Flux Method for Preparing Crystals

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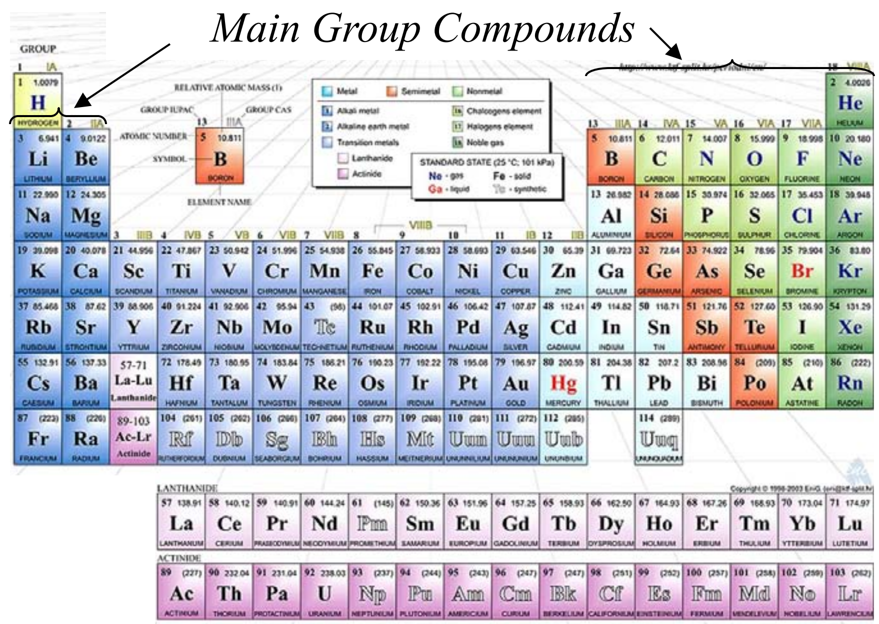


❑ Why materials synthesis?

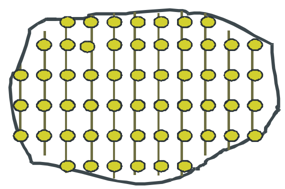
If you can make samples, then you can pursue the science that appeals to you: Magnetic materials, metals, insulators, superconductors, etc.

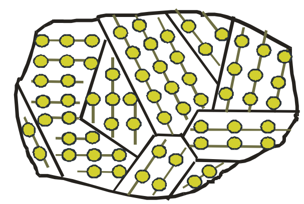
If you know how to cook, you can create what you want.

Pizza

Seafood Stew

❑ Definition of crystal?





In a crystal, the constituent atoms are arranged in an orderly repeating pattern extending in all three spatial dimensions.

Spatial extent of the ordered regions (crystallites):

Crystal	poly-/micro-crystalline	nanocrystalline	amorphous
~ mm	~ µm	~ nm	< nm

❑ Why single crystals?

- **Aesthetics – gemstones**

Ruby

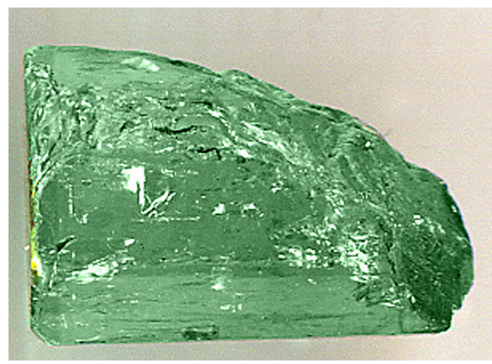
Al_2O_3
with ~ 1% Cr

Diamond

C

Sapphire

Al_2O_3
with ~ 0.01 % Ti & Fe



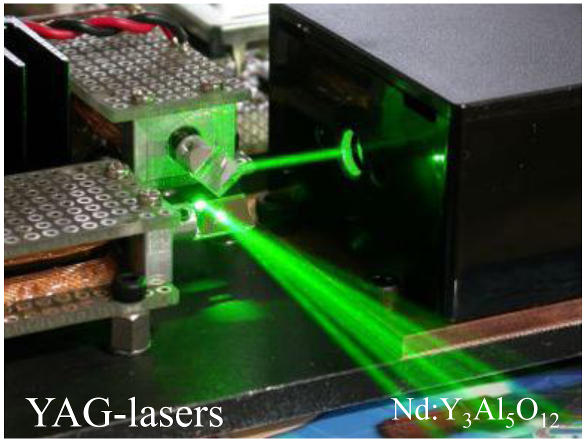
Emerald

$Be_3Al_2(SiO_3)_6$
With Cr or V dopants

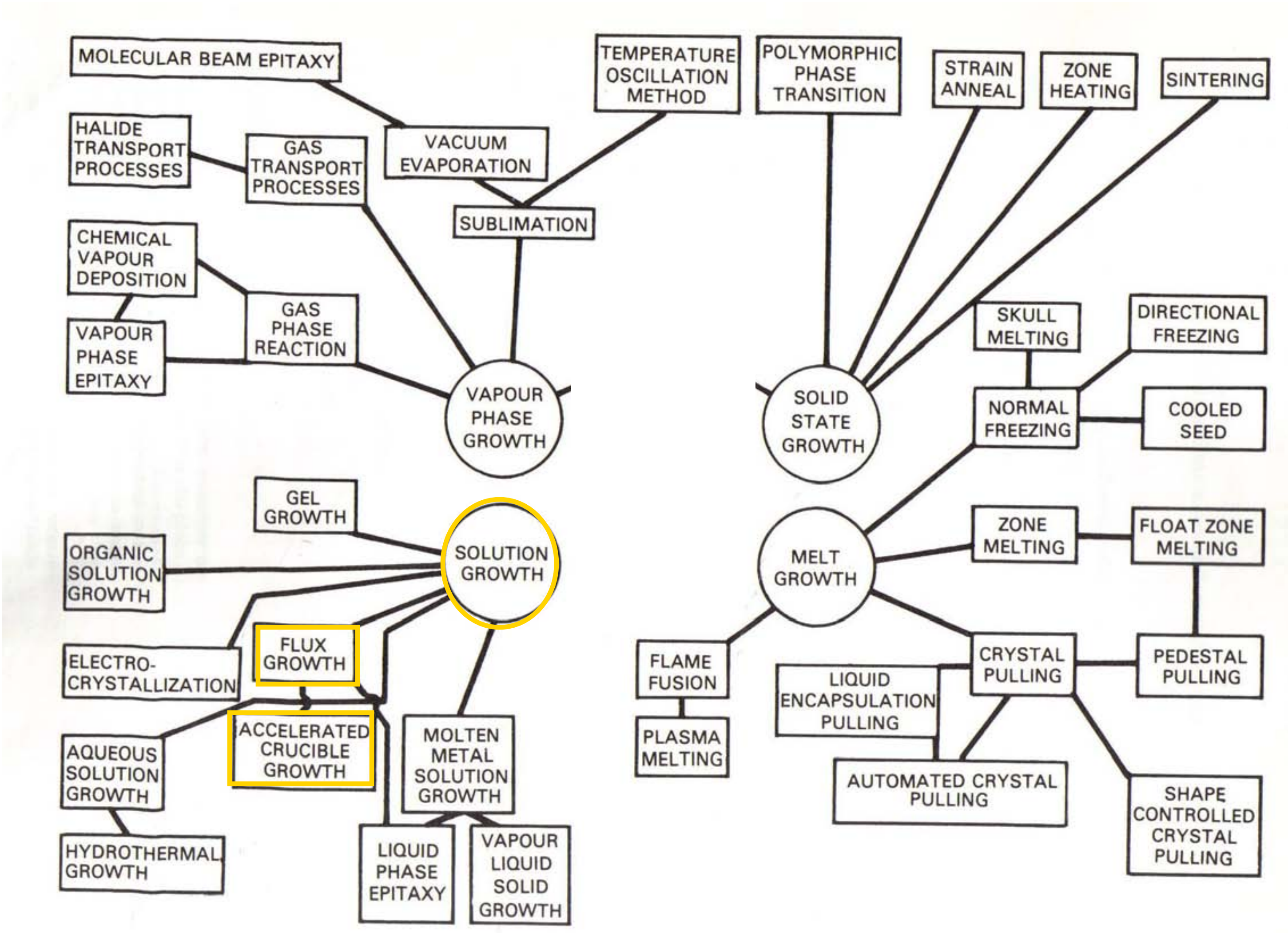
❑ Why single crystals?

• **Find intrinsic properties (no grain boundaries, anisotropic)**

• **Application in devices**

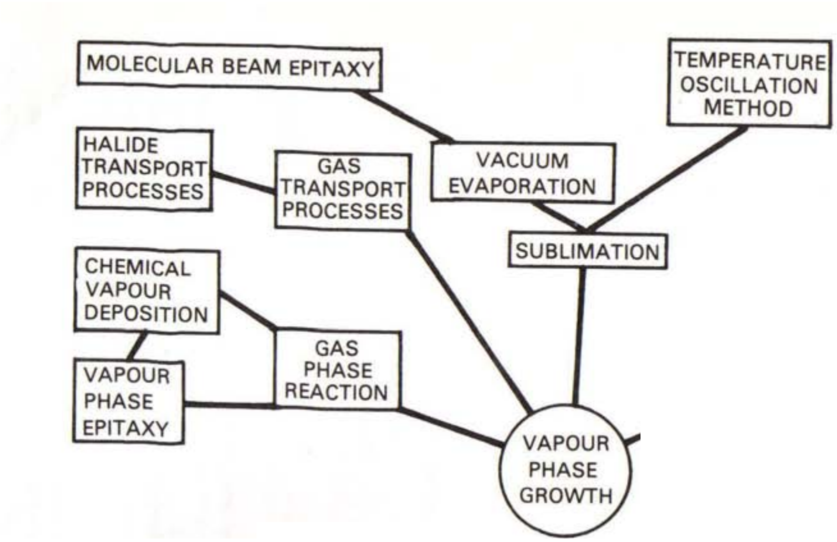


❑ What are the crystal growth techniques?



B. R. Pamplin, Crystal Growth, Pergamonpress (1980).

❑ What are the crystal growth techniques?



