Methods of Bulk Crystal Growth

In Condensed Matter and Materials Physics

Vernneuil

Czochralski

Bridgeman

Micropulling

(Floating) zone melting

Crystal growth from the liquid melt

Flux method

Hydrothermal

Crystal growth from liquid solutions

Chemical vapor transport

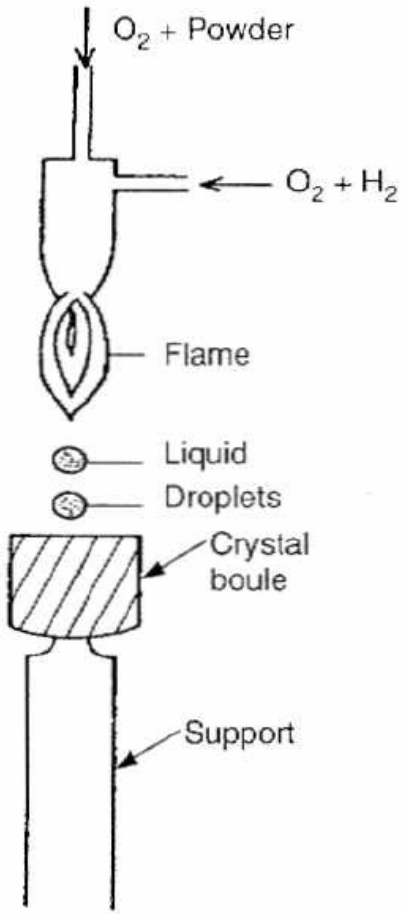
Electrochemical methods

Other methods

Application of high pressures and magnetic fields

Verneuil Method

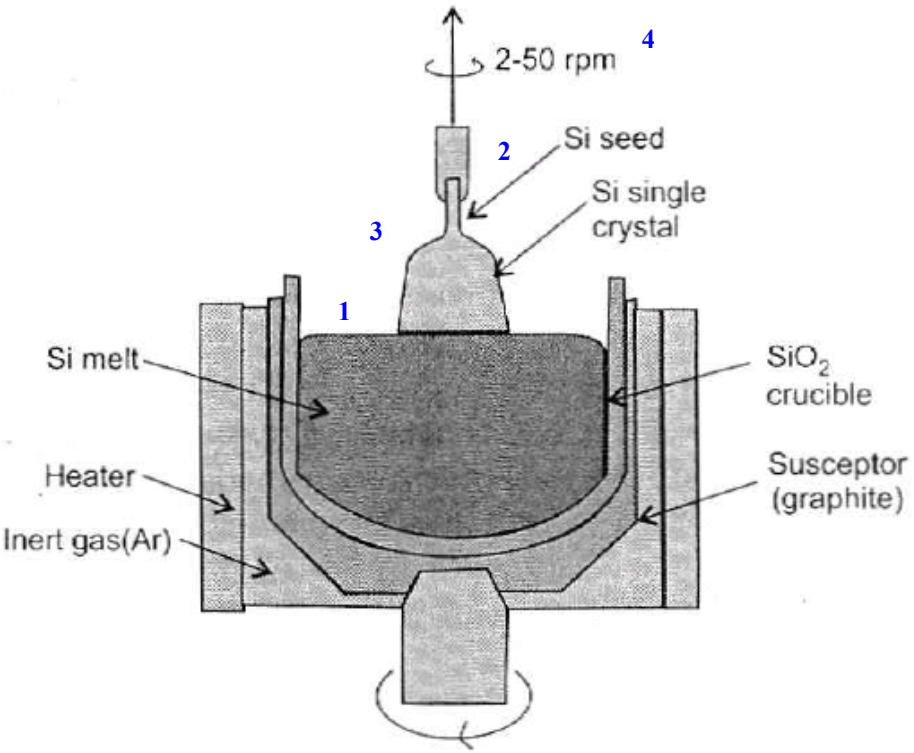
One of the first crystal growth methods



- Stream of powder mixed in high T flame (Hydrogen – Oxygen torch)
- Melts, forms droplets and falls on seed crystal which is held by support rod
- Crystal growth by solidification
- High crystal growth rates (10mm/h)
- Hard to avoid defects since cooling rate of the molten layer at the droplet – seed surface is not controlled and has large fluctuations
- Some oxide crystals: Al_2O_3

Czochralski

Crystal pulling from congruent melt
Standard method for Si wafers for devices
Melt crystallizes epitaxially on the seed



From Yu and Cardona: *Fundamentals of Semiconductors* Springer Verlag 1996

Liquid encapsulated CZ growth: layer of B_2O_3 above the melt helps prevent volatile loss

1. Cylindrically shaped boules pulled from a bath of molten Si contained in silica crucible under Ar atmoshpere. Crucible is kept at T slightly above melting point.
2. Seed (small crystal of Si) is inserted in a bath, then rotated. Once inserted, thermal shock generates dislocations on the crystal
3. Dislocations are eliminated by necking – high pull rate is introduced (4-6mm/min) which reduces diameter of the growing crystals to 25 – 30% of the seed size. High pull rates introduces growth velocity greater than velocity of dislocation motion
4. Pulling rod and crystal are oppositely rotated few tens rpm's (homogeneity *x*,T)
- After necking, usual growth rates are 0.1 to 1mm/min. Both growth rates and temperature of the bath are adjusted
- Si crystals is oriented the same way as seed crystal (melt crystallizes epitaxially)
- Solid – liquid interface very important.
- Solidification of Si releases heat of fusion ΔH_m = 50.21 kJ/mole Si
- Axial and radial temperature gradients can introduce defects and dislocations
- Impurities oxygen and carbon
- Inert atmoshpere, high P help compounds
- Materials: Si, GaAs, $Y_3Al_5O_{12}$ (YAG)

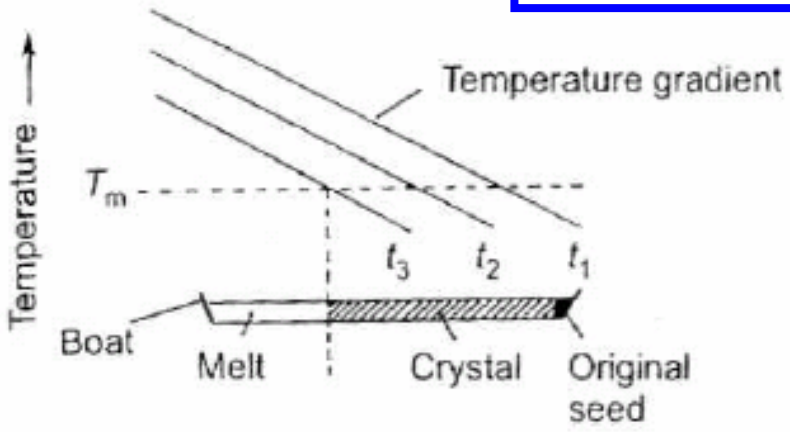
Czochralski pulling furnace

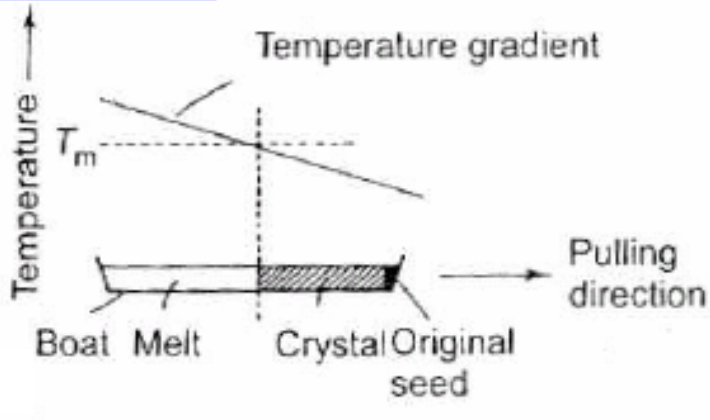
MnSi <110> seeded growth

CEA Grenoble (courtesy of Gerard Lapertot)

Bridgeman and Stockbarger

Crystal pulling from congruent melt
Temperature Gradient





Bridgeman

T gradient (ΔT) along crucible is kept constant

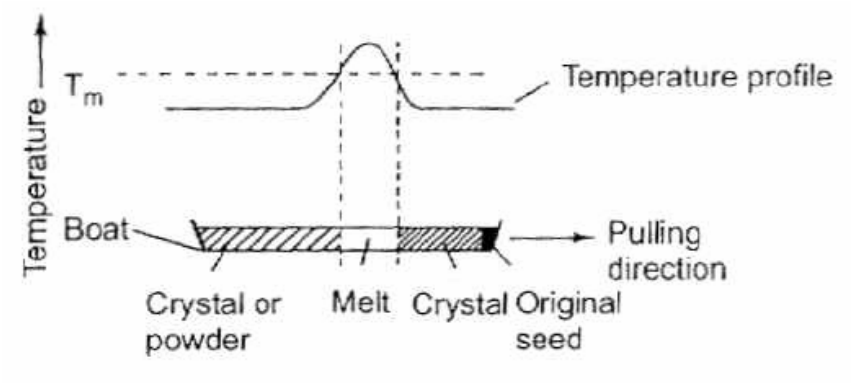
T of the furnace is reduced with time

Crystallization front (melting T) moves progressively along the length of the crucible

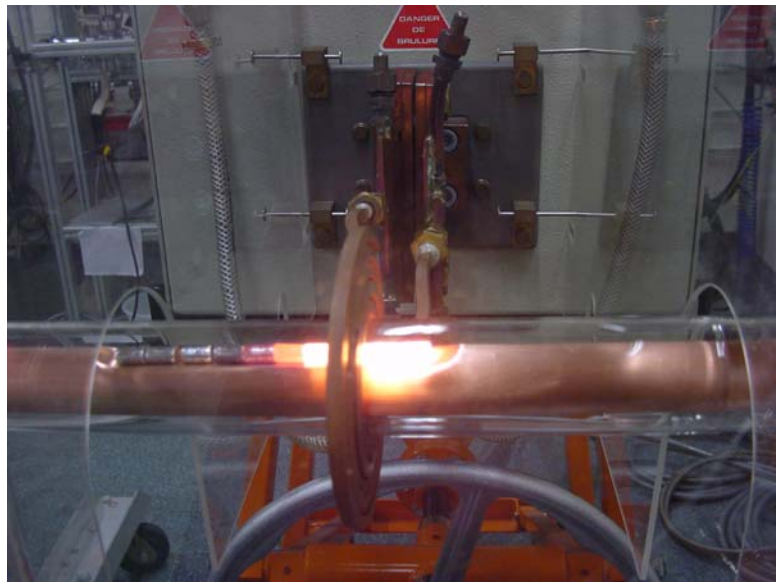
Stockbarger method: crucible is moved relative to furnace in which both ΔT and T are constant

Zone melting

Crystal pulling from congruent melt
Peaked temperature profile



Temperature profile along the crucible is peak shaped, with T exceeding Tm only in narrow region. Crucible is translated relative to the heater and the hot zone, material melts and crystallization front moves along the crucible



Horizontal Zone Melting/purification/growth cold copper boat – RF

CEA Grenoble (courtesy of Gerard Lapertot)

Floating zone refinement – purification of rod like crystals:
Solubility of impurities will be higher in the hot molten region than in cooler part surrounding this region.
Impurities prefer to dissolve in molten zone and are removed out of the crystal as the heater is translated

Floating Zone Purification of (Si) crystals

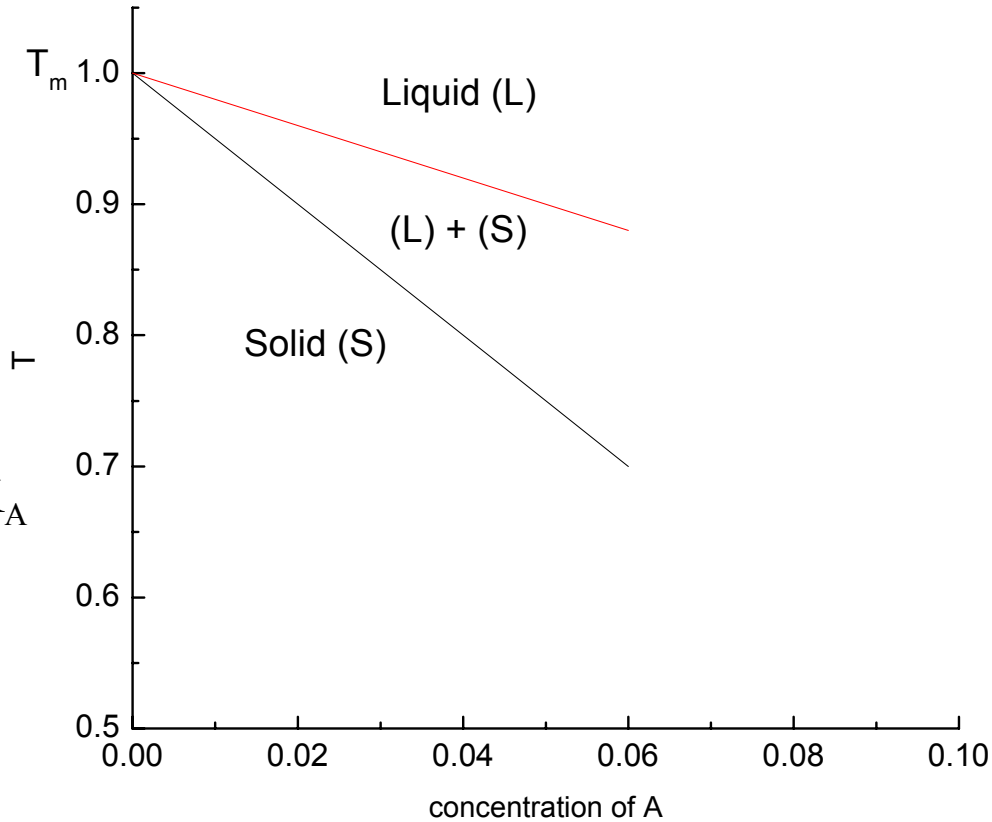
- Most atoms are more soluble in liquid than in solid
- Segregation coefficient is ratio of equilibrium concentrations of atom A:

$$K_A = c_A(\text{solid})/c_A(\text{liquid})$$

- Estimate of K_A is possible from equilibrium phase diagrams: solutes A that depress melting point of Si have $K_A < 1$, those that increase have $K_A > 1$
- For dillute limit of A in Si segregation coefficient is:

$$K_A = s_L/s_S$$

where s_L and s_S are slopes of liquidus and solidus curves



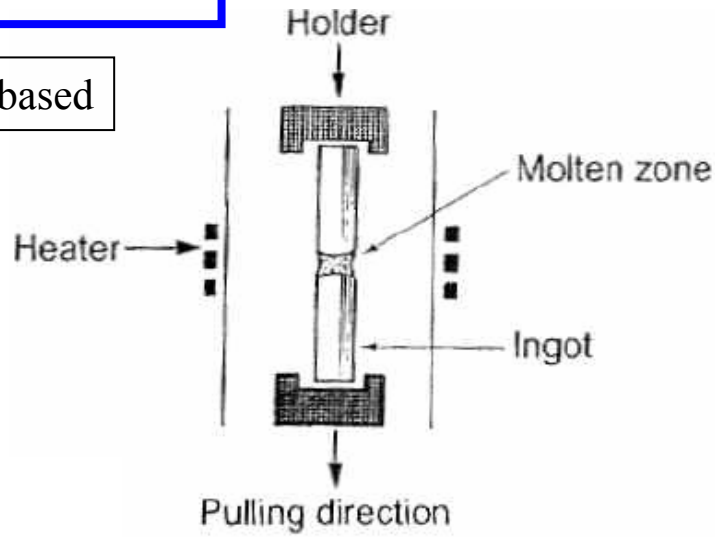
Most impurities have $K < 1$ – if there is impurity with c_0 in the solid rod, the first melted portion of the rod will have $Kc_0 < c_0$. Concentration of impurities is higher in end parts, but molten zone can be remelted and it will have $c \sim Kc_0 << 1$

