

- grown from supersaturated solution
- crystal seed
- slow cooling

a frequency converter - converts the infrared light at 1053 nm into the ultraviolet at 351 nm

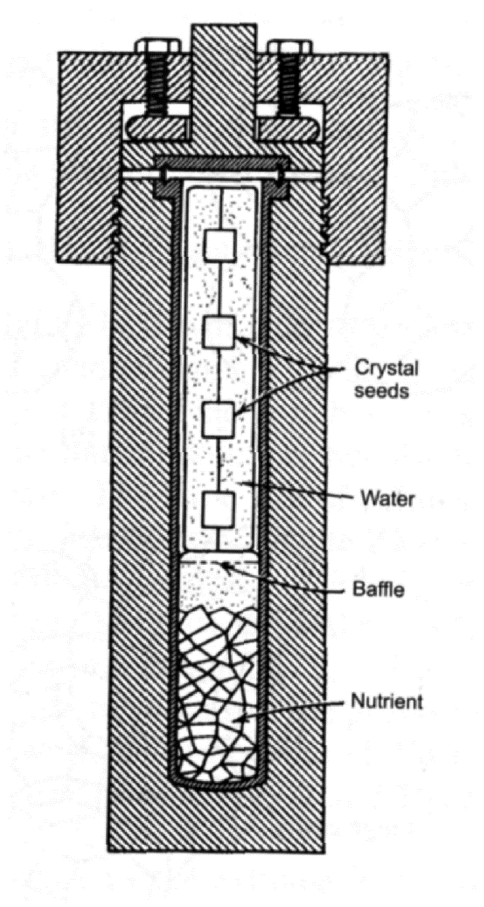
Hydrothermal Crystallization/Synthesis

1957 - Bell Labs
Autoclave with Water medium
High temperature growth, above normal boiling point

Water acts as a pressure transmitting agent
Water functions as solubilizing phase
Often a mineralizing agent is added to assist with the transport of reactants and crystal growth
Speeds up chemical reactions between solids

Crystal growth hydrothermally involves:

- **Temperature gradient reactor = autoclave**
- **Dissolution of reactants at one end**
- **Transport with help of mineralizer to seed at the other end**
- **Crystallization at the other end**



Hydrothermal Crystallization/Synthesis

Useful technique for the synthesis and crystal growth of phases
- unstable in a high temperature preparation in the absence of water
- materials with low solubility in water below 100 °C

Hydrothermal growth of quartz crystals
Annual global production hundreds of tons of quartz crystals
Uses of single crystal quartz: Radar, sonar, piezoelectric transducers, monochromators, XRD

Water medium, nutrients 400 °C, seed 360 °C, pressure 1.7 kbar
Mineralizer 1M NaOH

A mineralizer is a complexing agent (not too stable) for the reactants/precursors that need to be solublized (not too much) and transported to the growing crystal

Role of the mineralizer - control of crystal growth rate
Choice of mineralizer, temperature and pressure
Solubility of quartz in water is important

Hydrothermal Quartz Synthesis

Hydrothermal growth of quartz crystals: $SiO_2 + 2\,H_2O \rightleftarrows Si(OH)_4$

0.3 wt% even at supercritical temperatures >374 ^oC

Need mineralizing reactions:

NaOH mineralizer, dissolving reaction, 1.3-2.0 kbar

$3\,SiO_2 + 6\,OH^- \rightleftarrows Si_3O_9^{6-} + 3\,H_2O$

Na_2CO_3 mineralizer, dissolving reaction, 0.7-1.3 kbar

$CO_3^{2-} + H_2O \rightleftarrows HCO_3^- + OH^-$
$SiO_2 + 2\,OH^- \rightleftarrows SiO_3^{2-} + H_2O$

NaOH creates growth rates about 2x greater than with Na_2CO_3 because of different concentrations of hydroxide mineralizer