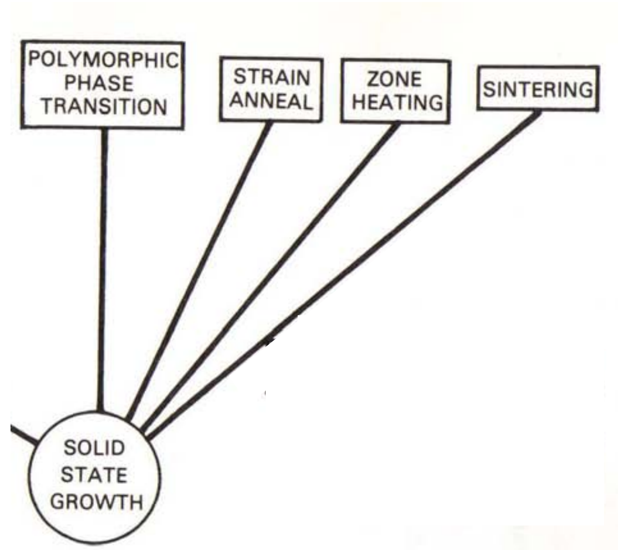
Growth from gas phase – 'precipitation' from gas phase

- solid → gas → xtal
- Chemical vapor transport – need a transport agent
- Pulsed laser deposition – need a substrate or seed

Issues:

- Induce a phase transition – homogeneous gas phase to solid + unsaturated gas
- Control conditions for supersaturation, usually by control of temperature gradients

❑ What are the crystal growth techniques?



Growth from a mixture of solids *(no melting)*
• kinetic and thermodynamic factors are important

Issues:
• Crystals are micron size
• Phase segregation, grain boundaries

❑ What are the crystal growth techniques?

Growth from the liquid phase

• solid → liquid → solid

• Variations are Bridgman, Czochralski (pulling), Kyropoulos (top seeding), Verneuil (flame fusion), tri-arc, skull melting, image float-zone

Issues:

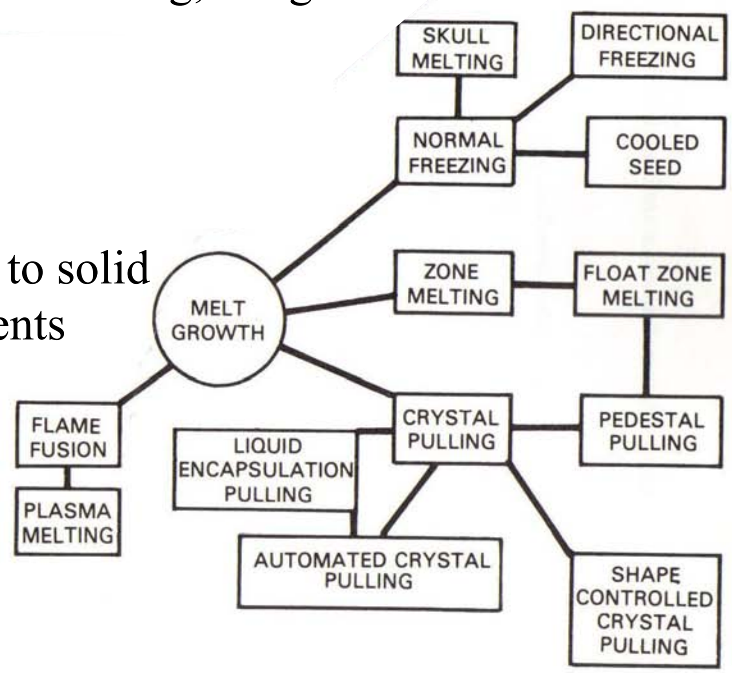
• Induce a phase transition – liquid to solid

• Control of temperature and gradients

• High melting points > 2000 °C
(confirmation of melting!)

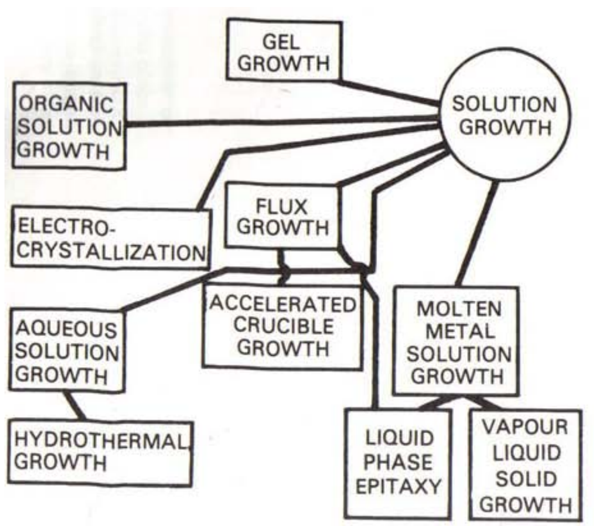
• Reactivity of crucible

• Control nucleation (seed crystal)



❑ What are the crystal growth techniques?

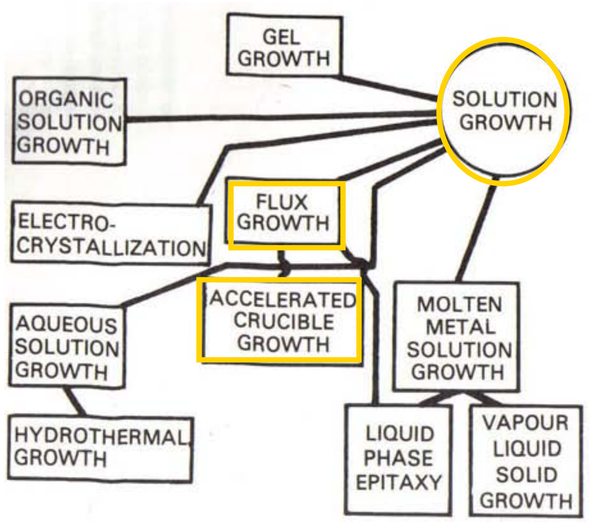
Growth from solution – precipitation from supersaturated solution
• Aqueous & organic solvents
• Inorganic solvent (flux, high T)
• Hydrothermal (high P & T)



Issues:
• induce a phase transition – homogeneous solution to solid + unsaturated solution
• control conditions for supersaturation– concentration (evaporation of solvent), temperature (solubility or saturation is a function of temperature)
• reactivity of container (crucible)
• inclusion of solvent in crystals

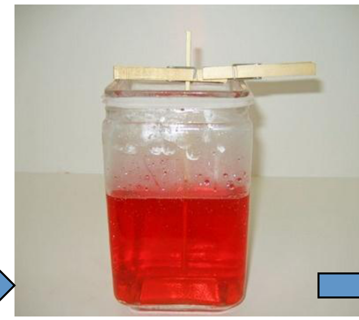
❑ Why solution growth?

<u>Advantages</u>:
- Grow congruently and incongruently melting materials
- Need relatively simple equipment
- Has short growth-time scales
- Need small amounts of materials



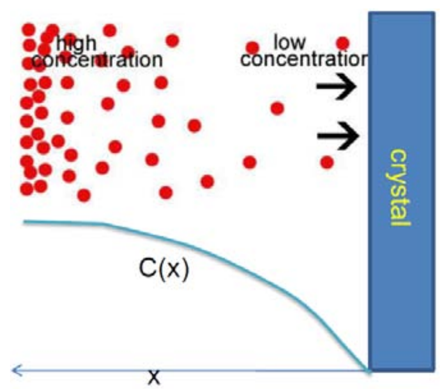
<u>Disadvantages</u>:
- Not too large a crystal (mm to cm)

e.g. Rock candy

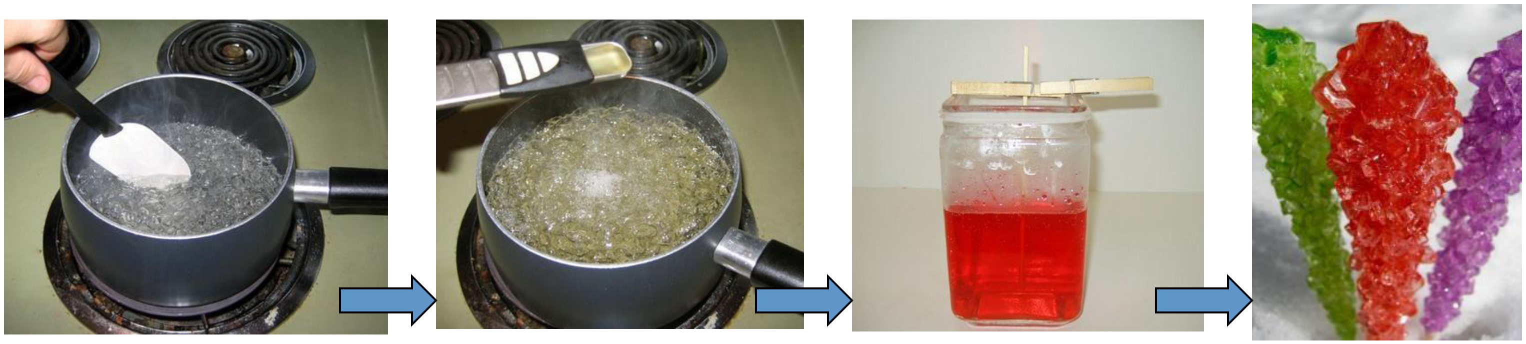


- *Find the right solvent and dissolve the starting materials*
- *Crystallize with time and temperature*

<u>Important</u>: Solvent should have reasonable solubility & Diffusivity



e.g. Rock candy



- *Find the right solvent and dissolve the starting materials*
- *Crystallize with time and temperature*

- **Flux Growth** is solution growth at high temperature
- Flux (melt; solvent) can be metals (Ni, Fe, etc.), oxides (B_2O_3, Bi_2O_3), hydroxides (KOH, NaOH), salts (BaO, PbO, PbF_2), eutectic binaries

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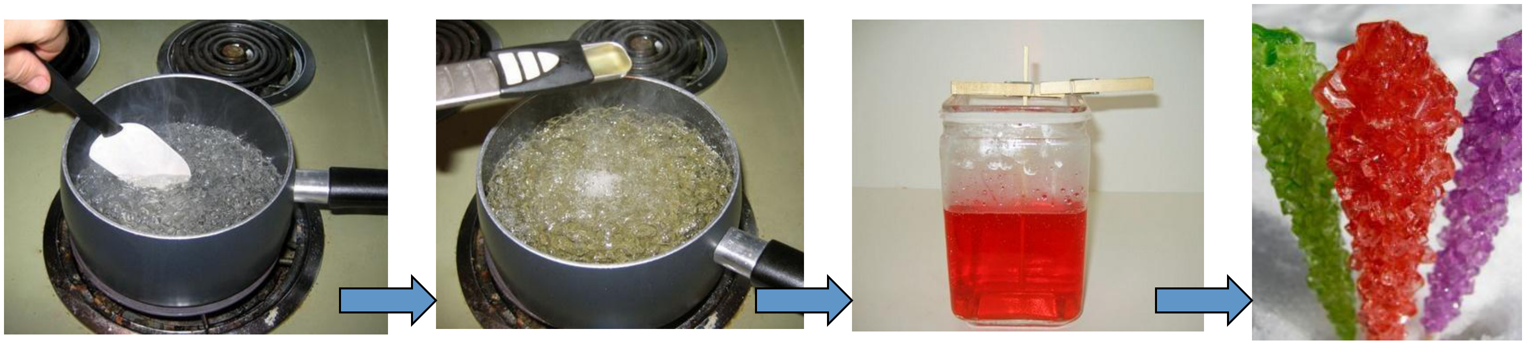
e.g. Rock candy