Floating Zone Crystal Growth

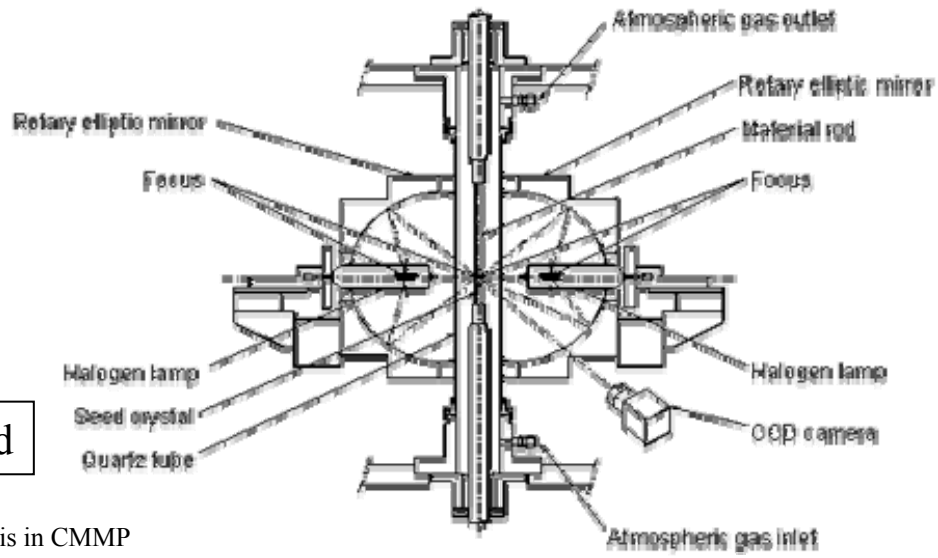
Crystal pulling from congruent melt
Peaked temperature profile

- Growth from the liquid phase which is not in the contact with any container
- Main source of impurities is therefore eliminated
- Starting material is a polycrystalline rod mounted vertically and held at both ends under vacuum or gas in contact with a seed crystal. Small crystal is placed at the other end to initiate the growth, necking procedure is used to eliminate dislocations
- Only a short section of the rod is locally heated by lamp (mirrors) or radio frequency coils. It is kept in place by surface tension forces
- Molten zone is rotated to promote uniformity and slowly pulled to create grown crystal
- Impurity level usually 100 times less than CZ growth

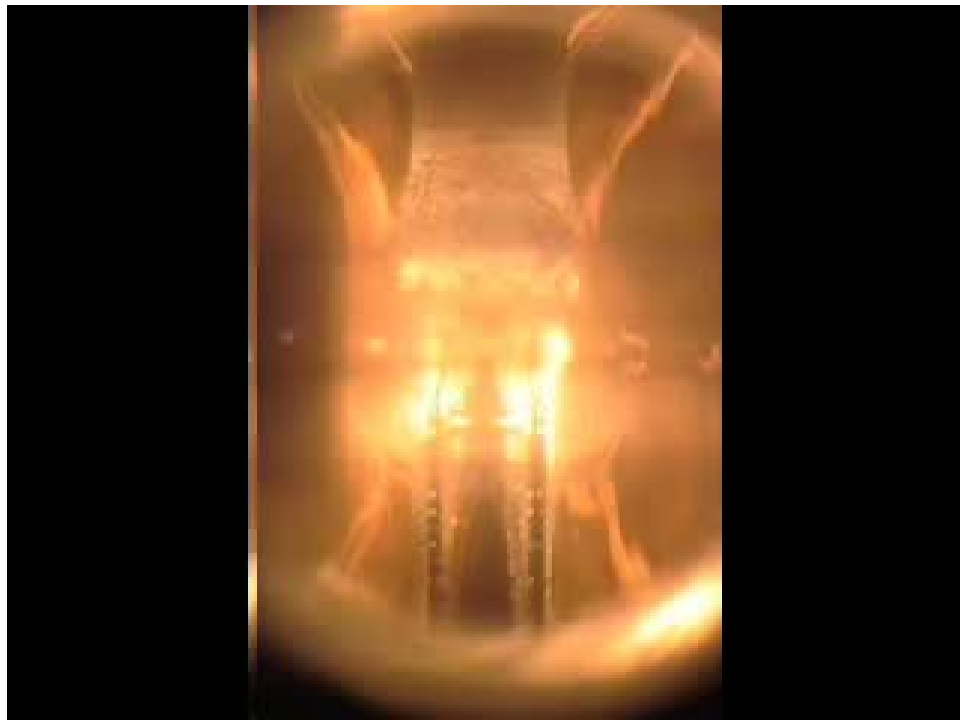
RF based



Lamp based

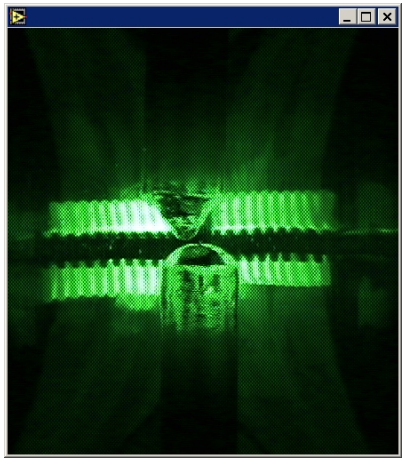


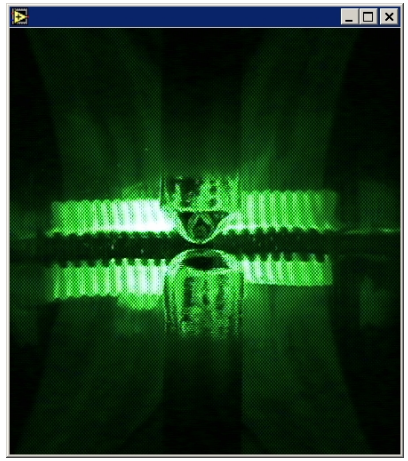
Traveling solvent floating zone

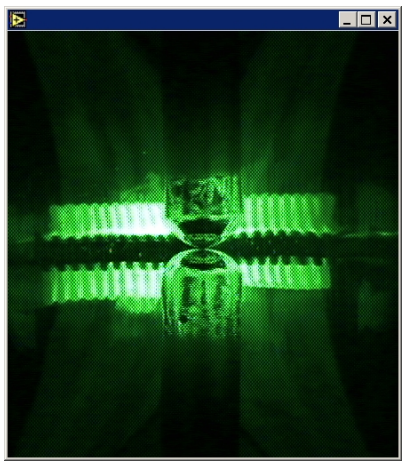


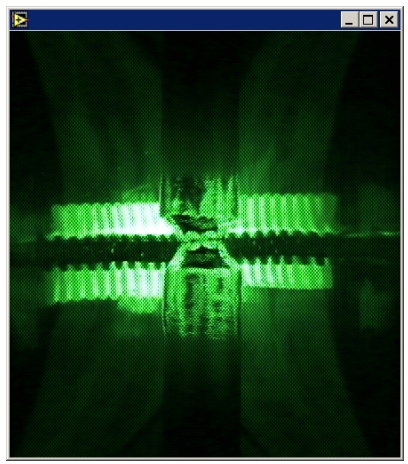
TSFZ Furnace at BNL Courtesy of Genda Gu

Starting the growth …

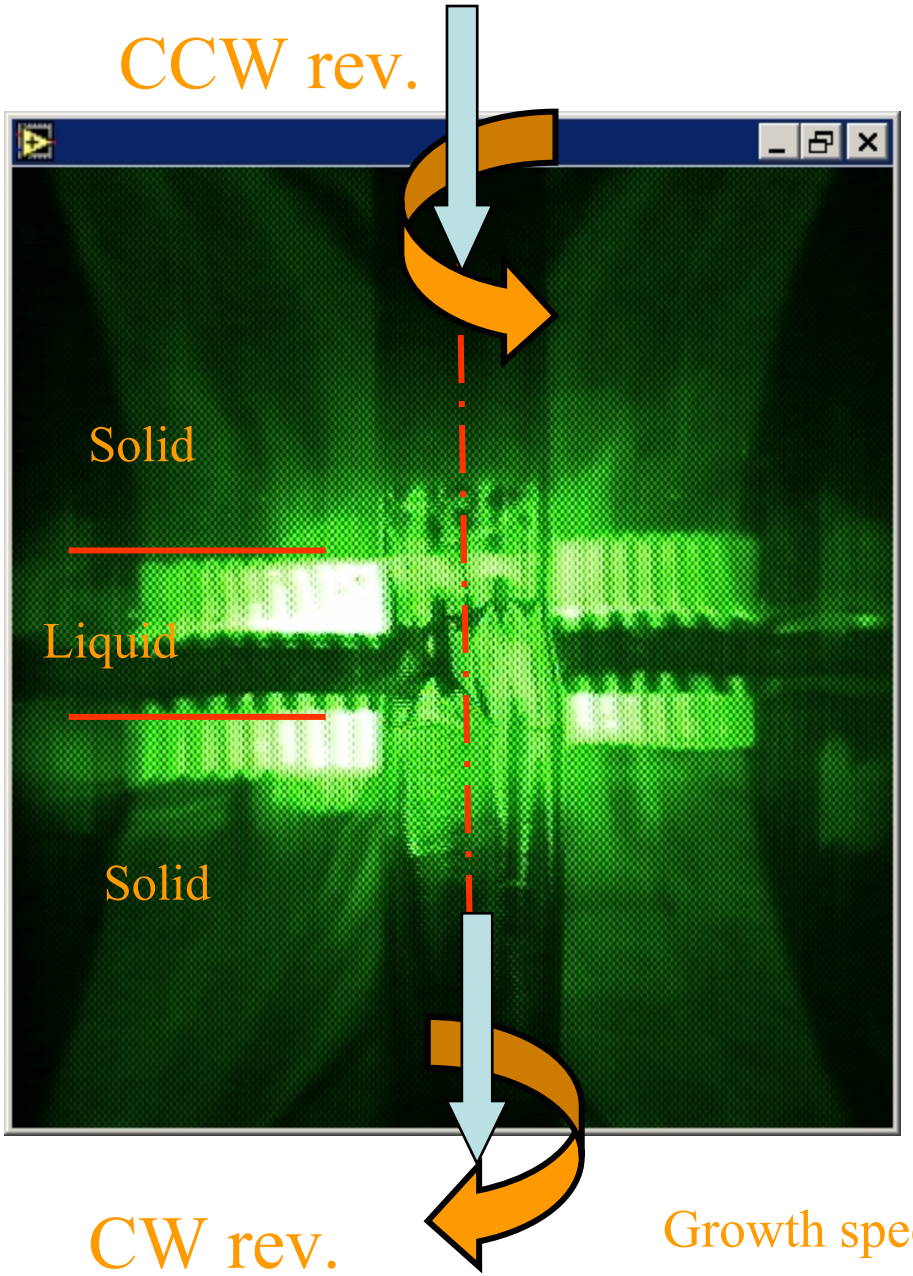








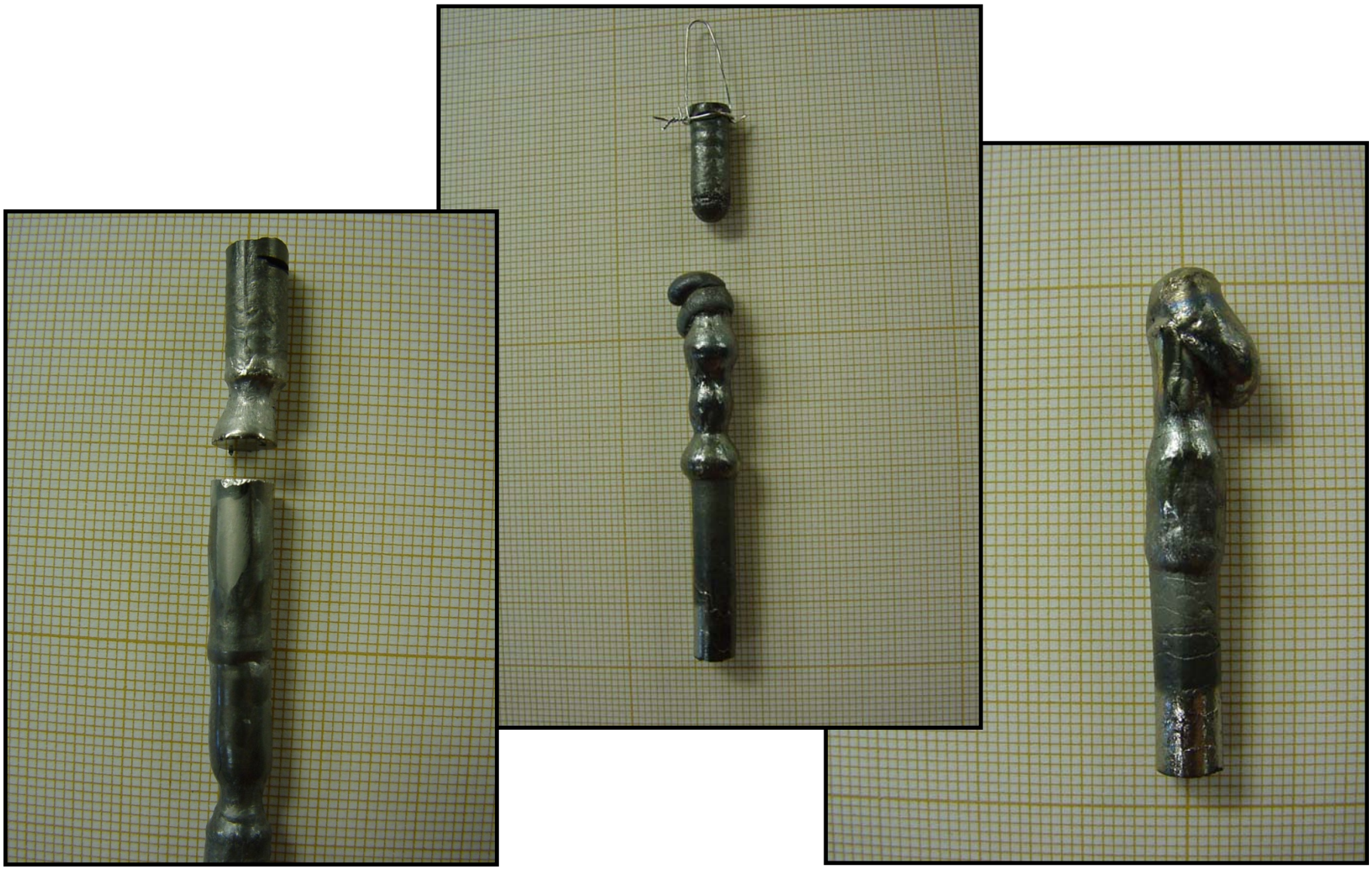
Pushing down rod to feed the hot spot …
Wait for thermal equilibrium …
>> hemispherical melt