Hydrothermal Synthesis

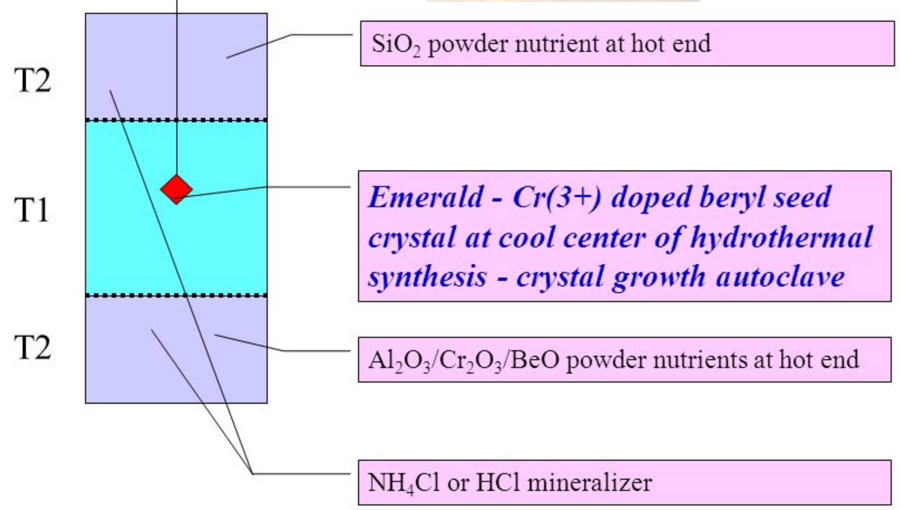
Some materials have negative solubility coefficients, crystals grow at the hotter end in a temperature gradient hydrothermal reactor

Example: α-$AlPO_4$ (Berlinite) - important for its high piezoelectric coefficient (larger than α-quartz with which it is isoelectronic) used as a high frequency oscillator
Powdered $AlPO_4$ cool end of reactor - negative solubility coefficient!!!
H_3PO_4/H_2O mineralizer, $AlPO_4$ seed crystal at hot end

Emeralds $Cr^{3+}/Be_3Al_2Si_6O_{18}$
SiO_2 powder at hot end 600 °C, NH_4Cl or HCl/H_2O mineralizer, 0.7-1.4 kbar, cool central region for seed, 500 °C, $Al_2O_3/BeO/Cr^{3+}$ dopant powder mixture at other hot end 600 °C

$6\ SiO_2 + Al_2O_3 + 3\ BeO \rightleftarrows Be_3Al_2Si_6O_{18}$

Beryl contains $Si_6O_{18}^{12-}$ six rings



Hydrothermal Synthesis

Metal crystals

Metal powder at cool end 480 °C, Mineralizer 10M HI / I_2
Metal seed at hot end 500 °C
Dissolving reaction that also transports Au to the seed crystal:

$$Au + 3/2\ I_2 + I^- \rightleftarrows AuI_4^-$$

Metal crystals grown this way include: Au, Ag, Pt, Co, Ni, Tl, As

Diamonds

$$Ni + C + H_2O \rightleftarrows \text{diamond}$$

Carbon films on SiC fibers

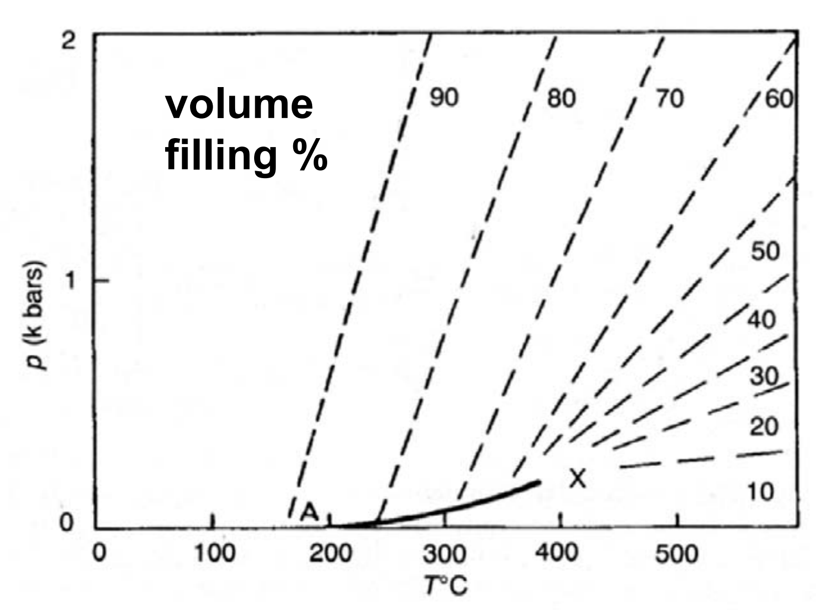
$$SiC + 2\ H_2O \rightleftarrows C + 2\ H_2 + SiO_2 \qquad 100\ \text{MPa},\ \ 300\text{-}\ 600\ ^oC$$