• *Find the right solvent and dissolve the starting materials*

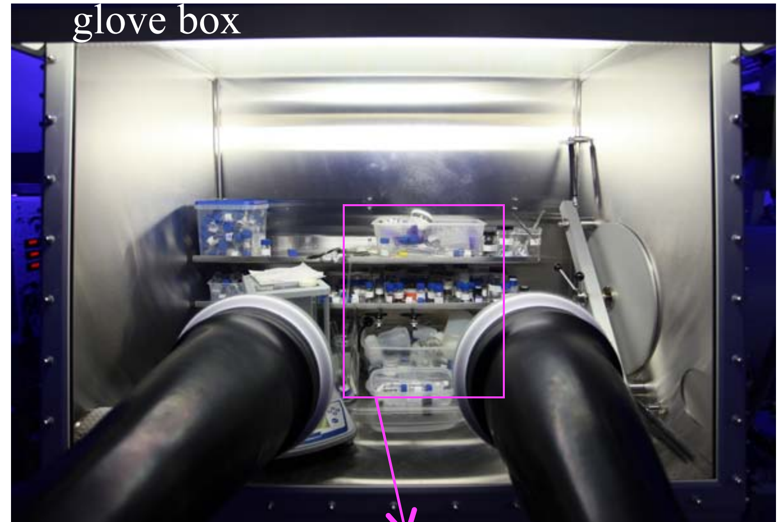
• *Crystallize with time and temperature*

Key characteristics for fluxes

- Have low melting temperature
- Be easily separated from the products
- Not form stable compounds with the reactants
- Have a large difference between boiling & melting temp.

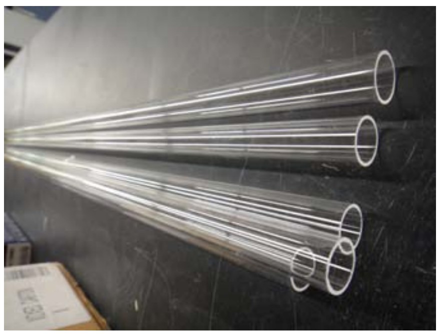
❑ What are flux growth needs?

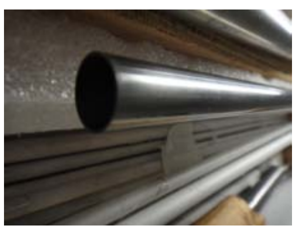
- Elements
- Cutting tools



❑ What are flux growth needs?

- Crucibles
- Tubes (reaction under ambient conditions not possible)

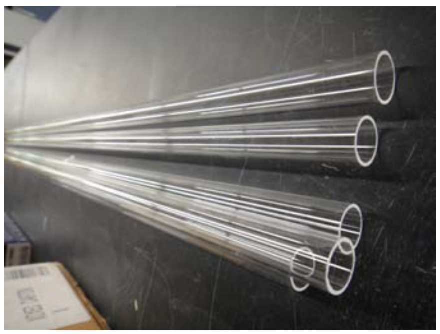


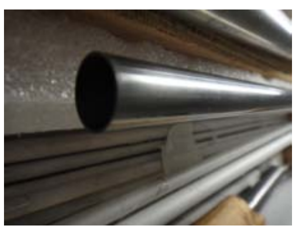


	T_{max} (°C)	$T_{melting}$ (°C)
borosilicate glass (Pyrex)	515	820
gold	1013	1064
silica (quartz)	1200	1853
platinum	1720	1770
alumina (Al_2O_3)	1900	2072
zirconia (ZrO_2)	2000	2700
magnesia (MgO)	2400	2852
tantalum	1400	3017

❑ What are flux growth needs?

- Crucibles
- Tubes (reaction under ambient conditions not possible)

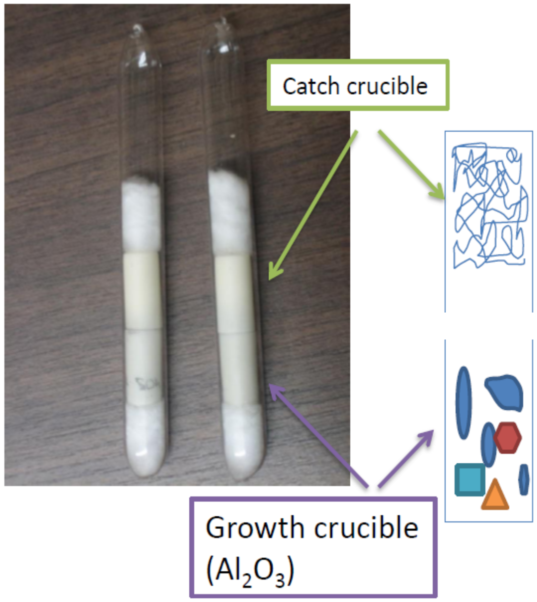




Elements	Container & tube choices
Alkali & alkaline-earth metals	Ta, steel
Al, Ga	Al_2O_3, MgO, BeO
Mg	MgO, Ta, graphite or steel
Cu, Ag, Au	graphite, MgO, Al_2O_3, Ta
Fe, Co, Ni	Al_2O_3, ZrO_2
Zn, Cd, Hg	Al_2O_3
In	Al_2O_3, Ta
Rare-earth metals	Ta, Mo, W, BeO
Bi, Sn	Al_2O_3, SiO_2, graphite
Sb	SiO_2, graphite

❑ What are flux growth needs?

- Arc melt
- Glass sealing station



❑ What are flux growth needs?

- Furnaces

SiC heating elements (T_{max}= 1500 °C)
$MoSi_2$ heating elements (T_{max} = 1700 °C)

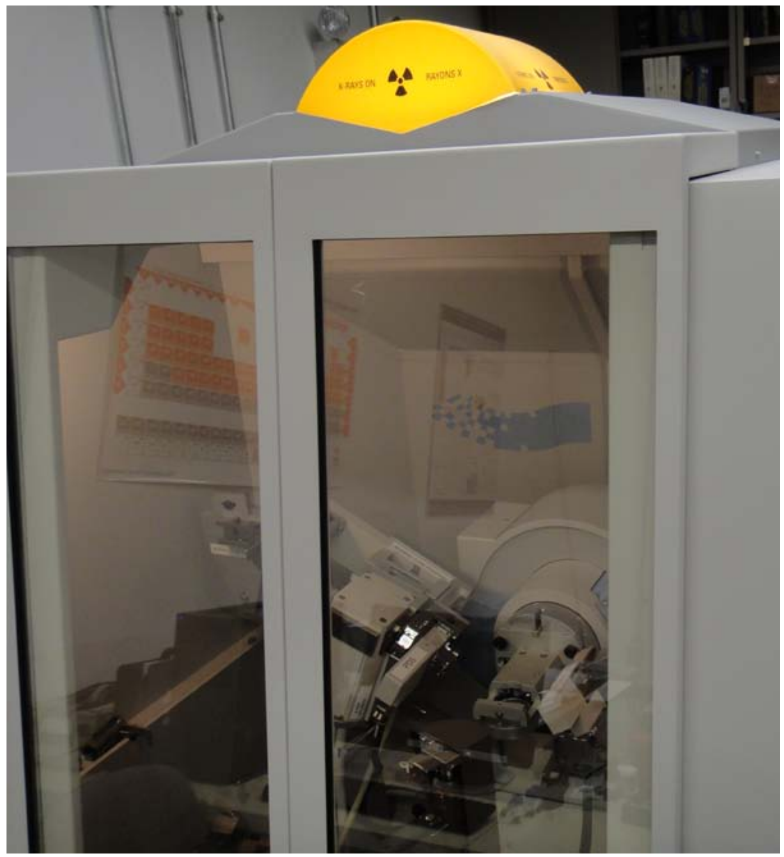
❑ What are flux growth needs?

- Centrifuges

- Chemical etchers (e.g. for Al, use NaOH; for Ga or In, use HCl)
- Mechanical removal tools

❑ What are flux growth needs?

- Energy dispersive spectrometer
- X-ray diffractometer (powder or single crystal)



❑ Where to start?

❖ (1) Review basic literature on flux growth

Growth of single crystals from molten metal fluxes
Fisk, Z. and Remeika, JP

Gschneidner Jr, KA and Eyring, L. (eds) (1989)
Handbook on the Physics and Chemistry of Rare Earths
12 , p. 53. Elsevier , Amsterdam

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

Growth of single crystals from metallic fluxes

By P. C. CANFIELD and Z. FISK

Los Alamos National Laboratory,
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The Metal Flux: A Preparative Tool for the Exploration of Intermetallic Compounds

Mercouri G. Kanatzidis, Rainer Pöttgen,* and Wolfgang Jeitschko**

The Design, Discovery, Growth and Physical Properties of Novel Intermetallic Compounds

Paul C. Canfield

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Introduction to Techniques for Crystal Growth or In the Age of Nano, Why Bother to Grow Crystals?

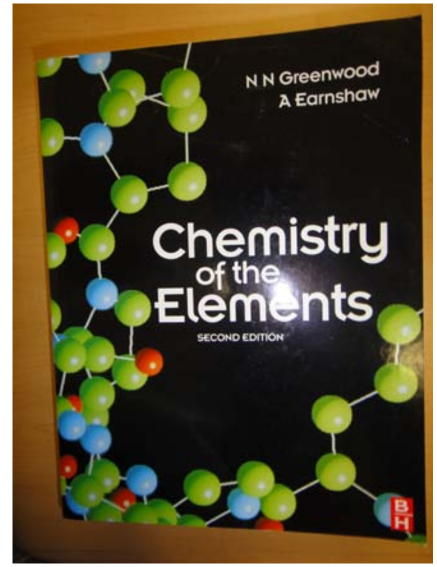
J.E. Greedan, BIMR McMaster University

❑ Where to start?

❖ (2) Learn about the elements

e.g. reactivity, toxicity, general properties

Atmosphere control may be crucial –
i.e. samples can't be made in air!