Polycrystalline feed rod

Growth speed ≈ 10mm/h

The real life …

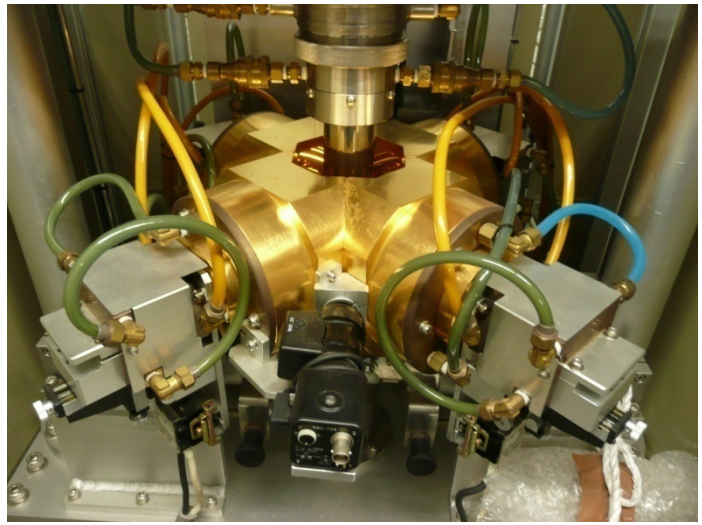


CEA Grenoble, *courtesy of G. Lapertot*

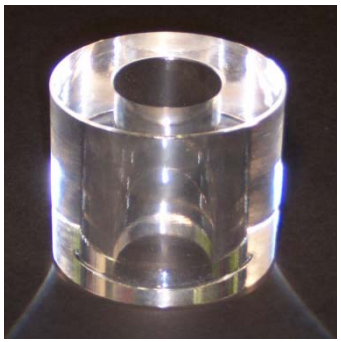
TSFZ Furnaces

ISU - Ames

Two mirror, four mirror

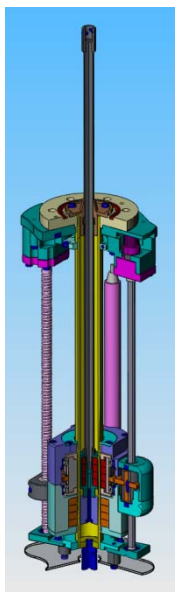


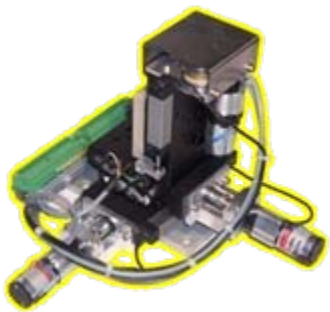
High pressure floating zone



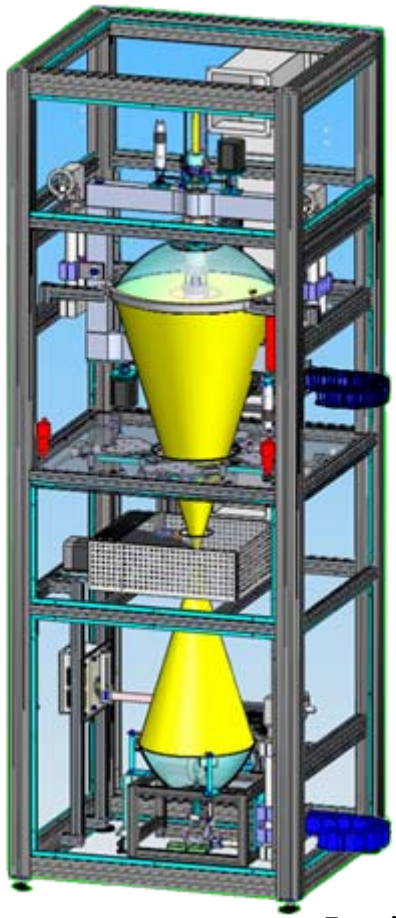
High pressure – 15 MPa (2200 PSI)

High precision pulling drives
> 0.1 mm/h, pressure independent



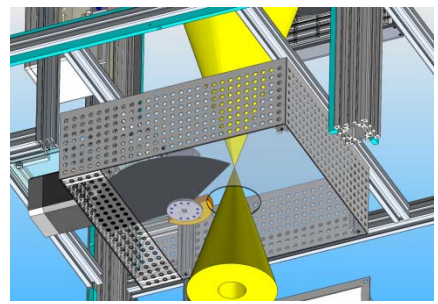


In situ control of lamp x-y-z position



Temperature up to 3000°C (5400 F)
Xe arc lamp 3 – 5 – 7 kW

In situ scan of zone temperature



In situ temperature measurement by
two color pyrometer using a light shutter

IFW Dresden, Germany, *Courtesy of Günter Behr*

Micropulling

Avoids large consumption of material (~ 1g)

Considerable crystalization speed (1mm/min.)

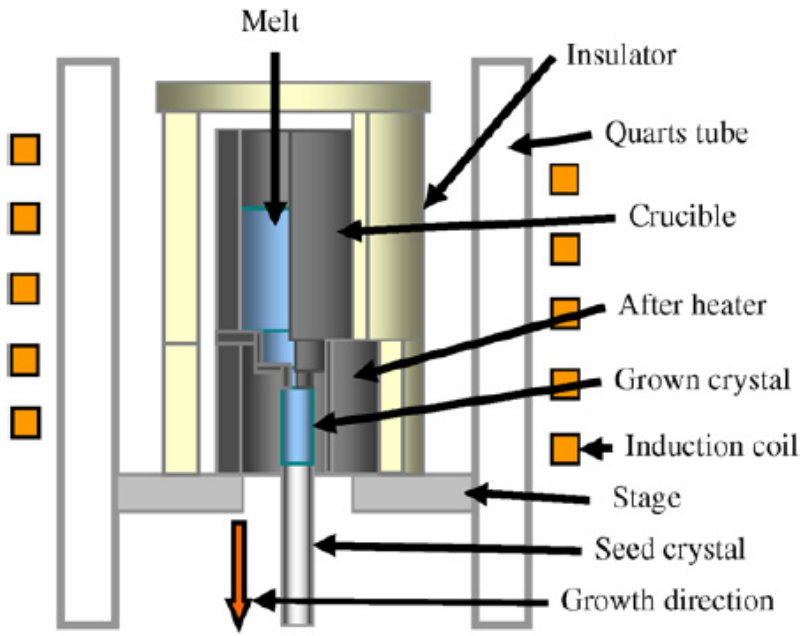
Crucible used as a shaper of material

Resistive, RF and other types of heating

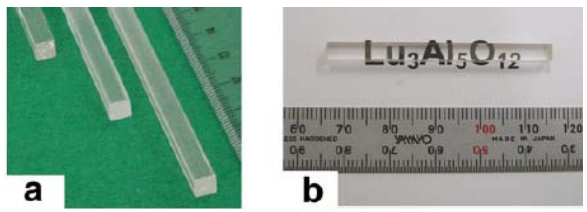
Small diameters of grown crystals are possible
So that there is small ΔT in the core and periphery\

High temperatures and gas environments are possible

Device – size shaping is possible

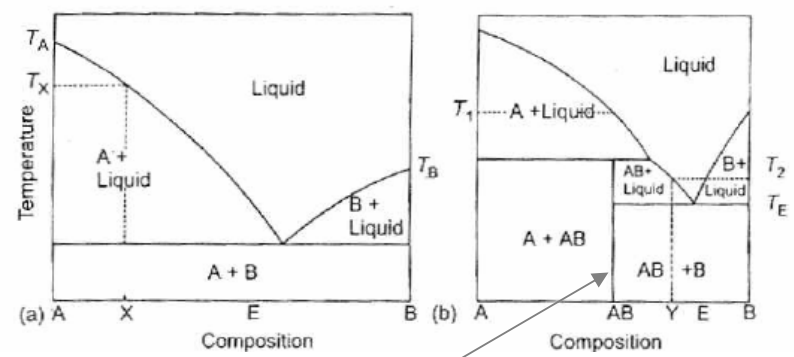


Optical Materials 30, 6 (2007)



Crystal growth from melts

Starting state is (often) homogeneous solution with fast atomic diffusion
Synthesis occurs at lower temperatures than Tm
Suitable for exploratory synthesis



Material is dissolved (solute) in suitable non – reactive solvent
Crystallization driven by reducing solubility of solute (lower T) or by increasing solute concentration in the solution (evaporation

Solvent may coexist with the crystal on many length scales:
Atomic substitution or interstitial, grain inclusion, surface blobs
Some measurement techniques may be affected but some are not

Making incongruently melting compound AB: X = Y, not AB

Reduce melting point of pure solute by forming solution (Flux)

Consider a system where A is solute and B is solvent:
With addition of B, melting point of A-B mixture decreases.

Slow cooling of composition X between TX and TE will make crystals of A + some liquid ('flux") whose composition C=C(T)

At TE solid eutectic mixture of large A crystals and small B crystallites

Goal: to extract crystals appropriate for particular measurement + free of secondary phase influences

Solvents can be low melting point metals with low vapor pressure:
Ga, In, Sn, Sb, Pb, Bi, Al,

Elements with higher vapor pressure
Zn, Cd, Te, Se, S, As, I

Inorganic (often complex) compounds
InS, Sb_2S_3, Bi_2O_3, SnF_2, KF, Na_2B4O_7….

Other solvents using advanced high T, P techniques and methods
Cu, Ce, Ni, Co, Si, Ge, N

ACADÉMIE DES SCIENCES. SÉANCE DU 10 JANVIER 1910.

CHIMIE MINÉRALE. — *Sur deux nouveaux phosphures de nickel.* Note de M. **Pierre Jolibois**, présentée par M. H. Le Chatelier.

Mes essais ont porté sur le nickel. Pour effectuer la réaction je suis parti d'un alliage de nickel et d'étain à 5 pour 100 de nickel. J'ai vérifié que l'on pouvait isoler de ce dernier le composé NiSn déjà décrit par Vigouroux (²) et par Guillet (³). En enfermant dans des tubes en verre d'Iéna vides d'air 21ᵍ d'alliage avec des quantités de phosphore variant de 1ᵍ à 4ᵍ après avoir chauffé le tube à 700°, j'ai isolé au moyen de l'acide chlorhydrique concentré et chaud de petits cristaux prismatiques très bien formés. Leur composition est voisine de NiP^2.

Pr. H Le Chatelier 1850-1936

New Fe-As superconductors are made using this method

Handbook on the Physics and Chemistry of Rare Earths, Vol. 12
edited by K.A. Gschneidner, Jr. and L. Eyring

Chapter 81

GROWTH OF SINGLE CRYSTALS FROM MOLTEN METAL FLUXES

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PHILOSOPHICAL MAGAZINE B, 1992, VOL. 65, NO. 6, 1117–1123

Growth of single crystals from metallic fluxes

By P. C. CANFIELD and Z. FISK
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Los Alamos, New Mexico 87545, USA

Other references:
I. R. Fisher and P. C. Canfield, Journal of Crystal Growth 225 (2001) 155–161
M. G. Kanatzidis, R. Pttgen and Wolfgang Jeitschko, Angew. Chem. Int. Ed. 2005, 44, 6996 – 7023

High Temperature Intermetallic Solutions

I. R. Fisher and P. C. Canfield, Journal of Crystal Growth 225 (2001) 155–161

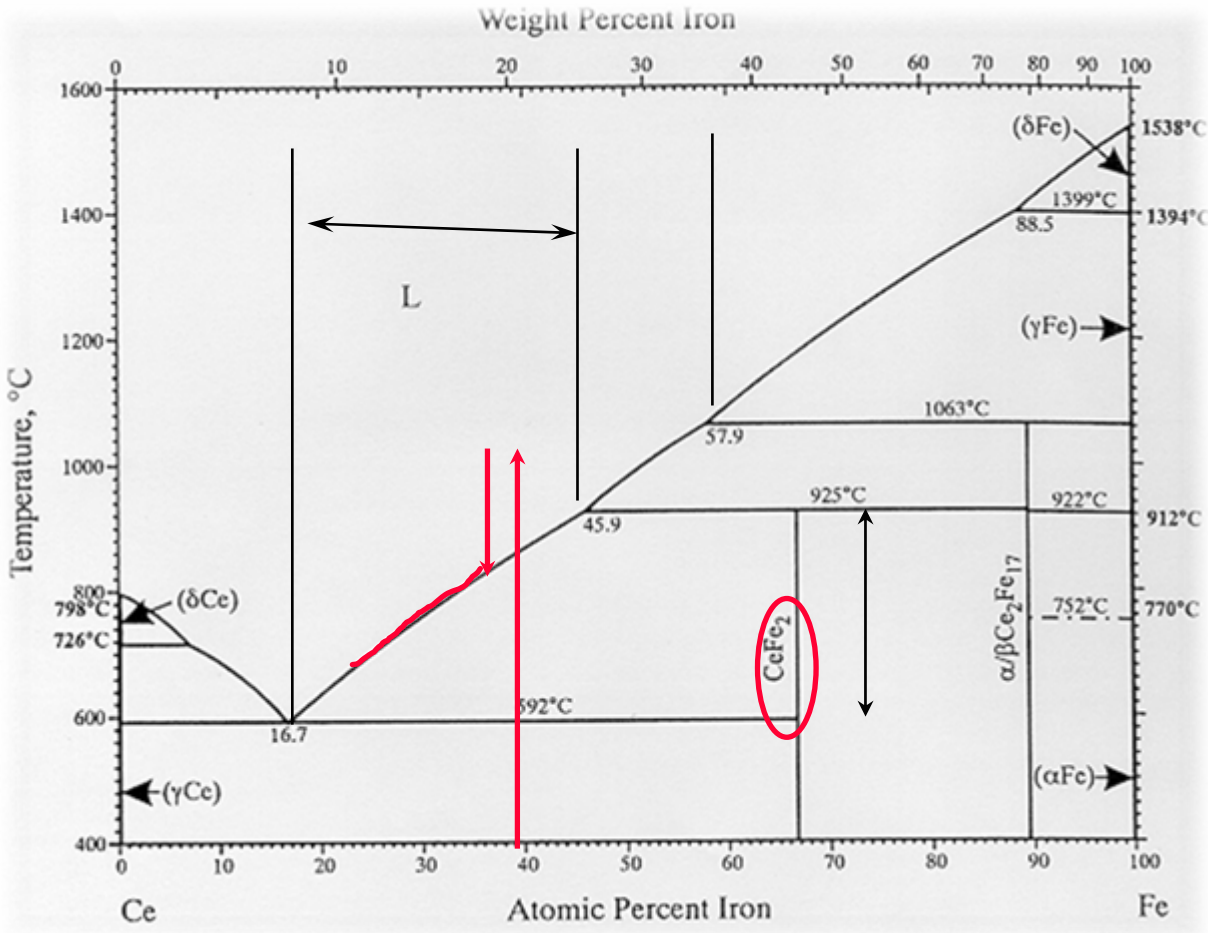
Single crystal samples allow for the measurement of the intrinsic properties of materials. In specific, they generally provide samples with less strain, higher purity, fewer grain boundaries, and natural growth habit. For basic studies of the electronic, magnetic, thermodynamic and structural properties of new or exotic materials the size of single crystals required rarely exceeds a cubic centimeter and often (with the exception of inelastic neutron scattering) crystals with dimensions of several mm on a side are more than adequate. Given that the majority of materials are incongruently melting, a technique that can grow a wide variety of congruently ***and*** incongruently melting materials with equal ease, with relatively simple equipment, in rather short time scales, is of great desirability. Growth from high-temperature metallic solutions is just such a technique. In addition it uses relatively small amounts of materials, making it much more economic than techniques such as Bridgman or Czochralski (CZ) growth, both of which require more substantial quantities raw material.