Zeolites

$$Al(OH)_3,\ SiO_2,\ NaOH,\ \text{template} \rightarrow M_{x/n}\ [(AlO_2)_x(SiO_2)_y].\ mH_2O$$

Hydrothermal Synthesis

Tables of pressure versus temperature for different initial volume filling of autoclave must be consulted to establish a particular set of reaction conditions for a hydrothermal synthesis or crystallization



Safety: an autoclave explosion

Pressure, volume, temperature tables

Critical point of water: 374.2 ^{o}C, 218.3 bar

Density of liquid water decreases with T
Density of water vapor increases with T

Density of gas and liquid water the same
0.32 g cm^{-3}, at the critical point

Liquid level in autoclave rises for > 32% volume filling

For 32% volume filling liquid level remains unchanged and becomes fluid at critical temperature

Bulk-Material Dissolution Technique

Large zeolite crystals: up to 3 mm, SOD, MFI, ANA, CAN, JBW

Autoclave, PTFE liner

quartz tube (SiO_2)	**TPAOH, HF, H_2O 200 °C, 25-50 days**
ceramic tube (SiO_2, Al_2O_3)	**NaOH, H_2O 100-200 °C, 7-20 days**

Small surface area, low dissolution rate, saturation concentration maintained, only a few nuclei are produced at the beginning, no large crystals formed in the stirred reactions, concentration gradients

Decomplexation Crystallization

Crystallization under ambient conditions, low temperature and pressure, provides kinetic products, control of crystal size and morphology, habit

AgX, X = Cl, Br, I
MX, M = H, Na, K, NH_4

$AgI + HI \rightleftarrows H^+ + [AgI_2]^-$ aqueous solution
Overlayer absolute ethanol, HI diffusion, decomplexation of AgI, hexagonal plates 5 mm

$AgX + 2\ NH_3 \rightleftarrows [Ag(NH_3)_2]^+ + X^-$
X = Cl, Br, slow evaporation (3-5 days), AgX crystals

Decomplexation Crystallization

$AgI + KI \rightleftarrows K^+ + [AgI_2]^-$

Concentration gives $K[AgI_2]$ crystals
Dilution by slow diffusion gives 20 mm AgI crystals
Warming gives AgI crystals
Inverse temperature dependence of AgI solubility in KI

$CuCl + HCl \rightleftarrows H^+ + [CuCl_2]^-$

$HgI_2 + KI \rightleftarrows [HgI_3]^- \rightleftarrows [HgI_4]^{2-}$

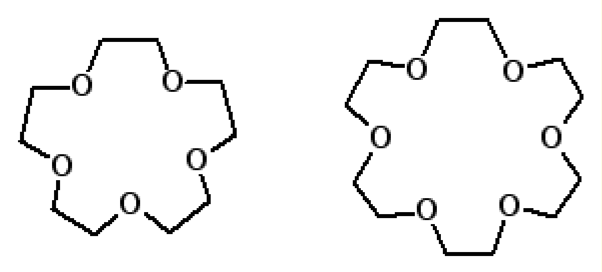
PbO + hot KOH solution
slow cooling provides PbO as 2 mm yellow needles and
1 mm red blocks

Complexation-Mediated Crystallization

Salts with high lattice energy: fluorides, carbonates, acetates

Solubilized in organic solvents by crown ethers
Crystallization provides uncomplexed salts

$NaOOCCH_3.3H_2O$ dissolves in cyclohexane with 15-crown-5
prismatic crystals



Complexation-Mediated Crystallization

Two soluble salts react to produce an insoluble phase
- aqueous solutions
- nonaqueous solvents

$CaCO_3$	**calcite**	**TD stable phase at room temp., in H_2O**
	vaterite	**kinetic product**
	aragonite	**TD stable at high temperature**