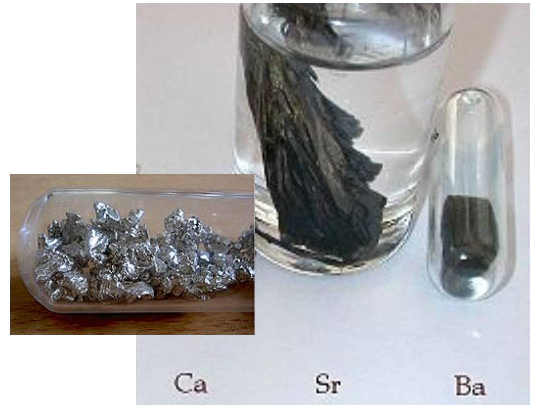


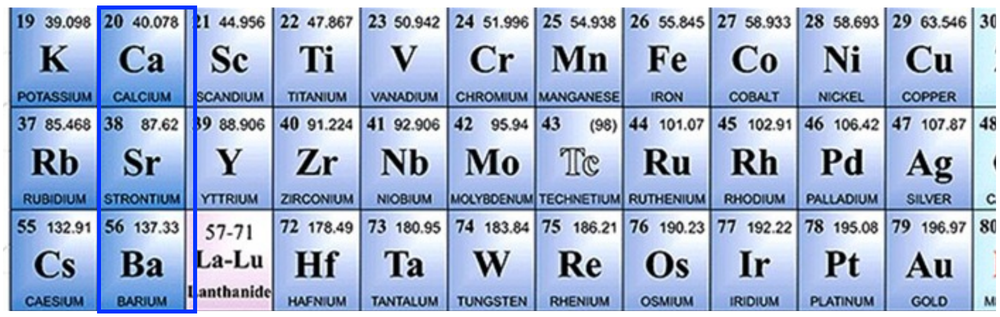
'Wikipedia' descriptions…

La: *" forms a hydrated oxide with moisture in air*
Na: *"burns with a yellow flame; reacts violently with water, oxidizes in air"*
K: *"oxidizes rapidly in air; very reactive with water; burns in contact with skin"*
Ba: *"reacts exothermically with oxygen, & violently with water"*
P: *"high reactivity; widely used in explosives, nerve agents, friction matches, fireworks"*
As: *"poisonous"; "frequently used for murder…"*

❑ Where to start?

❖ (2) Learn about the elements



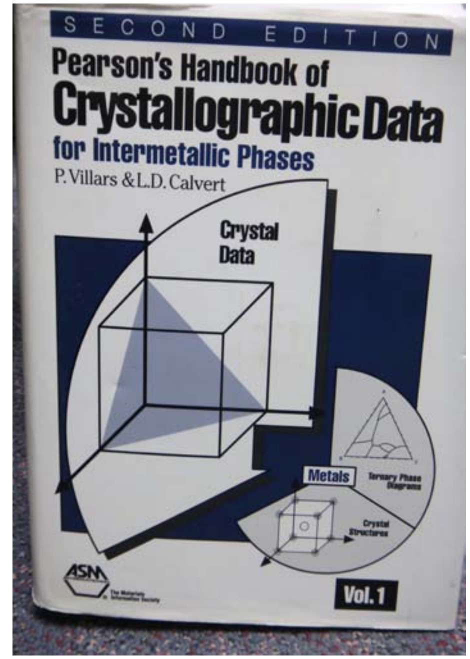


	IE (kJ/mol)	metal radius (pm)	T_{melt}(°C)	T_{boil} (°C)	$D_{20°C}$(g/cm^3)
Ca	590	197	842	1494	1.55
Sr	550	215	769	1382	2.63
Ba	503	222	729	1805	3.59

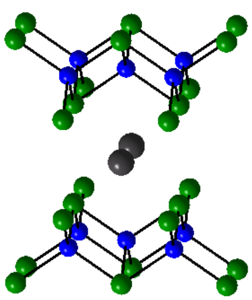
❑ Where to start?

❖ (3) Find structure data

Same structure-types may give similar physical properties!



e.g. Fe-based superconductor ($BaFe_{1.84}Co_{0.16}As_2$) has $ThCr_2Si_2$ structure.
Explore other Fe-based compounds with this structure:



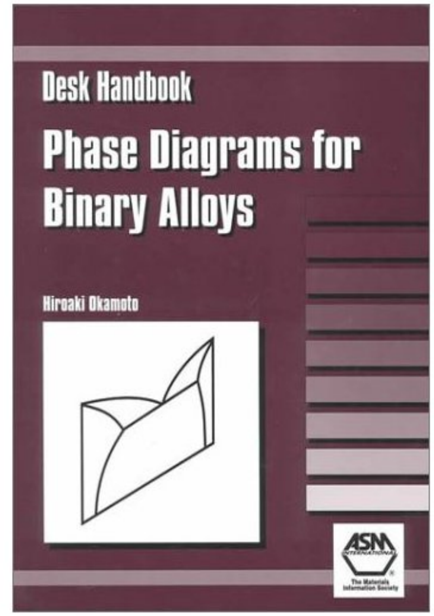
$EuFe_2As_2$	KFe_2As_2	$BaFe_2As_2$	$SrFe_2As_2$	$DyFe_2B_2$	$HoFe_2B_2$	$TmFe_2B_2$	$BaFe_2P_2$
$CaFe_2P_2$	$CeFe_2Ge_2$	$ErFe_2B_2$	$LuFe_2B_2$	YFe_2B_2	$CeFe_2P_2$	$GdFe_2B_2$	$TbFe_2B_2$
$CeFe_2Si_2$	$DyFe_2Si_2$	$ErFe_2Ge_2$	$EuFe_2P_2$	$DyFe_2Ge_2$	$ErFe_2Si_2$	$EuFe_2Si_2$	$LaFe_2Ge_2$
$LaFe_2P_2$	$SmFe_2Ge_2$	UFe_2Ge_2	$LaFe_2Si_2$	$NdFe_2Si_2$	$TlFe_2Se_2$	$ThFe_2Si_2$	YFe_2Si_2
UFe_2P_2	$GdFe_2Ge_2$	$NdFe_2Ge_2$	$TbFe_2Ge_2$	$YbFe_2Ge_2$	$LuFe_2Si_2$	$PrFe_2Si_2$	$SmFe_2Si_2$
$TmFe_2Si_2$	$YbFe_2Si_2$	$PrFe_2Ge_2$	$ThFe_2Ge_2$	$HoFe_2Si_2$	$SrFe_2P_2$	$TbFe_2Si_2$	$TlFe_2S_2$
UFe_2Si_2	$ZrFe_2Si_2$	. . .					

❑ Where to start?

❖ (4) Find the existing phase diagrams

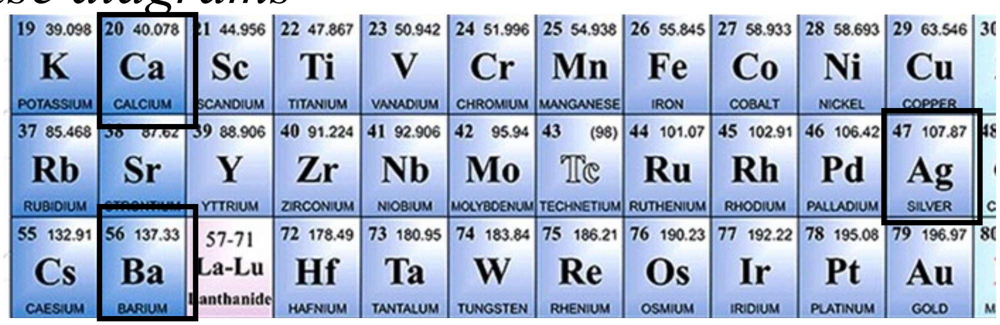
- Binary diagrams are a good start (may be your only option)

- Ternary, quaternary growths generally involve educated guesses.