Growth of single crystals from metallic solutions requires very simple equipment: box and vertical tube furnaces, a glass bench for evacuating and sealing quartz tubes, crucible materials and, in some cases, an arcmelter for pre-alloying elements and for working with Ta. Many of these details have been covered in the earlier two articles [1,2] and will not be reviewed here.

Given the reactivity of certain elements with Al_2O_3 (excessive Ce and Mg for example), a Ta crucible is sometimes needed. So as to allow for the decanting of the excess melt from the grown crystals a sealed Ta crucible with a built-in strainer is used. A simple, but effective version of such a crucible is referred to as a "3-cap crucible" because it can be made from a length of Ta tubing and three Ta caps, made of Ta sheet that have been machined to just fit inside of the Ta tube. One of the caps is arc-welded into the tube, closing it and creating a crucible, then the material is placed into the bottom of the crucible and the second cap, with holes drilled through it, is crimped into place just above the level of the solid material. Finally, the third cap is arc welded into place, sealing the crucible. Once the growth is completed the crucible can be inverted for decanting.

Molten Metallic Fluxes

Metallurgical phase diagrams allow us to determine step I - (stochiometry) and II - (T profile & final T)



Crystal $CeFe_2 \neq Ce_{0.33}Fe_{0.66}$

Starting from $Ce_{0.65}Fe_{0.35}$

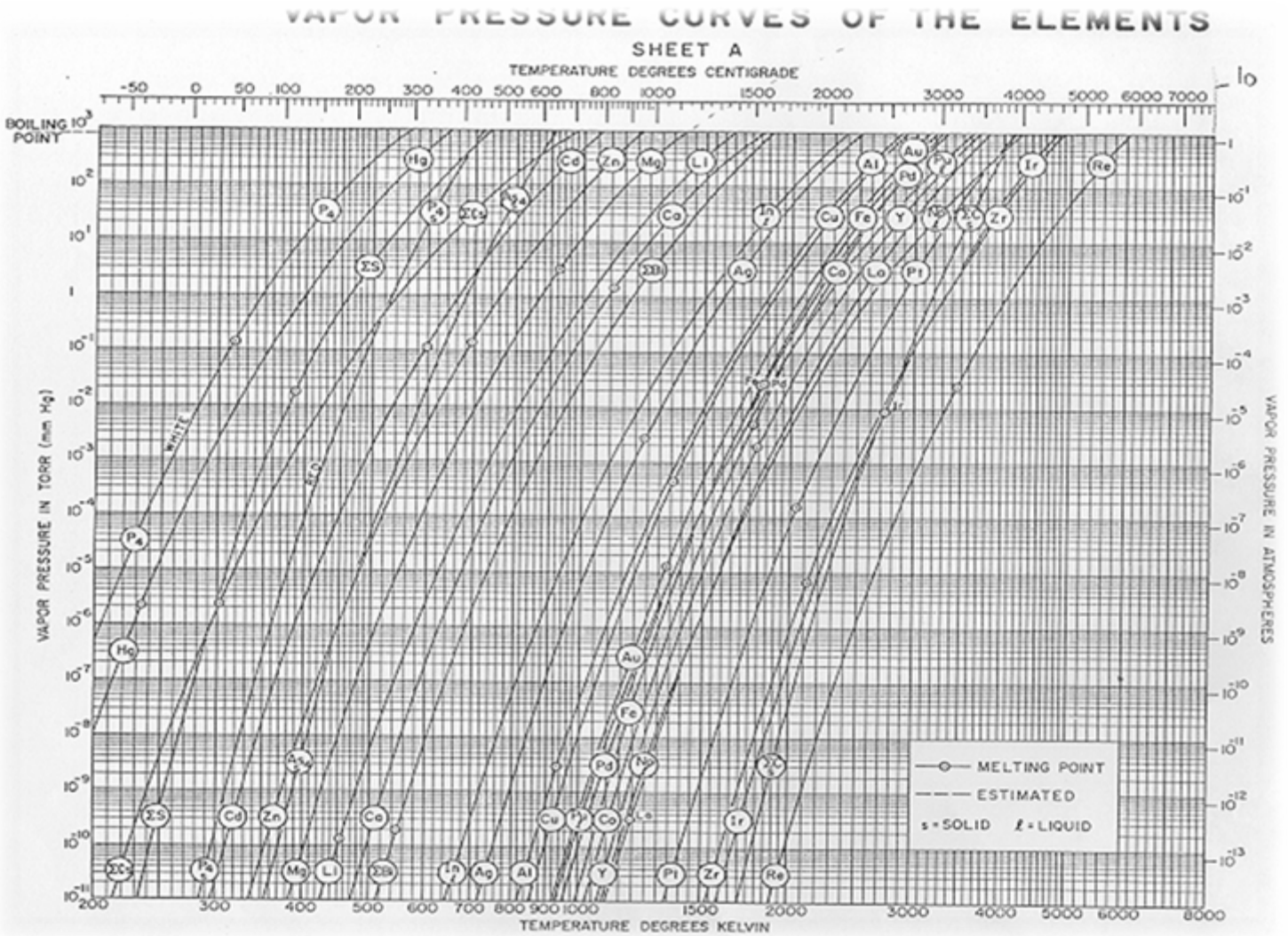
Tmax = 1050°

Tspin = 650°

Tantalum crucible

Vapor Pressure

Step III : Open or closed ampoule: vapor pressure = f (T)



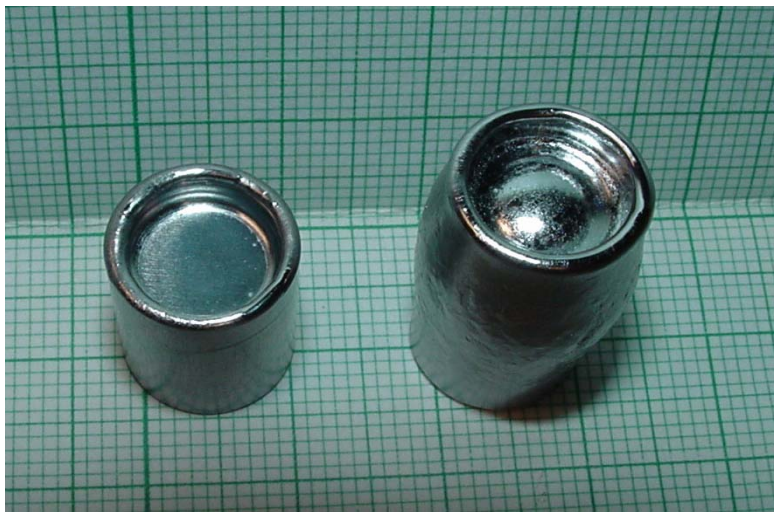
$ZrZn_2$

$SmRu_4P_{12}$

MgB_2

Yb, Eu....

Holding inside pressure .....or not !



CEA Grenoble *Courtesy of Gerard Lapertot*

Crucibles

Step IV: crucible choice

The material choice depends on relative compatibility between flux/crucible

Al_2O_3 90%

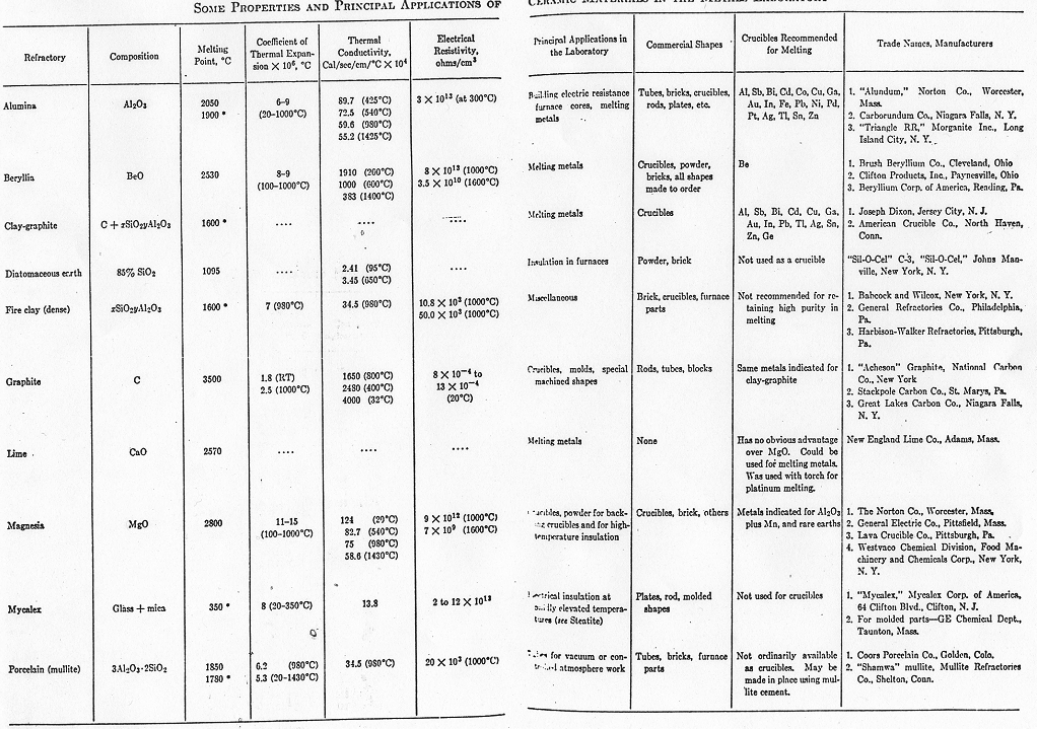
Ta, Mo, W, Pt 5%

Y_2O_3, MgO, ZrO_2 5%

Al_2O_3 [rare earth] ≤ 10%

$CeFe_2$ ⇒ Ta crucible

Yb vapors may react with quartz wool

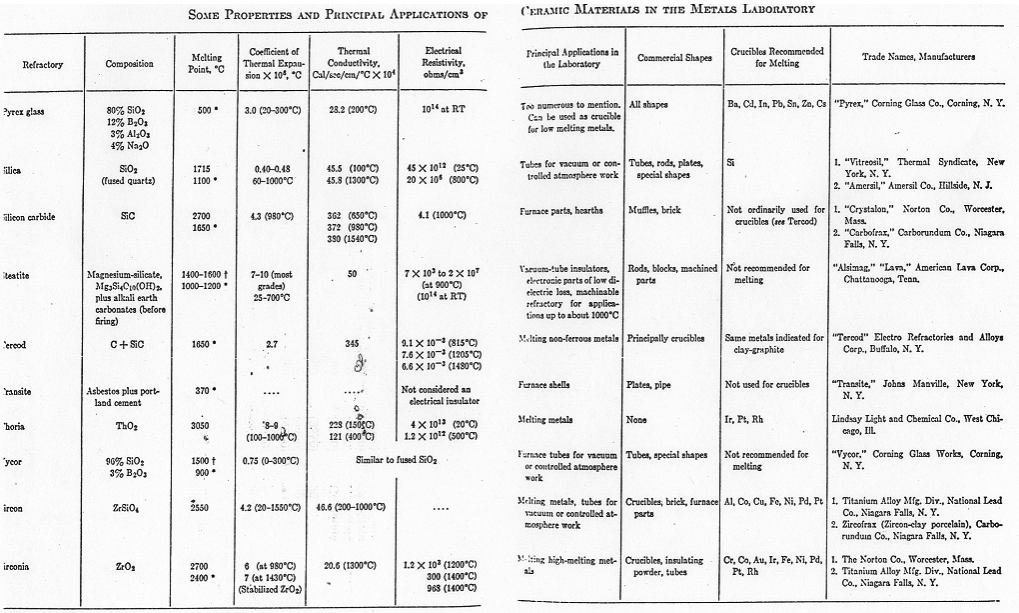


Some Properties and Principal Applications of

Refractory	Composition	Melting Point, °C	Coefficient of Thermal Expansion × 10⁶, °C	Thermal Conductivity, Cal/sec/cm/°C × 10⁴	Electrical Resistivity, ohms/cm³
Alumina	Al_2O_3	2050 1900 *	6–9 (20–1000°C)	89.7 (425°C) 72.5 (540°C) 59.6 (980°C) 55.2 (1425°C)	3×10^{13} (at 300°C)
Beryllia	BeO	2530	8–9 (100–1000°C)	1910 (200°C) 1000 (600°C) 383 (1400°C)	8×10^{13} (1000°C) 3.5×10^{10} (1600°C)
Clay-graphite	C + $zSiO_2yAl_2O_3$	1600 *	....	....	....
Diatomaceous earth	85% SiO_2	1005	....	2.41 (95°C) 3.45 (650°C)	....
Fire clay (dense)	$zSiO_2yAl_2O_3$	1600 *	7 (980°C)	34.5 (980°C)	10.8×10^3 (1000°C) 50.0×10^3 (1000°C)
Graphite	C	3500	1.8 (RT) 2.5 (1000°C)	1650 (800°C) 2480 (400°C) 4000 (32°C)	8×10^{-4} to 13×10^{-4} (20°C)
Lime	CaO	2570	....	....	....
Magnesia	MgO	2800	11–15 (100–1000°C)	124 (20°C) 32.7 (540°C) 75 (980°C) 58.6 (1430°C)	9×10^{12} (1000°C) 7×10^9 (1600°C)
Mycalex	Glass + mica	350 *	8 (20–350°C)	13.8	2 to 12 × 10^{13}
Porcelain (mullite)	$3Al_2O_3 \cdot 2SiO_2$	1850 1780 *	6.2 (980°C) 5.3 (20–1430°C)	34.5 (980°C)	20×10^3 (1000°C)