$CaCl_2$ (in MeOH) + $NaHCO_3$ (in MeOH, 18-crown-6)

Microcrystalline calcite
upon aging converts to nanocrystalline vaterite, surface stabilization by surface chelatation

The Gel Method

Large single crystals

Hydrogels: silicagel (water glass), polyvinyl alcohol, gelatin, agar

Silicate gel
Impregnation with metal or ligand, setting the gel = condensation, crosslinking, pH control of the condensation rate
Layered with the solution of ligand or metal
Slow diffusion, crystal growth

$CuSO_4$ + $[NH_3OH]Cl$ → Cu

$Pb(OAc)_2$ + Zn → Pb + $Zn(OAc)_2$

$Pb(OAc)_2$ + KI → PbI_2 + 2 KOAc

Liesegang rings, agates

$RbSnBr_3$, $CsSb_2I_5$ semiconductors

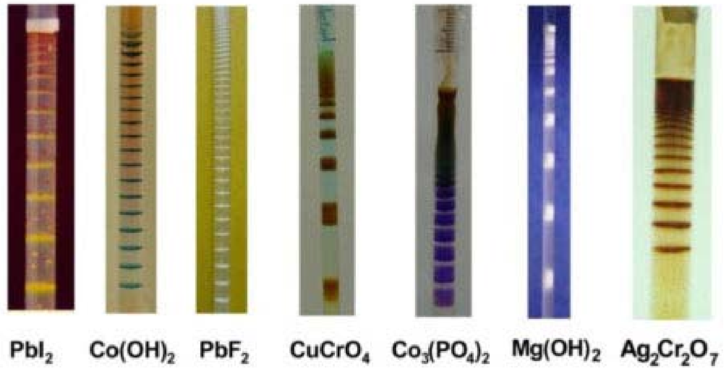


Figure 1: Typical Liesegang patterns grown in gels, for a number of sparingly soluble salts.

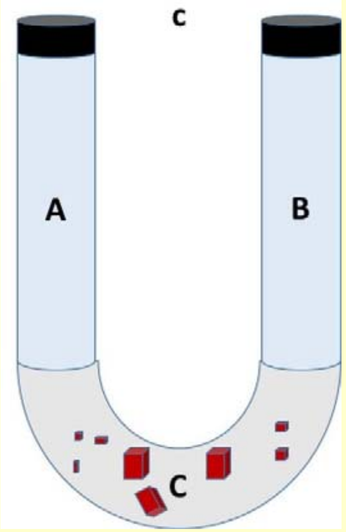
The Gel Method

Nonaqueous gels

PEO (MW = 100 000) in 1,2-dichloroethane + MeOH, EtOH, PrOH, DMF, CH_3CN, DMSO

Impregnation with metal or ligand
Layered with the solution of ligand or metal
Slow diffusion, crystal growth

U-tube, counter-diffusion A + B → C
Concentration programming, increasing concentrations



Ostwald rippening = larger xtals grow, smaller dissolve

Electrochemical Reductive Crystal Growth

Molten mixtures of precursors, product crystallizes from melt

Melt electrochemistry: Electrochemical reduction

$CaTi(IV)O_3$ (perovskite) / $CaCl_2$ (850 ^oC) → $CaTi(III)_2O_4$ (spinel)

$Na_2Mo(VI)O_4$ / $Mo(VI)O_3$ (675 ^oC) → $Mo(IV)O_2$ (large crystals)

$Li_2B_4O_7$ / LiF / $Ta(V)_2O_5$ (950 ^oC) → $Ta(II)B_2$

$Na_2B_4O_7$ / NaF / $V(V)_2O_5$ / $Fe(III)_2O_3$ (850 ^oC) → $Fe(II)V(III)_2O_4$ (spinel)