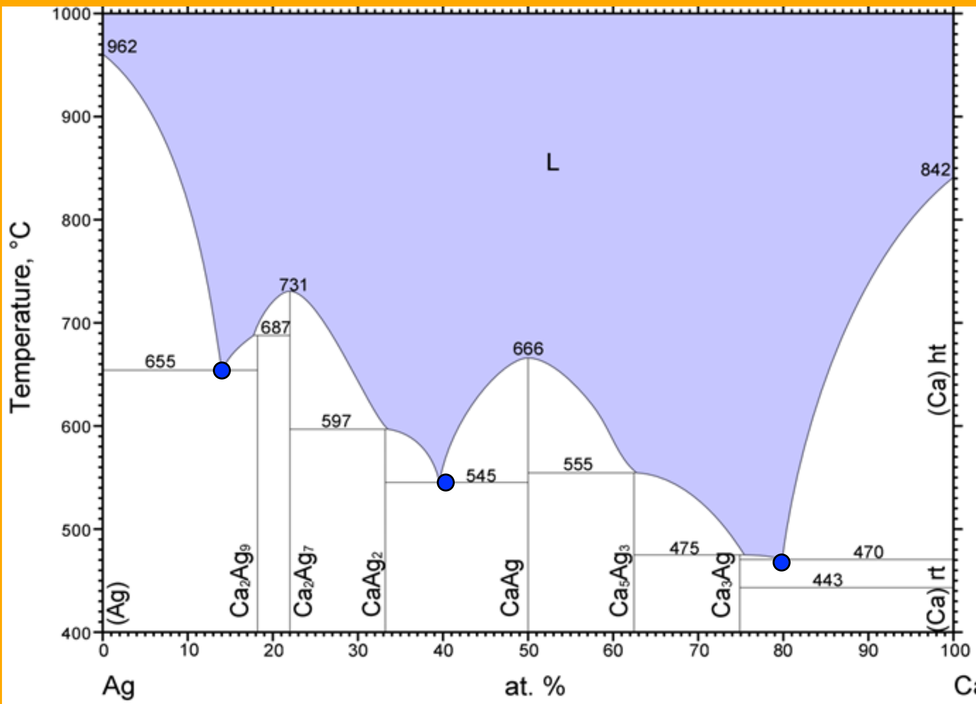


Let's review a few binary phase diagrams

Ca-Ag
Ba-Ag

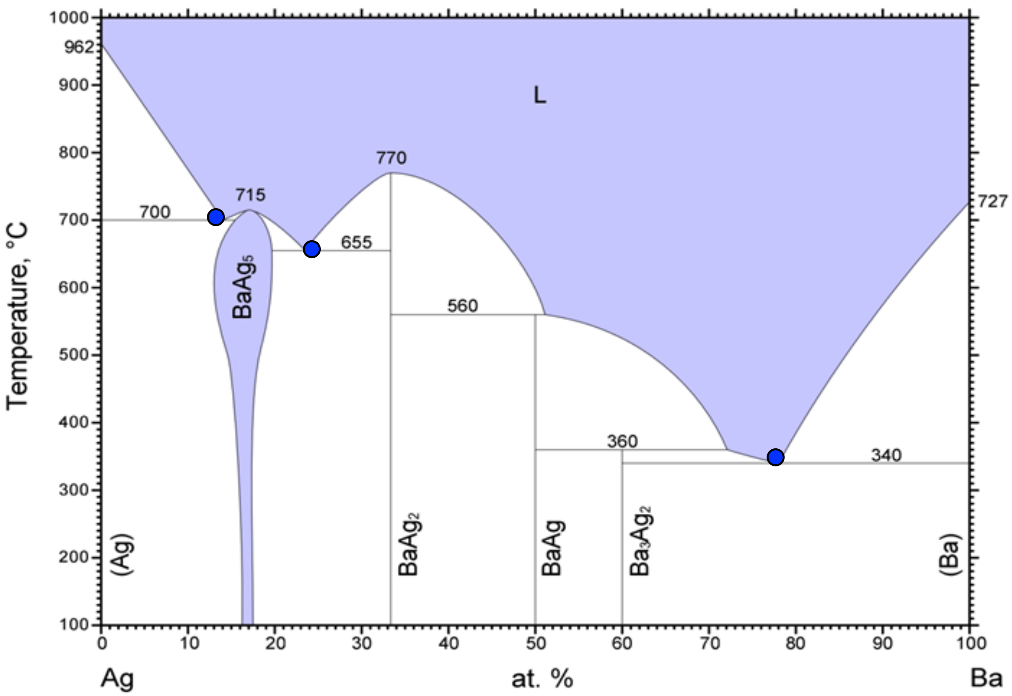


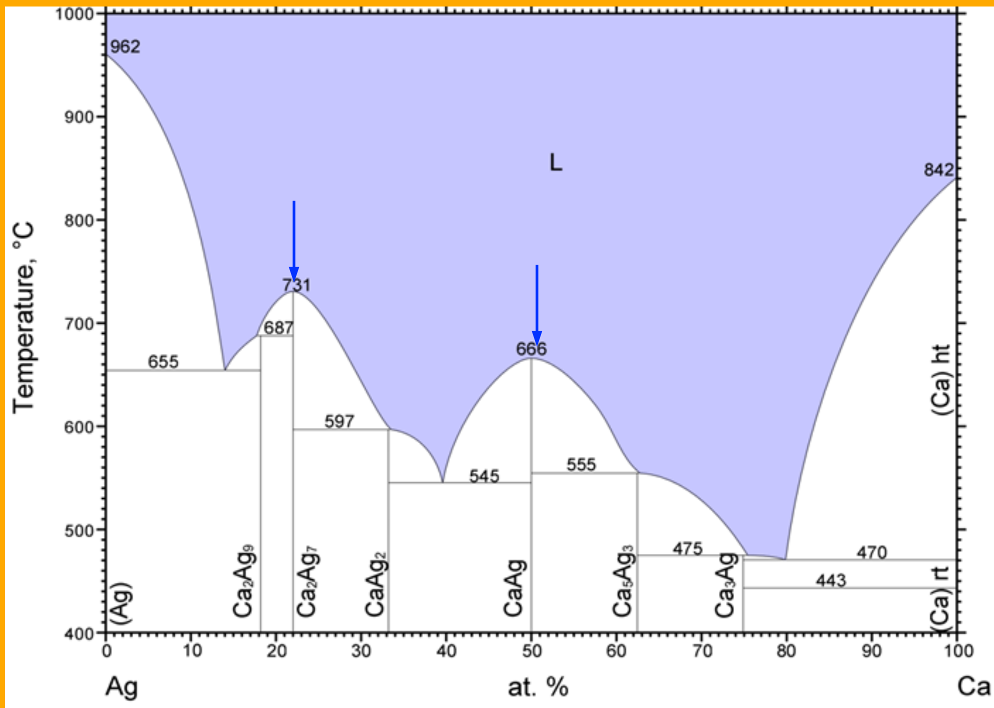
…detour



Eutectic point:

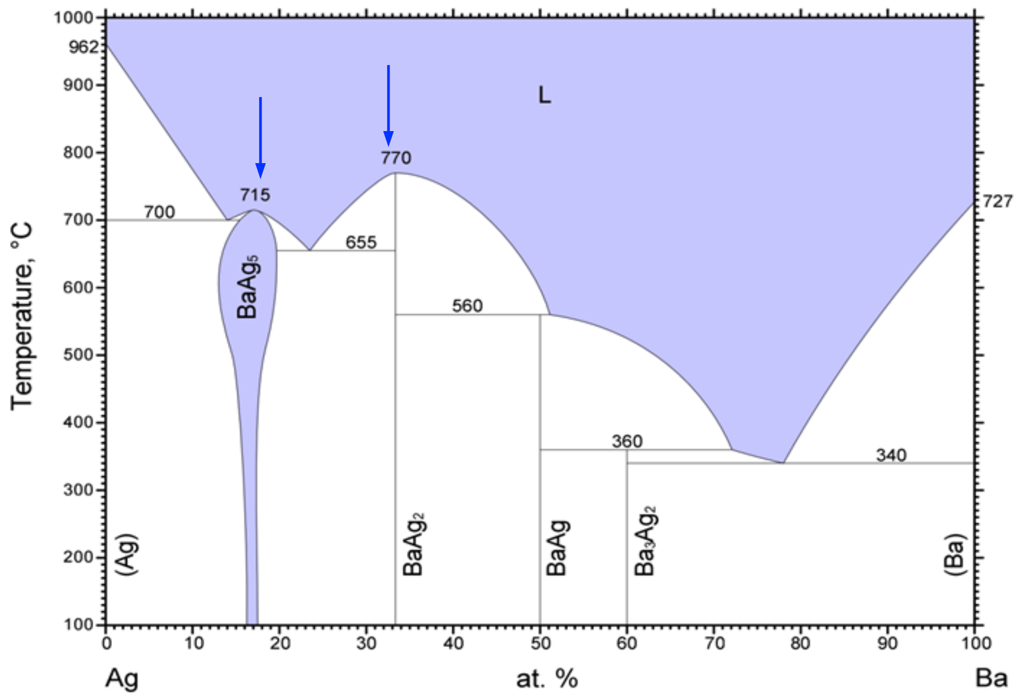
- Minima in liquid region
- Easily accessible liquid region

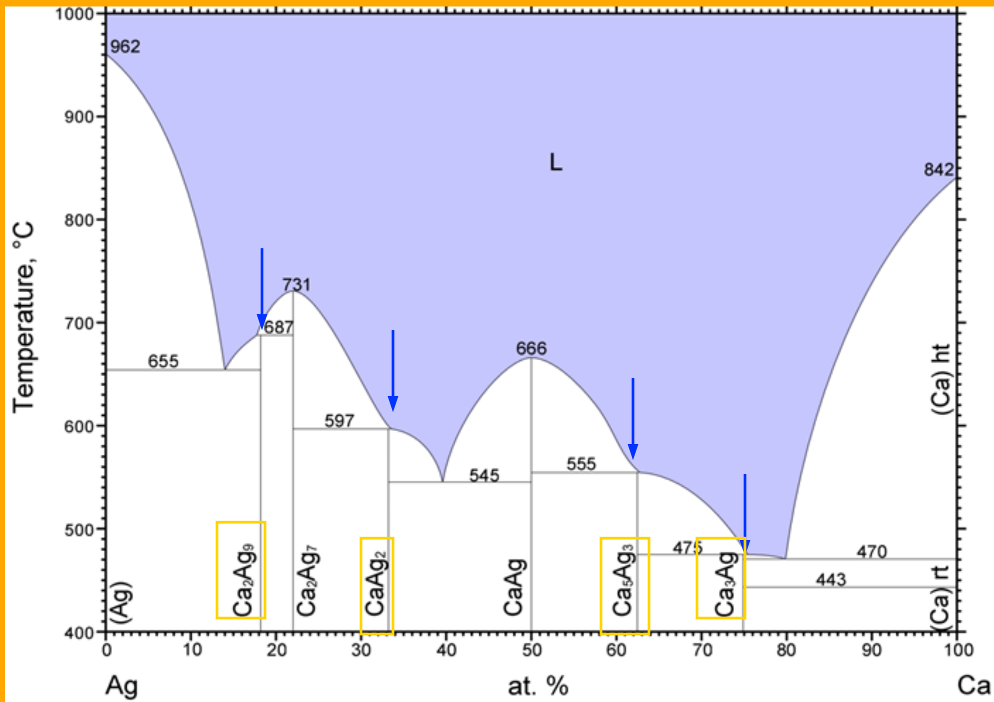




Congruent reaction:

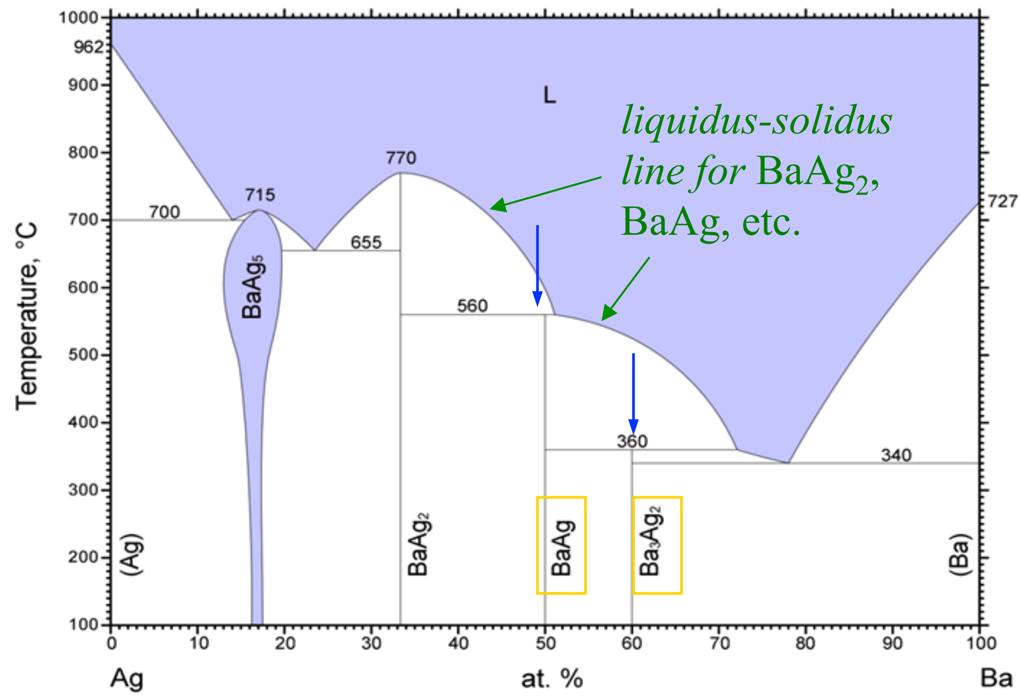
Transformation from a homogeneous liquid to a homogenous solid





Peritectic reaction:

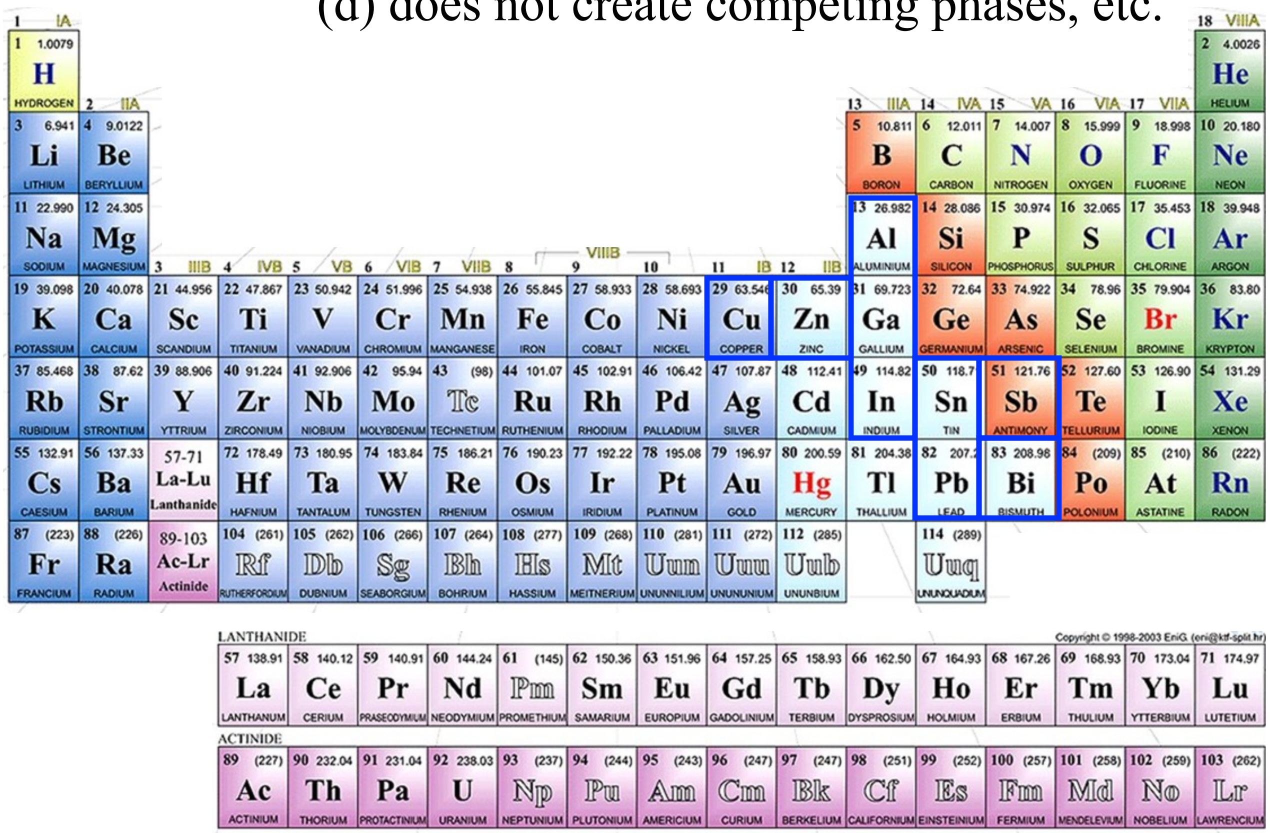
- Melt incongruently, i.e. decompose into a mixed solid and a liquid phase



❑ Where to start?

❖ (5) Find a good metallic flux for crystal growth

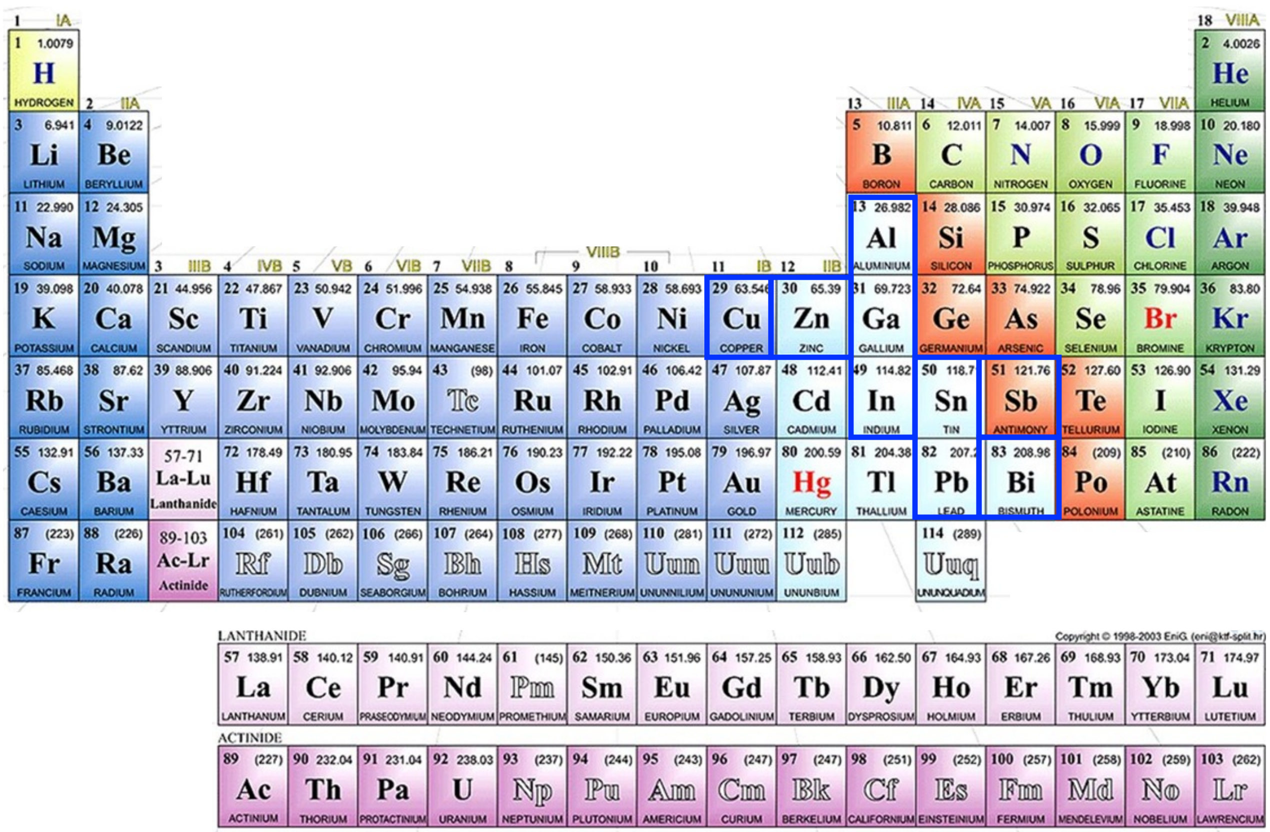
A good flux (a) has a low melting temperature,
(b) has a good solubility for the elements,
(c) does not enter crystal as inclusions, &
(d) does not create competing phases, etc.



Review of some metallic fluxes

Al
- T_{melt} = 660 °C
- attacks silica
- spin off Al in silica tubes or use NaOH

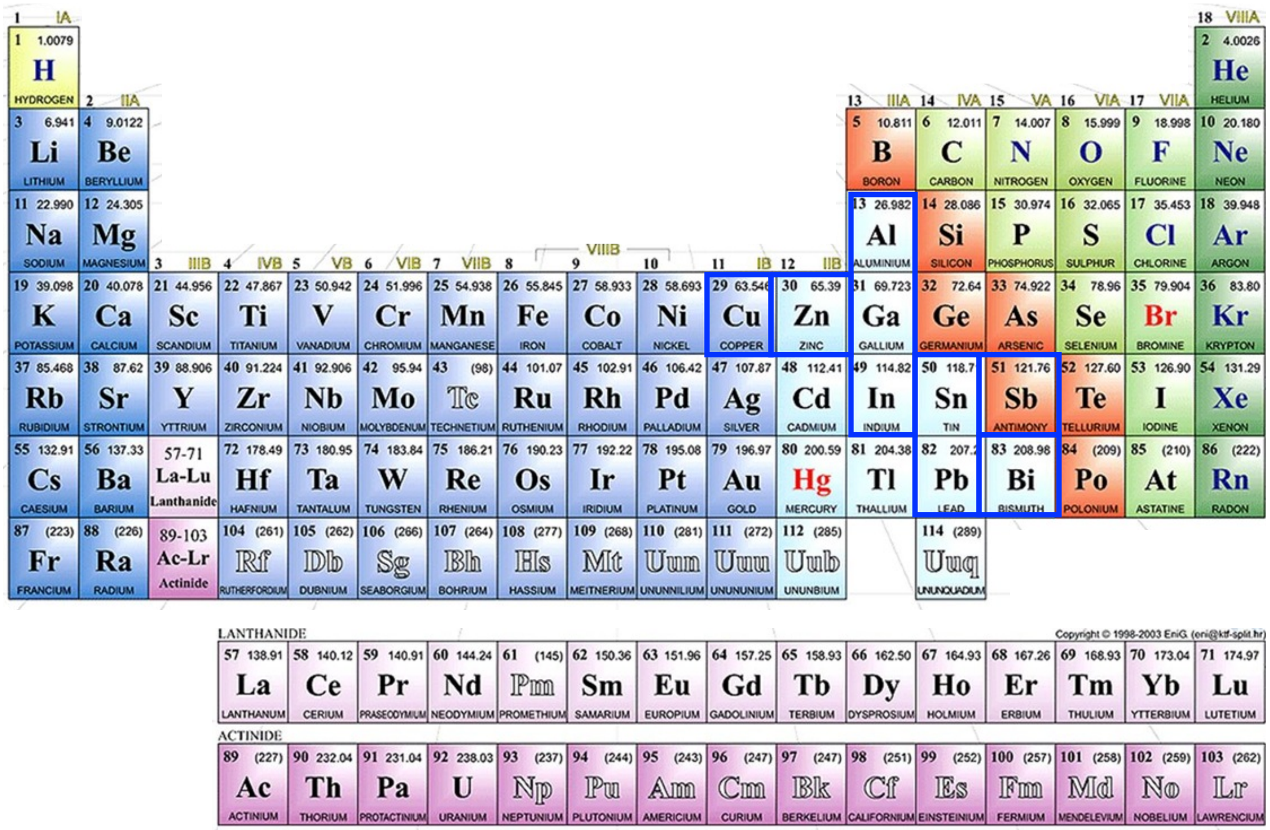
e.g. RB_4, $YbAlB_4$, RB_6, RBe_{13}, RAl_3, TiB_2, $CeSi_{2-x}$