Ceramic Materials in the Metals Laboratory

Principal Applications in the Laboratory	Commercial Shapes	Crucibles Recommended for Melting	Trade Names, Manufacturers
Building electric resistance furnace cores, melting metals	Tubes, bricks, crucibles, rods, plates, etc.	Al, Sb, Bi, Cd, Co, Cu, Ga, Au, In, Fe, Pb, Ni, Pd, Pt, Ag, Tl, Sn, Zn	1. "Alundum," Norton Co., Worcester, Mass. 2. Carborundum Co., Niagara Falls, N. Y. 3. "Triangle RR," Morganite Inc., Long Island City, N. Y.
Melting metals	Crucibles, powder, bricks, all shapes made to order	Be	1. Brush Beryllium Co., Cleveland, Ohio 2. Clifton Products, Inc., Paynesville, Ohio 3. Beryllium Corp. of America, Reading, Pa.
Melting metals	Crucibles	Al, Sb, Bi, Cd, Cu, Ga, Au, In, Pb, Tl, Ag, Sn, Zn, Ge	1. Joseph Dixon, Jersey City, N. J. 2. American Crucible Co., North Haven, Conn.
Insulation in furnaces	Powder, brick	Not used as a crucible	"Sil-O-Cel" C-3, "Sil-O-Cel," Johns Manville, New York, N. Y.
Miscellaneous	Brick, crucibles, furnace parts	Not recommended for retaining high purity in melting	1. Babcock and Wilcox, New York, N. Y. 2. General Refractories Co., Philadelphia, Pa. 3. Harbison-Walker Refractories, Pittsburgh, Pa.
Crucibles, molds, special machined shapes	Rods, tubes, blocks	Same metals indicated for clay-graphite	1. "Acheson" Graphite, National Carbon Co., New York 2. Stackpole Carbon Co., St. Marys, Pa. 3. Great Lakes Carbon Co., Niagara Falls, N. Y.
Melting metals	None	Has no obvious advantage over MgO. Could be used for melting metals. Was used with torch for platinum melting.	New England Lime Co., Adams, Mass.
...cibles, powder for back-... crucibles and for high-temperature insulation	Crucibles, brick, others	Metals indicated for Al_2O_3 plus Mn, and rare earths	1. The Norton Co., Worcester, Mass. 2. General Electric Co., Pittsfield, Mass. 3. Lava Crucible Co., Pittsburgh, Pa. 4. Westvaco Chemical Division, Food Machinery and Chemicals Corp., New York, N. Y.
...trical insulation at ...ly elevated temperatures (see Steatite)	Plates, rod, molded shapes	Not used for crucibles	1. "Mycalex," Mycalex Corp. of America, 64 Clifton Blvd., Clifton, N. J. 2. For molded parts—GE Chemical Dept., Taunton, Mass.
...s for vacuum or con...lled atmosphere work	Tubes, bricks, furnace parts	Not ordinarily available as crucibles. May be made in place using mullite cement.	1. Coors Porcelain Co., Golden, Colo. 2. "Shamwa" mullite, Mullite Refractories Co., Shelton, Conn.



Some Properties and Principal Applications of

Refractory	Composition	Melting Point, °C	Coefficient of Thermal Expansion × 10⁶, °C	Thermal Conductivity, Cal/sec/cm/°C × 10⁴	Electrical Resistivity, ohms/cm³
Pyrex glass	80% SiO_2 12% B_2O_3 3% Al_2O_3 4% Na_2O	500 *	3.0 (20–300°C)	22.2 (200°C)	10^{14} at RT
Silica	SiO_2 (fused quartz)	1715 1100 *	0.40–0.48 60–1000°C	45.5 (100°C) 45.8 (1300°C)	45×10^{12} (25°C) 20×10^8 (800°C)
Silicon carbide	SiC	2700 1650 *	4.3 (980°C)	302 (650°C) 372 (980°C) 330 (1540°C)	4.1 (1000°C)
Steatite	Magnesium-silicate, $Mg_3Si_4O_{10}(OH)_2$, plus alkali earth carbonates (before firing)	1400–1600 † 1000–1200 *	7–10 (most grades) 25–700°C	50	7×10^3 to 2×10^7 (at 900°C) (10^{14} at RT)
Tercod	C + SiC	1650 *	2.7	345	9.1×10^{-2} (815°C) 7.6×10^{-2} (1205°C) 6.6×10^{-2} (1480°C)
Transite	Asbestos plus portland cement	370 *	....	....	Not considered an electrical insulator
Thoria	ThO_2	3050	8–9 (100–1000°C)	228 (150°C) 121 (400°C)	4×10^{12} (20°C) 1.2×10^{12} (500°C)
Vycor	96% SiO_2 3% B_2O_3	1500 † 900 *	0.75 (0–300°C)	Similar to fused SiO_2	
Zircon	$ZrSiO_4$	2550	4.2 (20–1550°C)	46.6 (200–1000°C)	....
Zirconia	ZrO_2	2700 2400 *	6 (at 980°C) 7 (at 1430°C) (Stabilized ZrO_2)	20.6 (1300°C)	1.2×10^3 (1200°C) 300 (1400°C) 963 (1400°C)

Ceramic Materials in the Metals Laboratory

Principal Applications in the Laboratory	Commercial Shapes	Crucibles Recommended for Melting	Trade Names, Manufacturers
Too numerous to mention. Can be used as crucible for low melting metals.	All shapes	Ba, Cd, In, Pb, Sn, Zn, Cs	"Pyrex," Corning Glass Co., Corning, N. Y.
Tubes for vacuum or controlled atmosphere work	Tubes, rods, plates, special shapes	Si	1. "Vitreosil," Thermal Syndicate, New York, N. Y. 2. "Amersil," Amersil Co., Hillside, N. J.
Furnace parts, hearths	Muffles, brick	Not ordinarily used for crucibles (see Tercod)	1. "Crystalon," Norton Co., Worcester, Mass. 2. "Carborfrax," Carborundum Co., Niagara Falls, N. Y.
Vacuum-tube insulators, electrode parts of low dielectric loss, machinable refractory for applications up to about 1000°C	Rods, blocks, machined parts	Not recommended for melting	"Alsimag," "Lava," American Lava Corp., Chattanooga, Tenn.
Melting non-ferrous metals	Principally crucibles	Same metals indicated for clay-graphite	"Tercod" Electro Refractories and Alloys Corp., Buffalo, N. Y.
Furnace shells	Plates, pipe	Not used for crucibles	"Transite," Johns Manville, New York, N. Y.
Melting metals	None	Ir, Pt, Rh	Lindsay Light and Chemical Co., West Chicago, Ill.
Furnace tubes for vacuum or controlled atmosphere work	Tubes, special shapes	Not recommended for melting	"Vycor," Corning Glass Works, Corning, N. Y.
Melting metals, tubes for vacuum or controlled atmosphere work	Crucibles, brick, furnace parts	Al, Co, Cu, Fe, Ni, Pd, Pt	1. Titanium Alloy Mfg. Div., National Lead Co., Niagara Falls, N. Y. 2. Zircofrax (Zircon-clay porcelain), Carborundum Co., Niagara Falls, N. Y.
Melting high-melting metals	Crucibles, insulating powder, tubes	Cr, Co, Au, Ir, Fe, Ni, Pd, Pt, Rh	1. The Norton Co., Worcester, Mass. 2. Titanium Alloy Mfg. Div., National Lead Co., Niagara Falls, N. Y.

Various quartz ampoule assembly

Al_2O_3/metal open

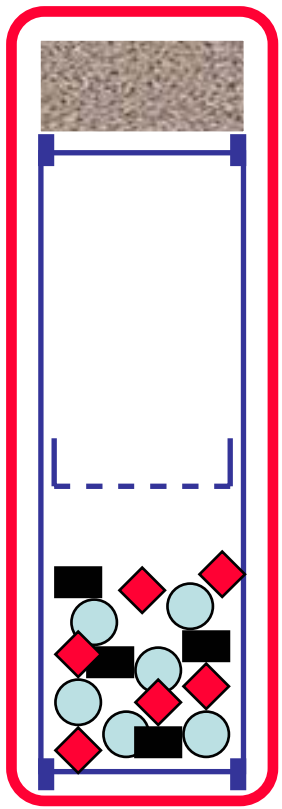
«$CeIn_3$»

initial

final

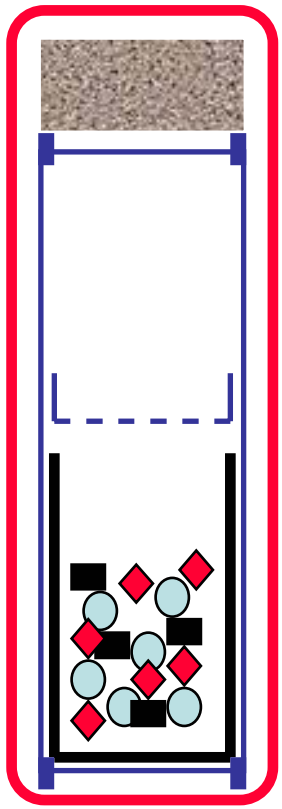
Welded Ta crucible

«$CeFe_2$»



hybride cera-metal

«$ZrZn_2$»



Chemical Compatibility

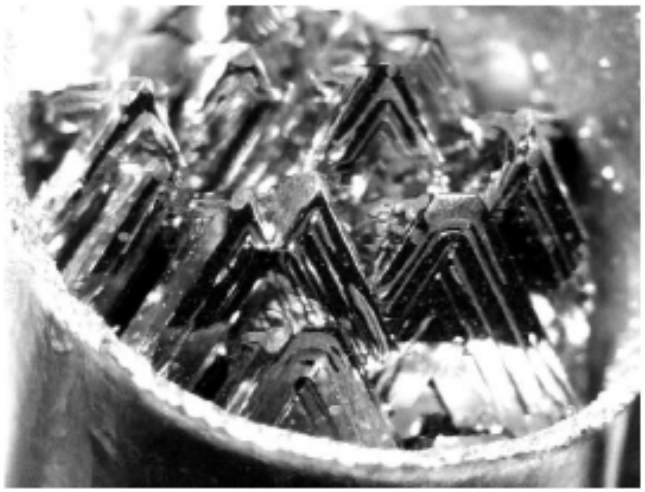


Fig. 1. Single crystals of $GdFe_2$ in remains of 15 mm OD Ta crucible. The larger facet edges are approximately 5 mm.

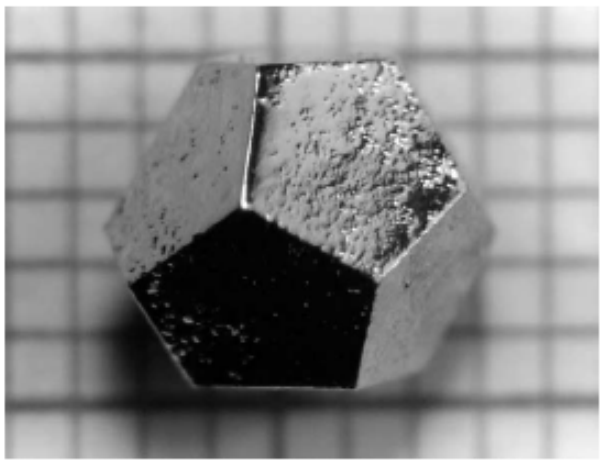


Fig. 3. Single grain of icosahedral $Ho_9Mg_{34}Zn_{57}$ on a mm-grid [7].

$GdFe_2$ crystals and $Ho_9Mg_{34}Zn_{57}$ quasicrystals from Ta crucible
I. R. Fisher and P. C. Canfield,
Journal of Crystal Growth 225 (2001) 155–161

CEA Grenoble *Courtesy of Gerard Lapertot*

poor chemical compatibility between materials

Advantages and Disadvantages of Flux Method

Advantages of flux growth :

- better RRR compared all T >Tf methods like CZ, Bridgman, Zone melting
  MnSi (140), $YbRh_2Si_2$ (130), $YbCu_2Si_2$ (120),
- Size depends on material but are ok lots of physics measurments (R, Cp…)
- Save money (low [rare earth, Rh, Pd, Ir], isotope - 100mg) / melts for CZ (10grs)
- resistive furnaces, relatively cheap crucible (13$ for Al2O3 or MgO).
- possibility to discover new phases - **EXPLORATORY**
- quick to start an experiment.
- possibility for solid solutions, isotope.

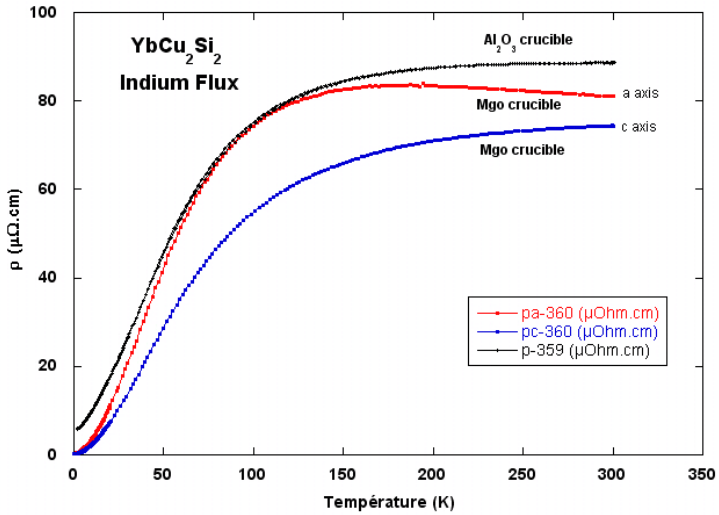
drawbacks :

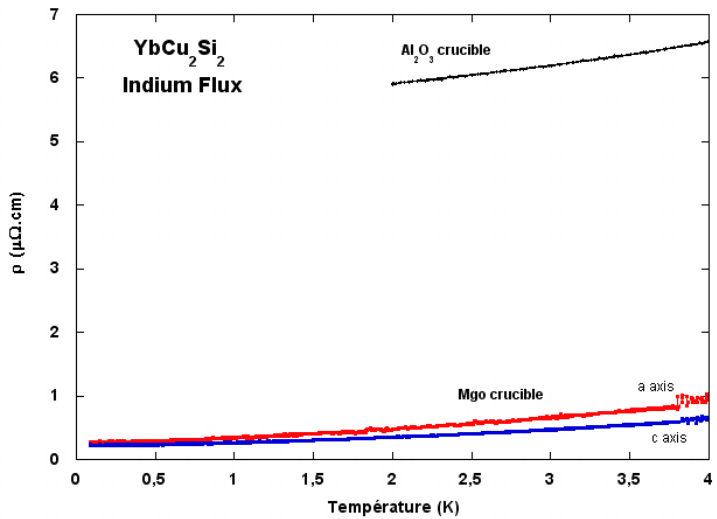
- Annealing is 'dangerous'
- Tmax quartz 1200° (1500°, H.F.) 2 steps.
- Chemical compatibility issues.
- No control/prediction of volume and direction of growth.