Na_2CrO_4 / Na_2SiF_6 → Cr_3Si

$Na_2Ge_2O_5$ / NaF / NiO → Ni_2Ge

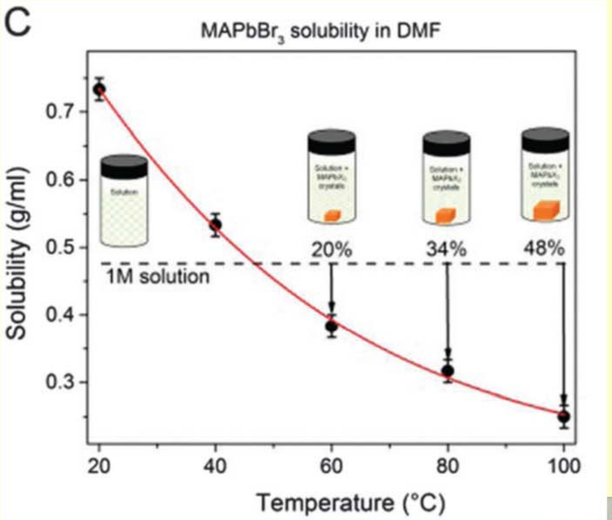
Phosphates → phosphides
Carbonates → carbides
Sulfates → sulfides

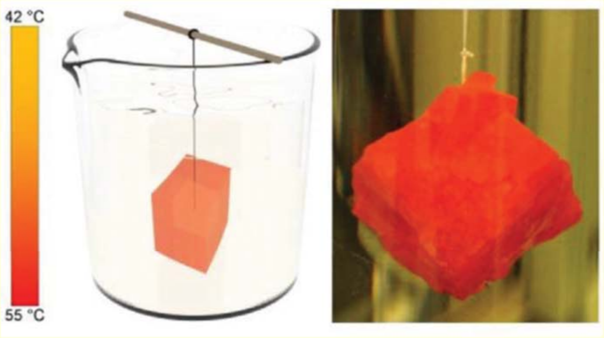
Inverse Temperature Crystallization

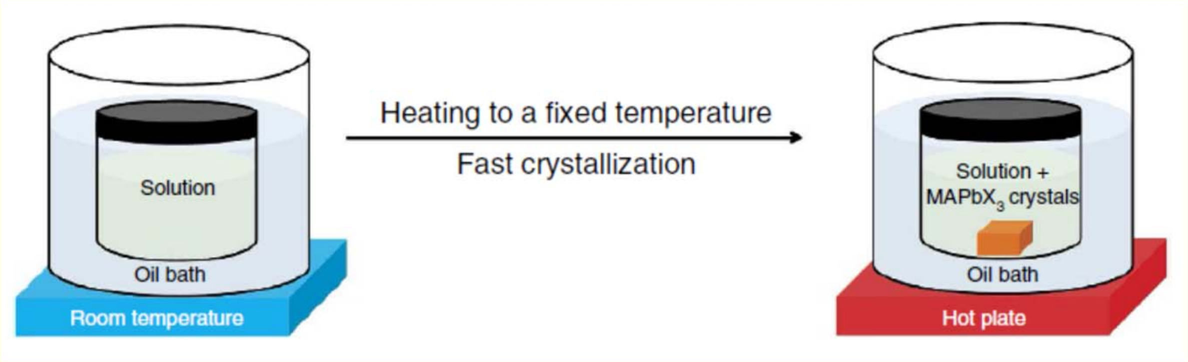
$MAPbX_3$ perovskites exhibit inverse temperature solubility behavior in certain solvents

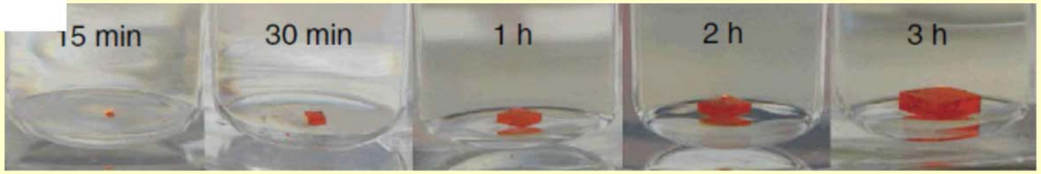
The solubility of $MAPbBr_3$ in DMF
0.80 ± 0.05 g ml^{-1} at r.t
0.30 ± 0.05 g ml^{-1} at 80 °C

methylammonium lead tribromide ($CH_3NH_3PbBr_3$)
high-energy radiation detectors