Review of some metallic fluxes

Ga
- T_{melt} = 30 °C
- tends to wet surfaces of grown crystal
- forms compounds with rare-earths

e.g. RSb, $R_2Pt_4Ga_8$

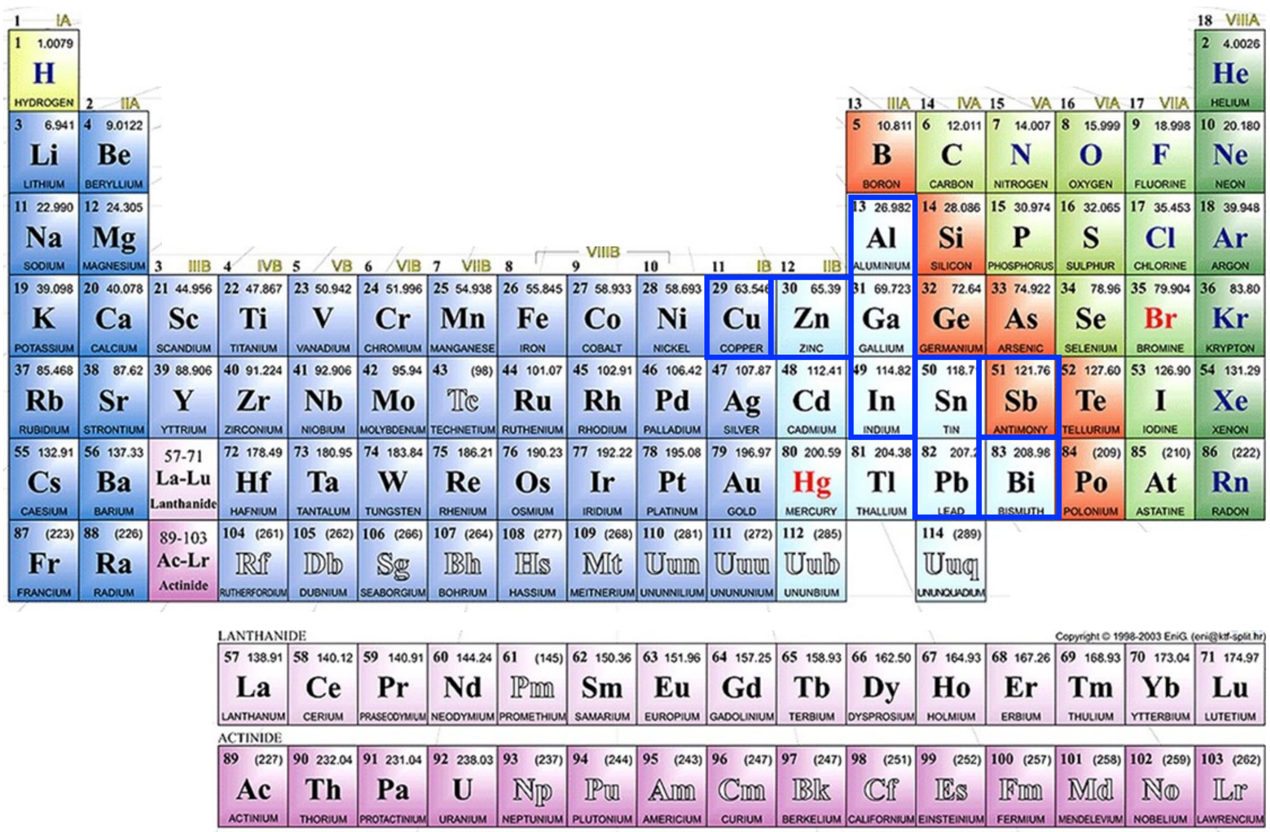


Review of some metallic fluxes

In

- T_{melt} = 157 °C
- Proven to be a good flux for $ThCr_2Si_2$-types
- T_C = 3.4 K

e.g. $CeCu_2Ge_2$, $CeNi_2Ge_2$, $TyCu_2Si_2$

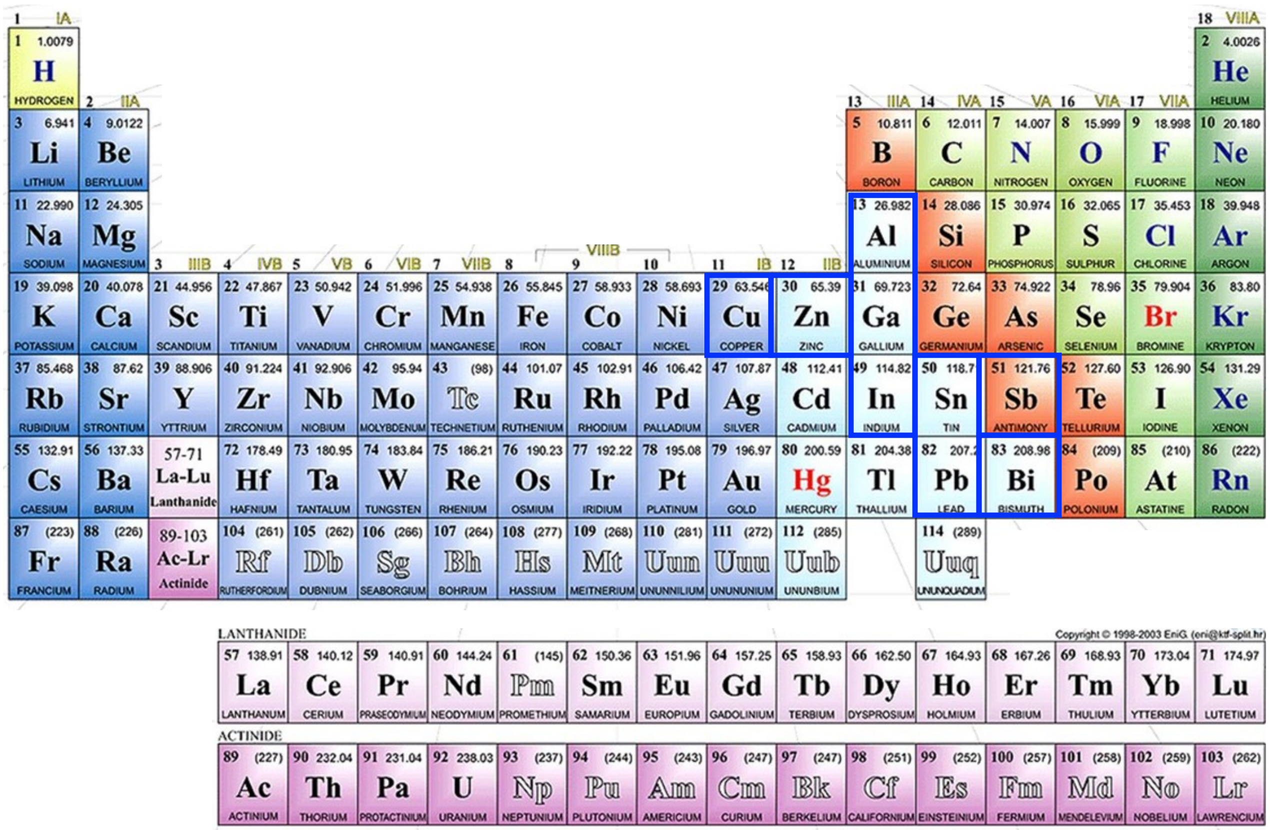


Review of some metallic fluxes

Sn; Pb

- T_{melt} = 232 °C; 327 °C
- form RPb$_3$, RSn$_3$ phases
- T_C = 3.7 K; 7.2 K

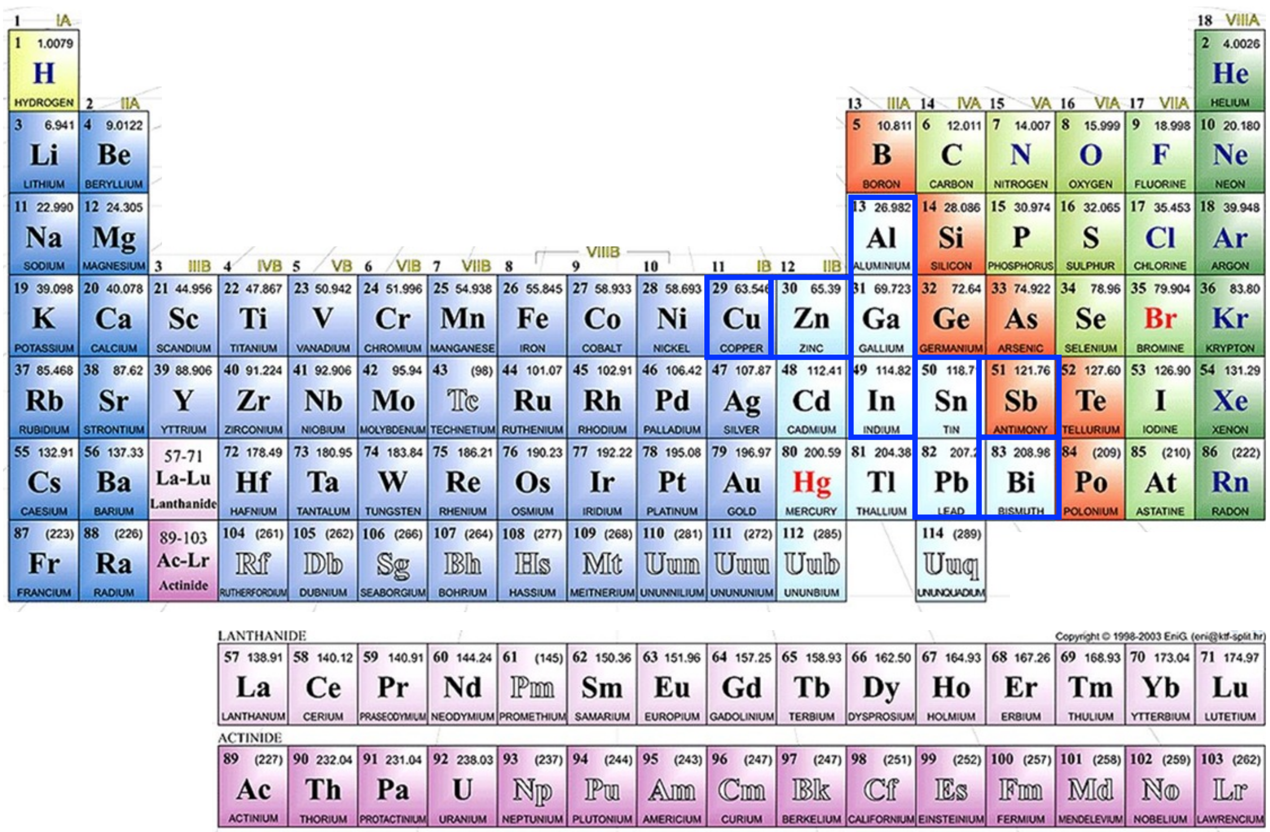
e.g. $YbCu_2Si_2$, TiNiSn, MnSnNi, *R*Sb; *R*BiPt, RPbPt