Flux and crucible interference

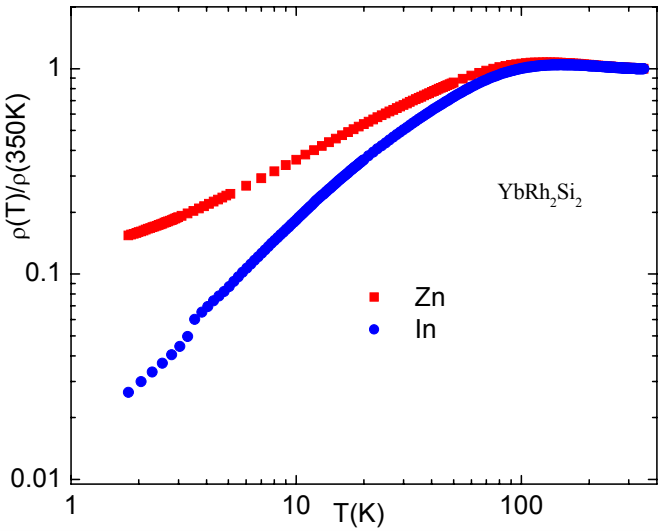
Al_2O_3 RRR 300-2K = 15

MgO RRR 300-2K
a axis = 171
c axis = 212





J. Cryst. Growth 304, 114 (2007)



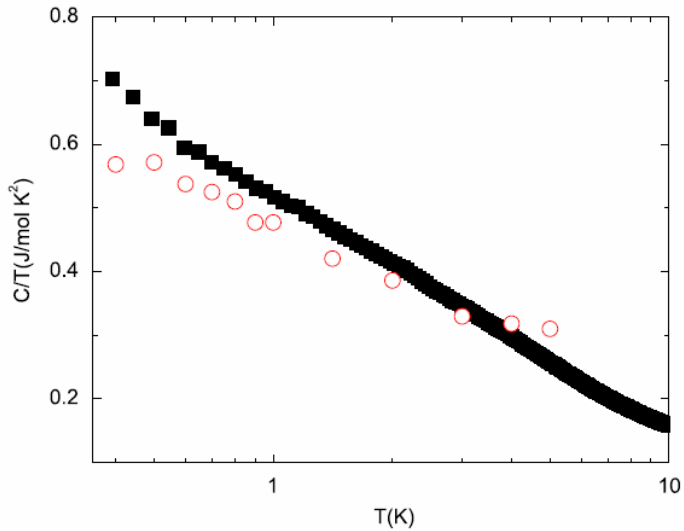
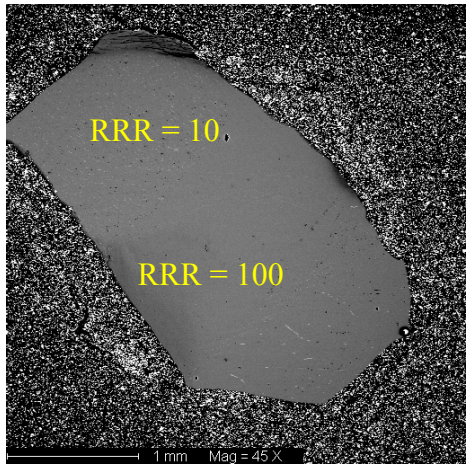
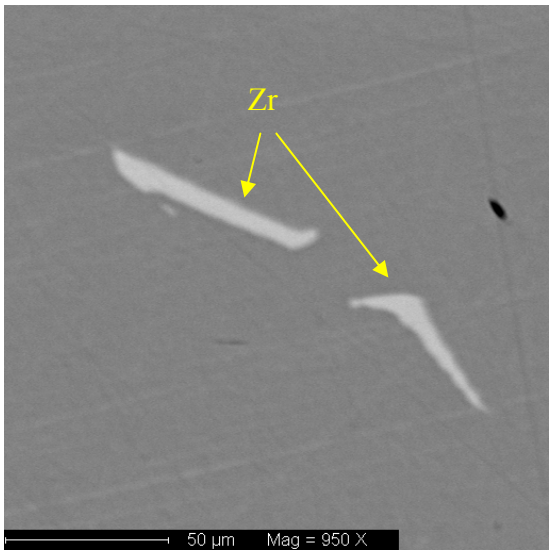


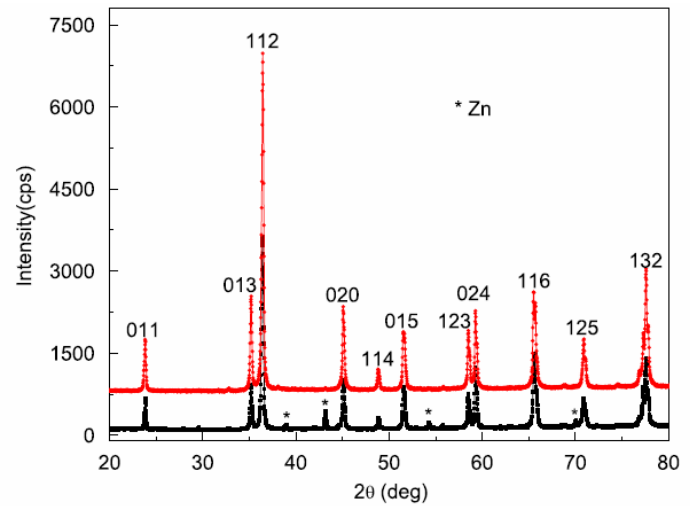
Fig. 5. Heat capacity of $YbRh_2Si_2$ grown from Zn melts. Open symbols are obtained on samples grown from In flux [8].

CEA Grenoble *Courtesy of Gerard Lapertot*

Example of Flux removal



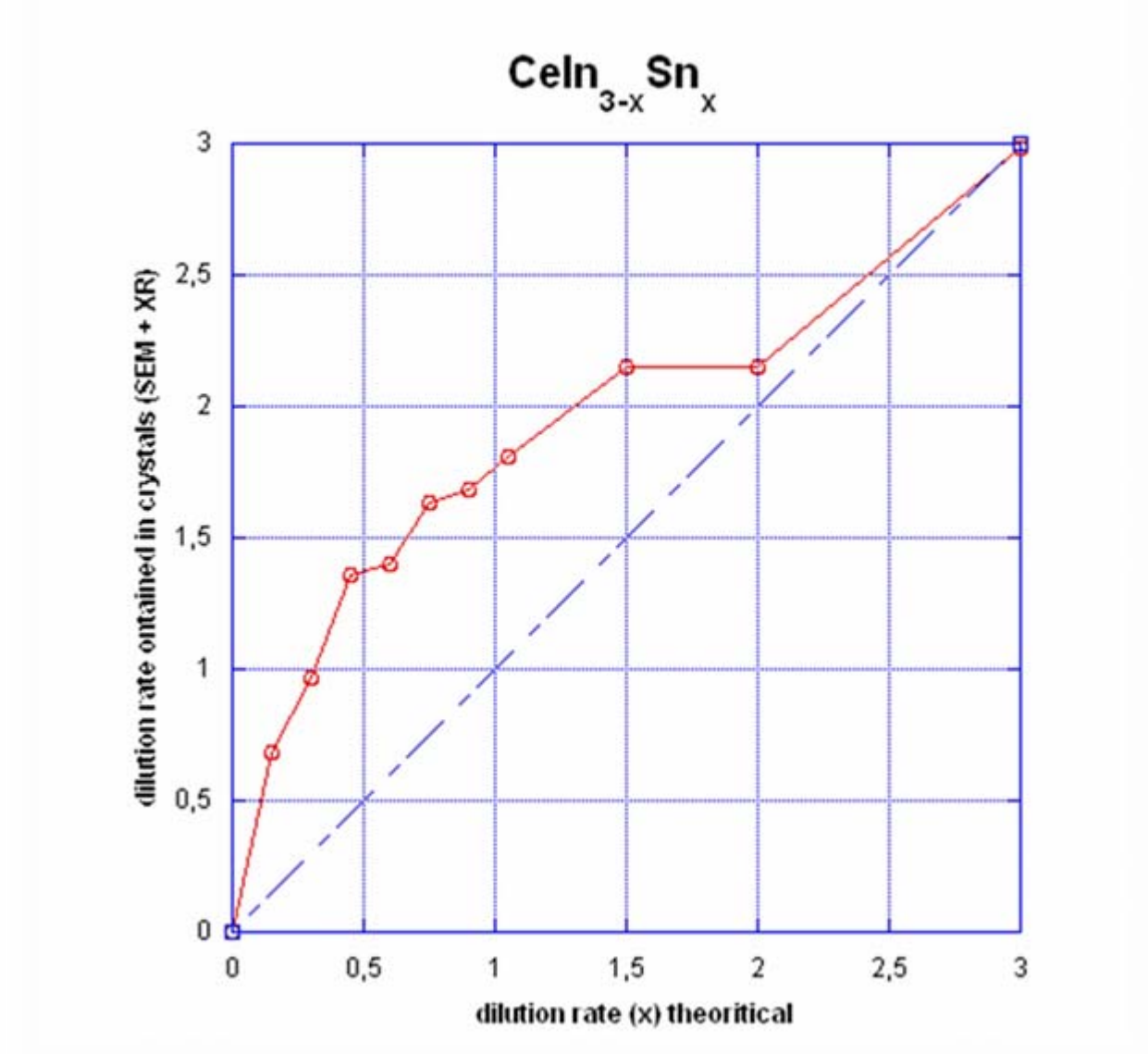




CEA Grenoble *Courtesy of Gerard Lapertot*

J. Cryst. Growth 304, 114 (2007)

Preferential solubility of components in crystals



Flux crystal growth laboratory

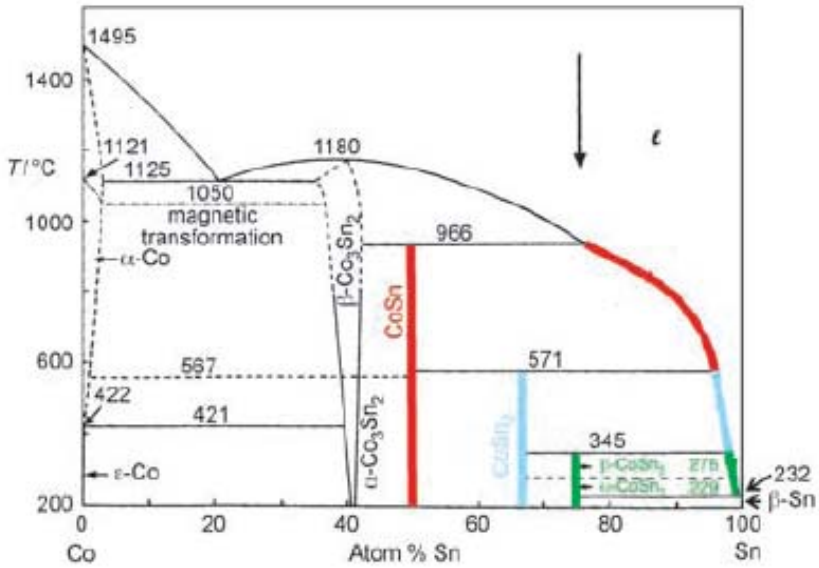
Petrovic lab at BNL

Petrovic lab at BNL

CEA Grenoble *Courtesy of Gerard Lapertot*

Petrovic lab at BNL

Incongruent AND congruent melters



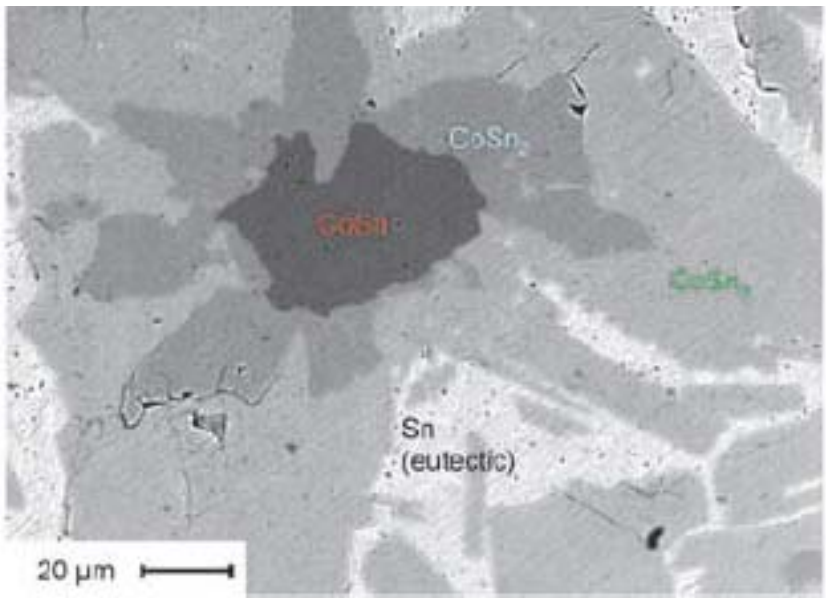


Figure 1. Peritectic reactions in the binary system Co–Sn. Top: the phase diagram of the Co–Sn system. By rapidly cooling a melt (liquidus, ℓ) of the approximate composition Co:Sn = 1:3 (large black arrow) crystals of composition CoSn are obtained first. Since these crystals have a higher Co content than the original melt, the liquid phase changes its composition on cooling along the red liquidus line. At 571 °C the crystals of CoSn start to react with the remaining melt, thereby forming a microcrystalline envelope of the compound $CoSn_2$. During this reaction, the liquid phase changes its composition along the blue line. After further cooling, at 345 °C, the melt, now with a Sn content of approximately 98 atom%, starts to react with $CoSn_2$ and forms another microcrystalline envelope this time of microcrystalline β-$CoSn_3$. Thereby the melt changes its composition along the green line. Finally, at 229 °C it solidifies, to form the eutectic, which consists of a matrix of a solid solution of Co in β-Sn with heterogeneous inclusions of α-$CoSn_3$. Bottom: A micrograph of a corresponding sample (with the slightly different overall composition Co:Sn = 1:4).[41] It is clear that well developed large crystals of α- or β-$CoSn_3$ cannot be grown by such a cascade of peritectic reactions. This sample has been cooled at the relatively slow rate of 100 °C h^{-1}. Nevertheless, it has not reached thermodynamic equilibrium. In its center it contains the remains of a primarily crystallized grain of CoSn, embedded in grains of $CoSn_2$. Before reaching equilibrium the sample had cooled to 345 °C, thus forming β-$CoSn_3$.