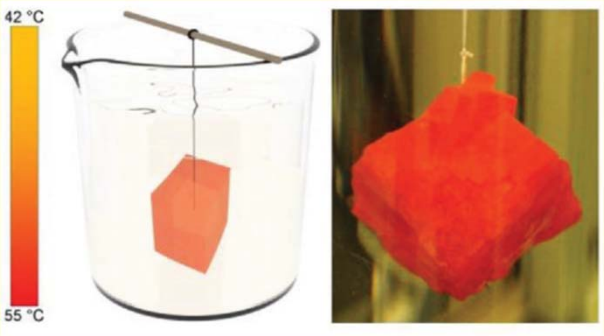


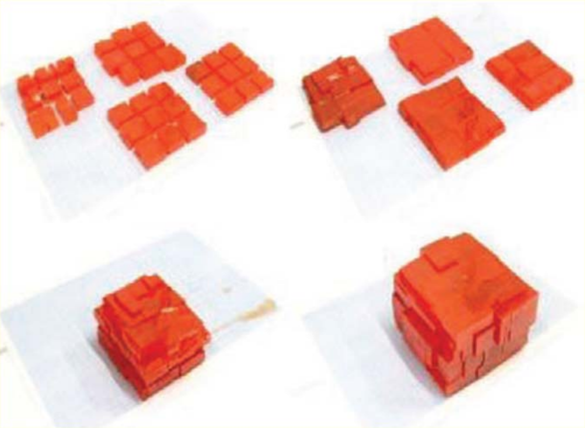


Oriented Crystal-Crystal Intergrowth

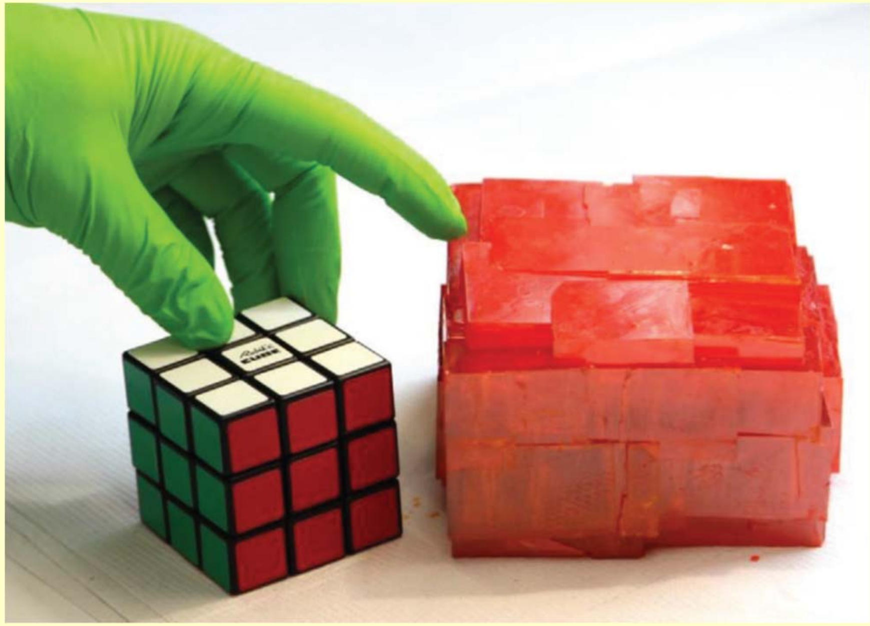
Inverse temperature crystallization

$MAPbX_3$ perovskites exhibit inverse temperature solubility behavior in certain solvents





methylammonium lead tribromide ($CH_3NH_3PbBr_3$)
high-energy radiation detectors



Synthesis of Amorphous Materials

Quenching of molten mixture of metal oxides with a glass former (P_2O_5, V_2O_5, Bi_2O_3, SiO_2, CaO, …), large cooling rates required (>10^7 K s^{-1})

Ion beam sputtering

Thermal evaporation

Thermal decomposition of organometallic precursors ($Fe(CO)_5$, …)
Amorphous Cr_2O_3, MnO_2, PbO_2, V_2O_5, Fe_2O_3

Sonochemical decomposition of organometallic precursors
$Fe(CO)_5$, $M(acac)_n$,…

Precipitation on metal hydroxides, transformation to hydrous oxides

MW heating of metal salt solution
Amorphous Cr_2O_3, Fe_2O_3