M. G. Kanatzidis, R. Pttgen and Wolfgang Jeitschko,
Angew. Chem. Int. Ed. 2005, 44, 6996 – 7023

High Temperature Intermetallic Solutions

Ternary compounds from quaternary melts

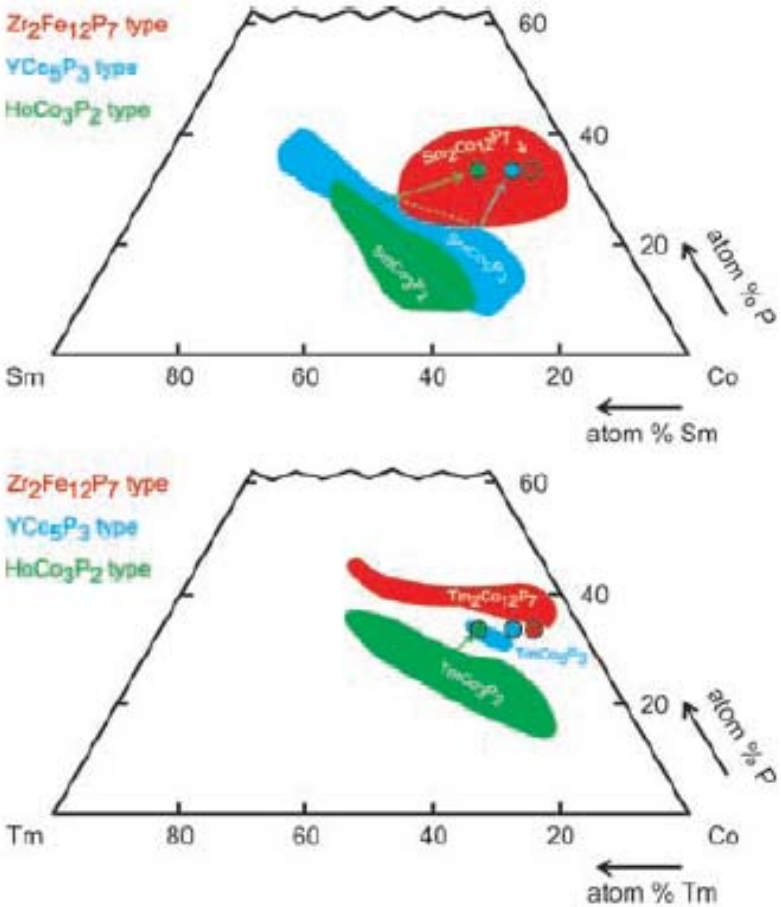


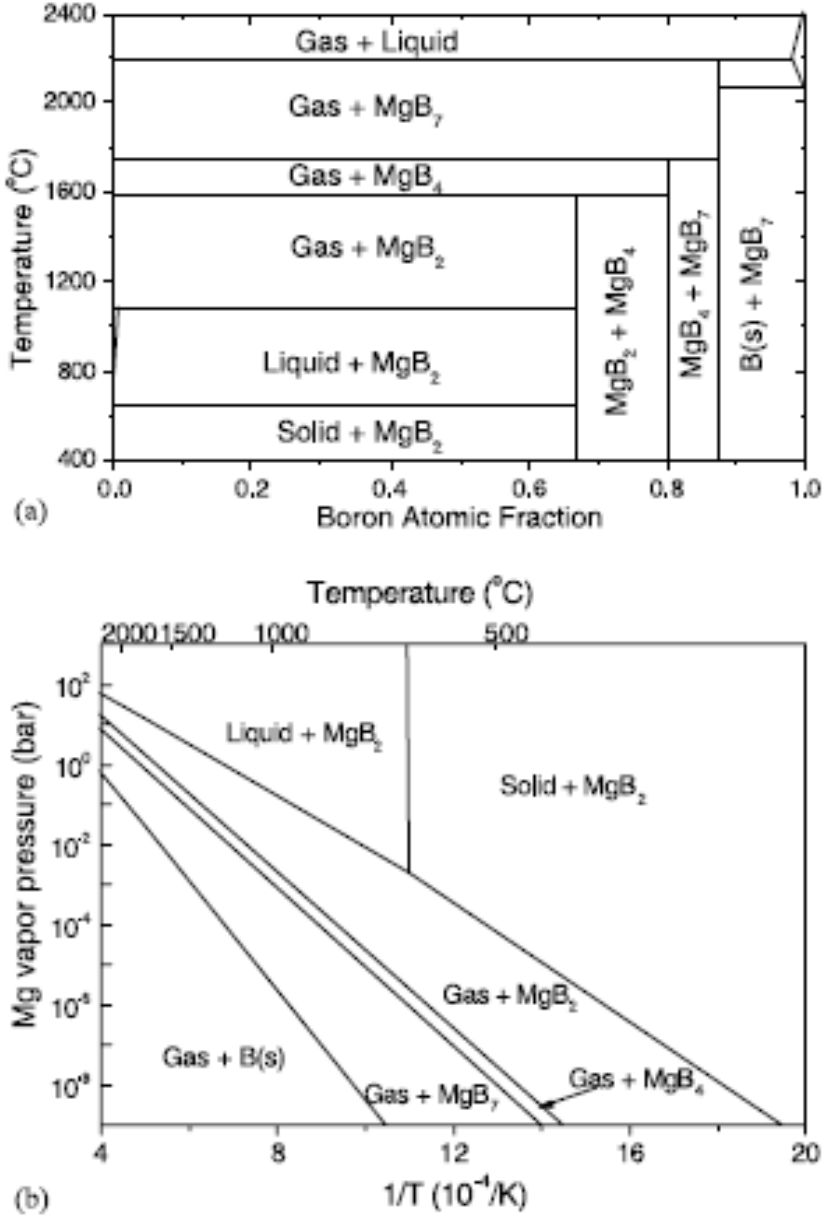
Figure 7. Sample compositions for the preparation of ternary Sm (top) and Tm (bottom) cobalt phosphides from a tin flux. All samples were prepared with 75 atom% tin as a flux. The diagrams indicate the ratio of the remaining 25 % of the elements samarium, thulium, cobalt, and phosphorus. The phase diagrams contain several ternary phosphide phases. Only the sample compositions resulting in ternary phosphides with $Zr_2Fe_{12}P_7$-type,[107a] YCo_5P_3-type,[112] and $HoCo_3P_2$-type[117a] structures are shown. The compositions of the ternary phosphides are indicated by large colored dots. All samples were equilibrated for two weeks at 850 °C and the tin-rich matrix was dissolved in diluted hydrochloric acid.[117b]

M. G. Kanatzidis, R. Pttgen and Wolfgang Jeitschko, Angew. Chem. Int. Ed. 2005, 44, 6996 – 7023

High Pressure Flux Growth

Growth of MgB_2 crystals: J. Karpinski et al., Physica C 385, 42 (2003)

to be studied on single crystals. Soon after the discovery of superconductivity in MgB_2, several laboratories started to work on single crystal growth. Unfortunately, conventional methods of crystal growth, like a growth from high temperature solutions in metals (Al, Mg, Cu, etc.) at ambient pressure, used for other borides, did not work for MgB_2. Since MgB_2 melts non-congruently, it is also not possible to grow crystals from a stoichiometric melt. MgB_2 crystals can be grown from a solution in Mg at high pressure, or from the vapor phase. Two methods result in submillimeter size single crystals: high pressure growth using an anvil technique [4–7] and heating of a mixture of Mg and B in closed metal container [8–10]. Larger crystals have been obtained using the first method. The solubility of MgB_2 in Mg is extremely low at temperatures below the boiling temperature of Mg (1107 °C) at ambient pressure (Fig. 1(a)), therefore crystals have to be grown at much higher temperature or by using another solvent. At higher temperatures at ambient pressure, Mg does not exist as a condensed phase, and therefore, in order to grow crystals from a solution in Mg, the pressure has to be increased. According to the calculated *P–T* phase diagram [11] (shown in Fig. 1(b)), crystal growth from a solution has to be performed in pressure and temperature conditions above the boiling line of Mg, which is the border between two regions in Fig. 1(b): liquid + MgB_2 and gas + MgB_2. However, for the stabilization the MgB_2 phase at temperatures above 1000 °C, not only high



High Pressure Crystal Growth

Growth of MgB_2 crystals: J. Karpinski et al., Physica C 385, 42 (2003)

partial pressure of Mg vapor is necessary, but also high hydrostatic pressure. There are several major problems, which have to be solved in order to grow crystals:

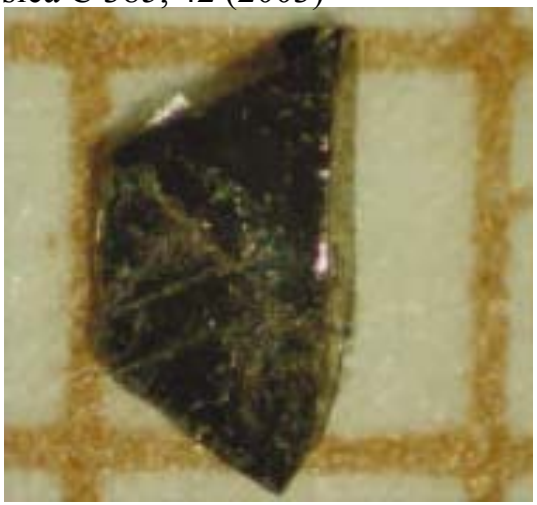
(a) The reactivity of the crucible material: at $T >$ 1000 °C, molten Mg is very aggressive towards all materials and destroys the crucible after a few hours.
(b) All metals used as a solvent form mixed compounds with Mg or MgB_2, which makes crystal growth of pure MgB_2 impossible from any solvent other than Mg.
(c) The solubility of MgB_2 in Mg is very small at low temperatures and therefore high temperature is necessary. However, the partial pressure of Mg vapor above molten Mg increases with temperature and at 1500 °C is of the order of 50 bar.
(d) MgB_2 decomposes above 1000 °C, at ambient pressure.

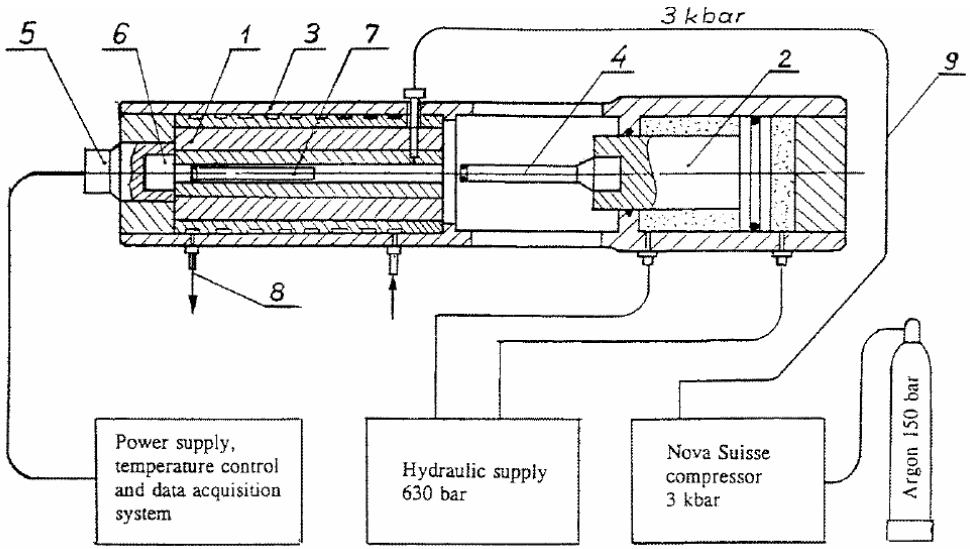
For experiments at Ar pressure, a mixture of Mg and B has been placed in a BN crucible in a high pressure furnace. The experiments have been performed at $P_{Ar} = 1$ kbar, at temperatures from 1450 up to 1700 °C. The experiment at $P_{Ar} = 14$ kbar was done at 1250 °C. As a result, hexagonal black crystals of the new nitride $MgNB_9$ were obtained, but no MgB_2 appeared. The source of nitrogen was the BN crucible. The growth of MgB_2 crystals at Ar pressure was also impossible from solutions containing Cu and Al, because Cu, used as a solvent, forms mixed compounds with Mg, while Al substitutes Mg in MgB_2.

Crystal growth experiments, using the anvil system, have been performed in the pressure range of 10–30 kbar. A mixture of Mg and B was put into a BN container of 6 mm internal diameter and 7 mm length. First, pressure was applied using a pyrophylite cube as a medium, then the temperature was increased during 1 h, up to the maximum of 1700–2200 °C, kept for 1–3 h, and decreased during 1–2 h. The result of a typical cubic anvil growth experiment is displayed in Fig. 2(a), showing a collection of MgB_2 and BN crystals, sticking together. MgB_2 plate like golden crystals (see Fig. 2(b) for example) were up to $1.5 \times 0.9 \times 0.2$ mm^3 in size and up to 230 μg in weight. In some experiments, hexagonal black crystals were obtained from the crystal growth process. Structural X-ray studies showed those to be a new nitride phase, namely $MgNB_9$ (Fig. 2(c)). The structure of this compound consists of two kinds of boron polyhedra separated by Mg and N atoms [7,15].

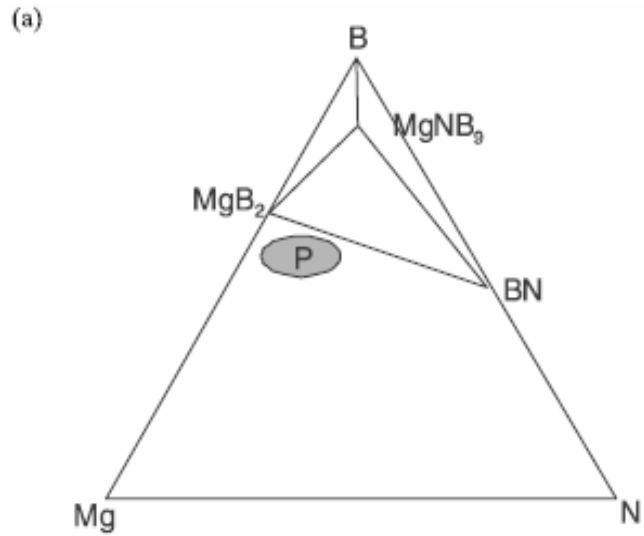
High Pressure Crystal Growth

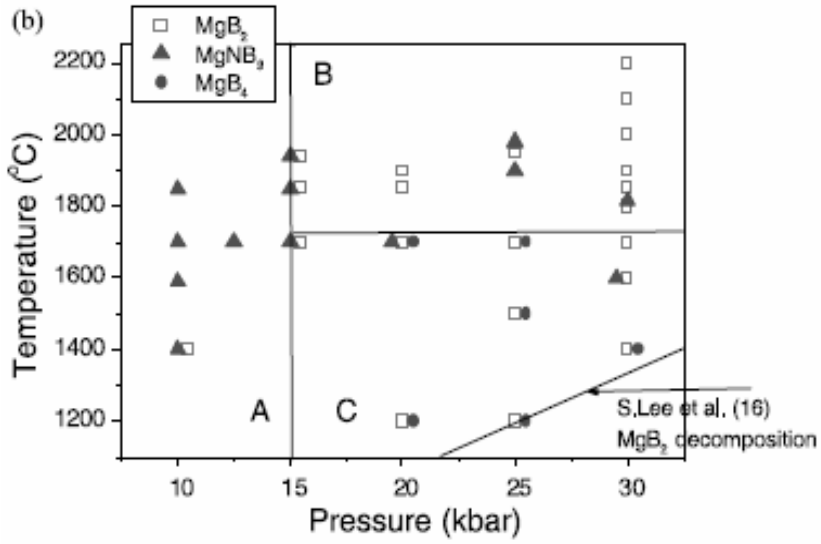
Growth of MgB_2 crystals: J. Karpinski et al., Physica C 385, 42 (2003)





High T_C cuprate oxides: Super.Sci.Technol. 12 R153 (1999)





Hydrothermal Crystal Growth

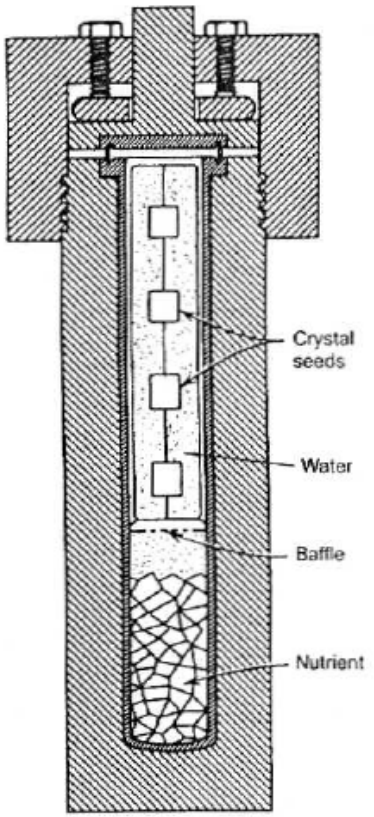
Chemical precipitation where solution-phase reaction occurs resulting in insoluble (sometimes crystalline) precipitate

Example: Synthesis of AgCl in aqueous solution

$AgNO_3$ (aq.) + NaCl(aq) → AgCl(s) +$NaNO_3$(aq)

Solvents are more effective in *supercritical state* – applied above (T_{cr}, P_{cr})
In the state where liquid and gaseous phase are indistinguishable solvent properties are enhanced

HYDROTHERMAL METHOD
Supercritical water + catalyst (ions from mineralizer that enhance solubility of the solute)



Hydrothermal bomb

T_1

$\Delta T = T_2 - T_1 > 0$

Material is dissolved at the bottom
and transferred to the top by convection
Solution becomes supersaturated and
crystallization occurs on the seeds

T_2

Advantage: synthesis of materials at low T
Disadvantage: mineralizer source of impurities
Oxide, sulfide materials, aluminosilicate zeolites (porous solids) ~ few Å cavities

Hydrothermal Crystal Growth Example

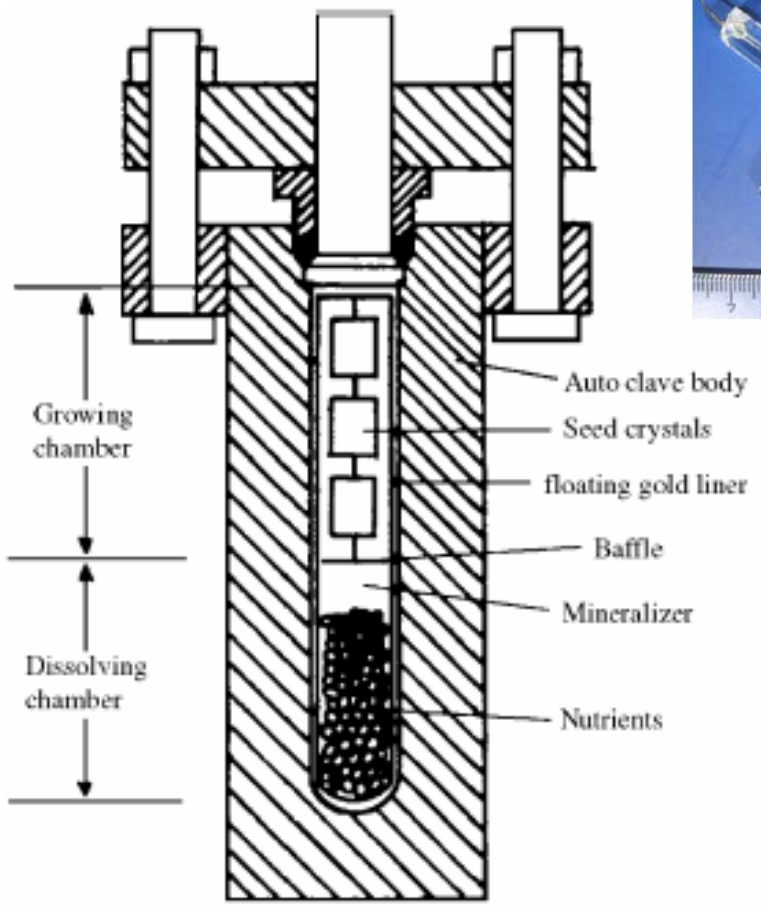
Growth of $KTiOPO_4$ crystals: used in optical devices (lasers)

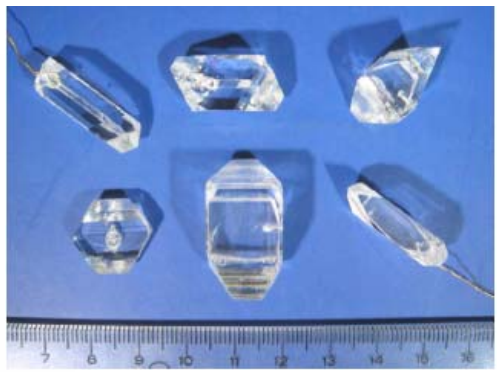
C. Zhang et al., J. Cryst. Growth 292, 394 (2006)

KTP single crystals were grown in an autoclave (Fig. 1) at a temperature range of 400–540 °C and a pressure range of 120–150 MPa. A "floating" closed gold liner is essential for preventing impurity incorporation from the autoclave inner surface and growth of high-quality KTP single crystals. The gold liner with a volume about 2400 ml is divided into two chambers by a baffle. The nutrition chamber contains solid nutrients (crushed flux KTP crystals) and the growing chamber contains seed crystals((0 1 1) orientation or point crystal) which were suspended by Au wires. A solution of K_2HPO_4 (2.0 mol/l), KH_2PO_4 (0.1 mol/l) and H_2O_2 (1 wt%) with a filling grade about 65–70% was used as the transporting media for dissolved nutrients. Suitable quantity of distilled water was supplied into the volume between the autoclave and the Au liner for pressure balancing.

The furnace produces the necessary temperature gradients which is about 50–70 °C between the two chambers, so as to create a convection current for the transportation of dissolved nutrients to the crystal seed located in the lower temperature chamber. Fig. 1 shows the schematic diagram of autoclave and crystal growth system and Table 1 shows the growth conditions of KTP single crystals grown by hydrothermal method.

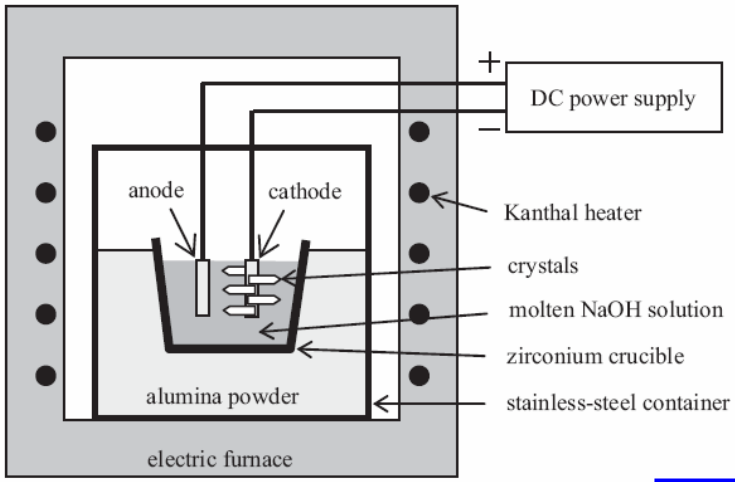
The experiments have shown that growth rates along the [0 1 1] are about 0.15–0.17 mm a day. The size of the biggest grown crystal was $14.5 \times 28 \times 17\,mm^3$. Fig. 2 shows the grown KTP crystals which were just taken out from the autoclaves after a run.





Basics of Electrochemical Methos

Passage of electric current through conducting liquid
Isothermal and irreversible (noneqiulibrium) process at constant temperature



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Electrochemical cell example for LaOOH crystal growth
Zirconium crucible holds solution of La_2O_3 in electrolyte NaOH
Electrochemical deposition at T ~ 400ºC in 0.4V potential for 96h.

$La_2O_3 + 2NaOH \rightarrow 2NaLaO_2 + H_2O$
$NaLaO_2 + H_2O \rightarrow La(OH)_3 + NaOH$
$La(OH)_3 \rightarrow La^{3+} + 3OH^-$

La^{3+} cations are attracted to cathode. OH^- are attracted to cathode by cations so

$La^{3+} + OH^- \rightarrow LaOOH + H_2O$

In general 3 methods of electrochemical crystal growth are possible:

1. Direct electrochemical decompositon of flux to yield product
2. Decomposition of compound dissolved in an inert solvent to yield product
3. Electrochemical transport

Electrolytic decomposition of $K_2Mo_2O_7$ at 600ºC
$K_2Mo_2O_7$ (l) → K_2Mo_4 (l) + MoO_2 (C) + O (g)

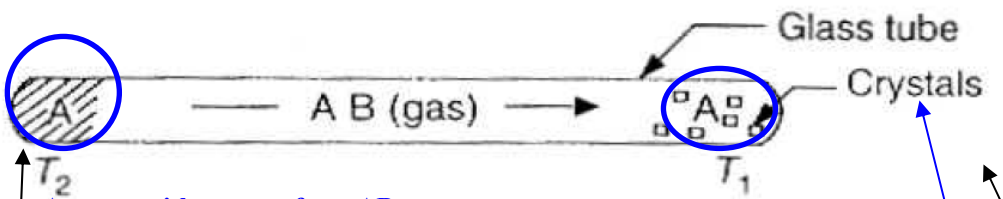
Melt composition changes as crystals are created;
if there is a width of formation crystals will have P(x)

Preparation of Na_xWO_3 ($0 \le x \le 1$)
$Na_2W_2O_7$ (l) → $(2/(2-x))Na_xWO_3$ (C) + $((2-2x)/2-x)Na_2WO_4$ (l) +$(x/(4-2x))O_2$ (g)

Synthesis of metal crystal – product is already in electrolyte
One electrode is desired product itself, the other inert or seed crystal
When current is applied, polycrystalline material is dissolved, transported via flux and precipitates on the seed crystal. Current controls the growth rate. Used for metal purification.

Chemical vapor transport reactions

Phase1: Heterogeneous reaction on the starting solid
Phase 2: Gas motion
Phase 3:Heterogeneous reverse reaction where the solid is formed



A reacts with a gas to form AB

Reverse reaction at different place (sublimation) results in reformation of A

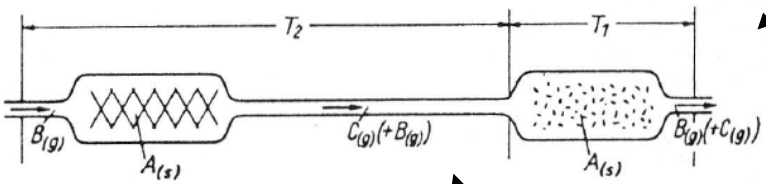
Two types of vapor transport reactions:

Endothermic $\Delta T = T_2 - T_1 > 0$
Synthesis of PtO_2: Pt (s) + O_2 (g) ↔ PtO_2 (g) (at 1200ºC)

Exothermic $\Delta T = T_2 - T_1 < 0$
Cr purification: Cr (s) + I_2 (g) ↔ CrI_2 (g)

Vapor phase transport of a solid substance A via gaseous intermediate AB formed by reaction with vapor transport agent B

Two transport mechanisms of AB:
1. gas stream in open tubes (when the reverse reaction proceeds rapidly)
2. thermal convection in closed tubes (all other cases)



Flow methods:

Thermal diffusion:

Consider endothermic reaction:
Zn (l) + S (l) → ZnS (s) at 800ºC, but faster with I_2 present (**0.5-5mg/cm^3 volume of tube**)

Other transport agents: Br_2, NH_4Cl, $TeCl_3$ or K_2PbCl_6 (for Cl), HCl (using extra capilaries and valves)

Reactions with (quartz) tube wall need to be considered (eg. Al transport in quartz). Sometimes quartz needs to be Protected by alumina, coating.

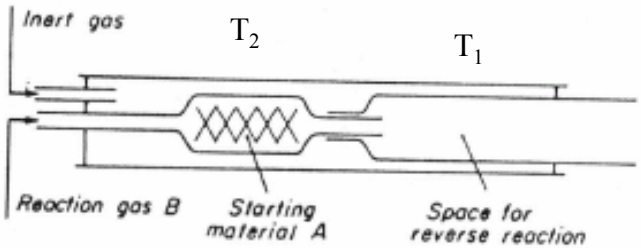
Gas flows (2-10 cm^3/h) through ΔT, space where gas can stay for a long time is useful for sublimation
Surface exposure to gas flow enhances reaction at T_2 (loose powders) – example PtO_2 reaction.

Gas B can be added at high T, depending on its properties, or it can be added to A in solid form initially.

Chemical vapor transport mechanism basics

Low P: mean free path of molecules is comparable with tube length – no collisions, material transported ~ charge surface area
Higher P: Gas motion determined by diffusion, for ΔT=const. rate of diffusion decreases with increasing total P
At even higher P thermal convection contributes

10^{-3}atm ≤ P ≤ 3atm.
molecular flow diffusion diffusion + convection



Can be adjusted with variable pressure gradient

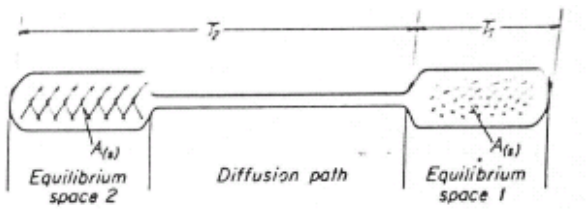
1. Flow method with carrier gas $iA(s,l) + kB(g) = jC(g)$

Amount of A deposited at T1 is
(difference between concentrations at 2 and 1):

$$n_A/n_{B0} = (i/j)[n_{C2}/n_{B0} - n_{C1}/n_{B0}] = i\Delta n_C/jn_{B0} \rightarrow n_A = (i/j)[\Delta P_C n_{B0}/P_{B0}]$$

For $P_C \ll P_B$

Where n ~ P. P_C is equilibrium pressure



2. Most applications: closed tubes, P where diffusion dominates

$$n_A = (i/k)n_B = (i/j)n_C$$