Review of some metallic fluxes

Sb
- T_{melt} = 630 °C
- stability of *R*-Sb phases

e.g. RSb_2, $U_3Sb_4Pt_3$, $PtSb_2$

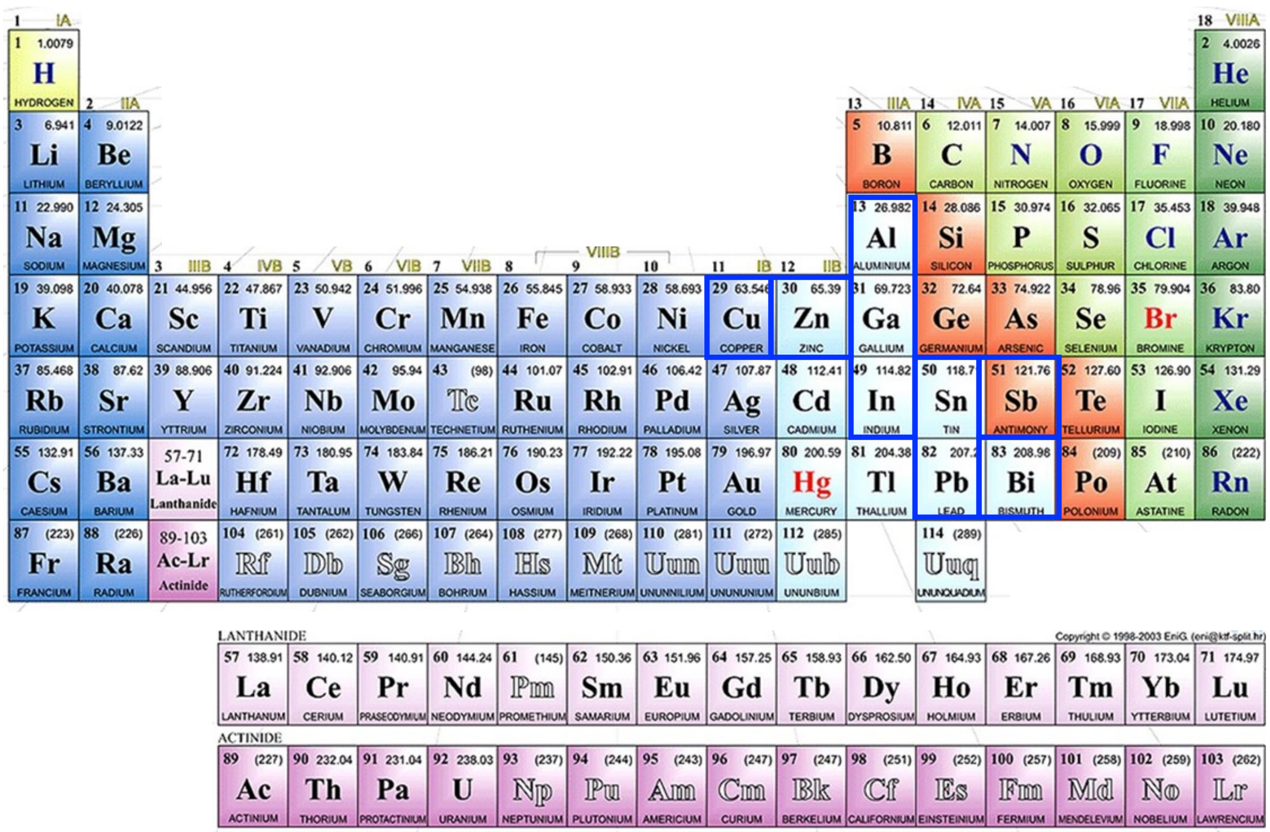


Review of some metallic fluxes

Zn T_{melt} = 420 °C e.g. InSb, GaSb, InAs, Si, Ge

Bi T_{melt} = 272 °C e.g. UPt_3, PtMnSb, NiMnSb, UAl_3, GaP, $ZnSiP_2$, $CdSiP_2$

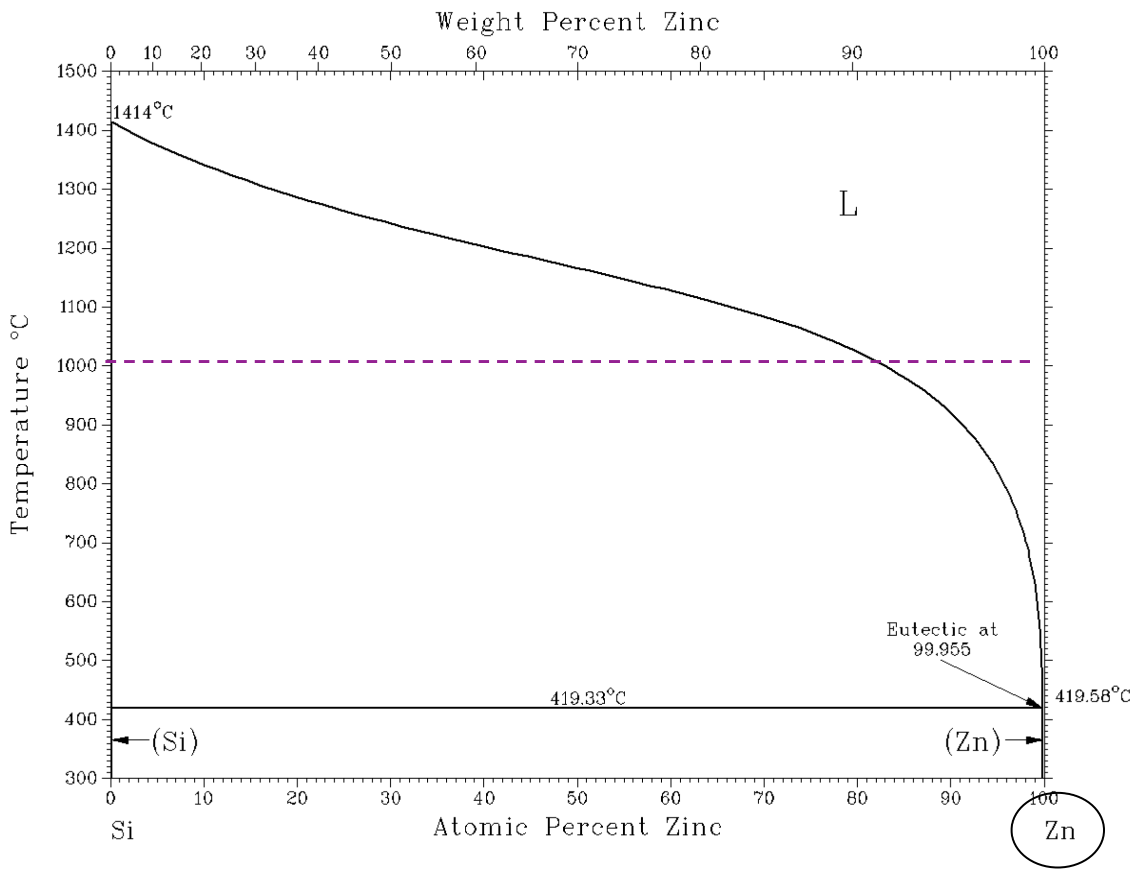
Cu T_{melt} = 1085 °C e.g. RPh_4B_4, RCu_2Si_2, V_3Si, RIr_2, UIr_3



❑ What are some examples?

(I) How to make Si? (T_{melt} = 1412 °C)

Let's aim for max temperature of our furnace of ~ 1000 °C
Look up solvents that are low melting: Bi, Sn, Zn, Ga, Al

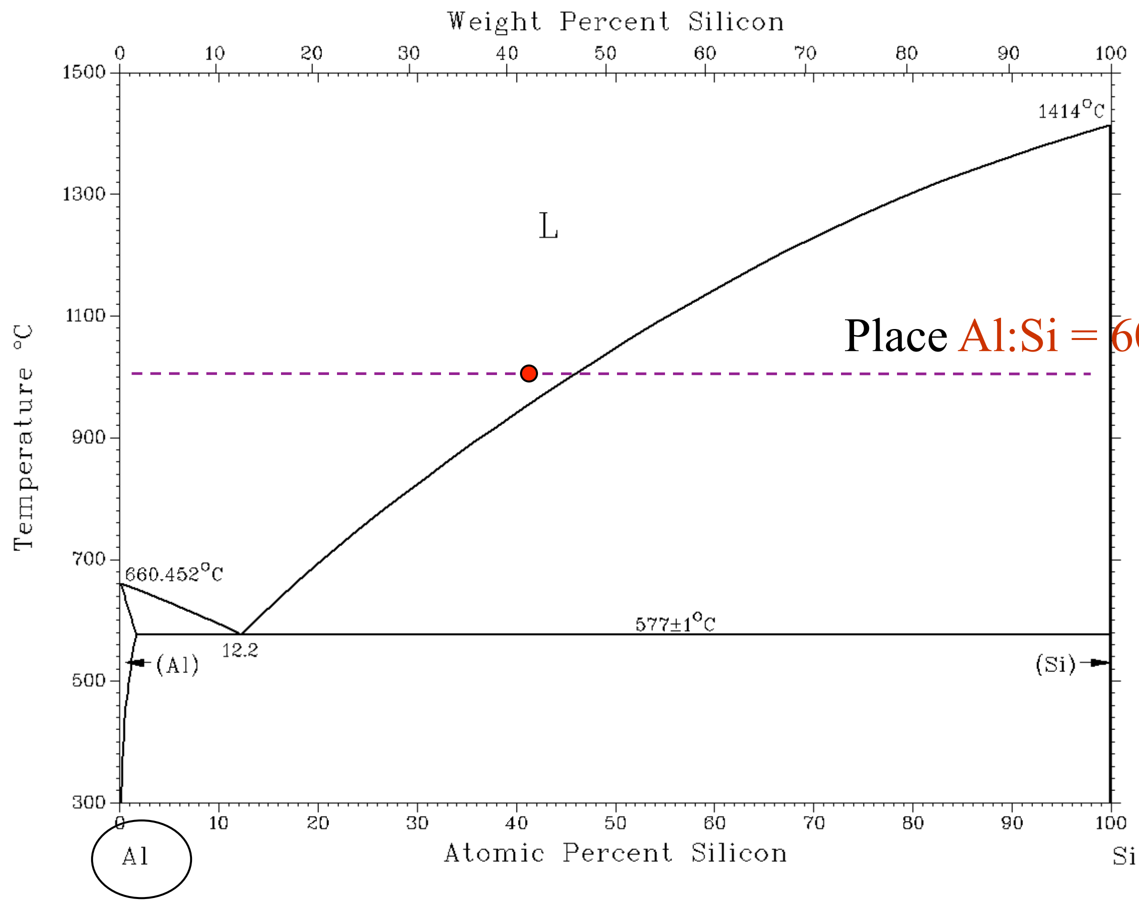


❑ What are some examples?

(1) How to make Si? (T_{melt} = 1412 °C)

Let's aim for max temperature of our furnace of ~ 1000 °C
Look up solvents that are low melting: Bi, Sn, Zn, Ga, Al

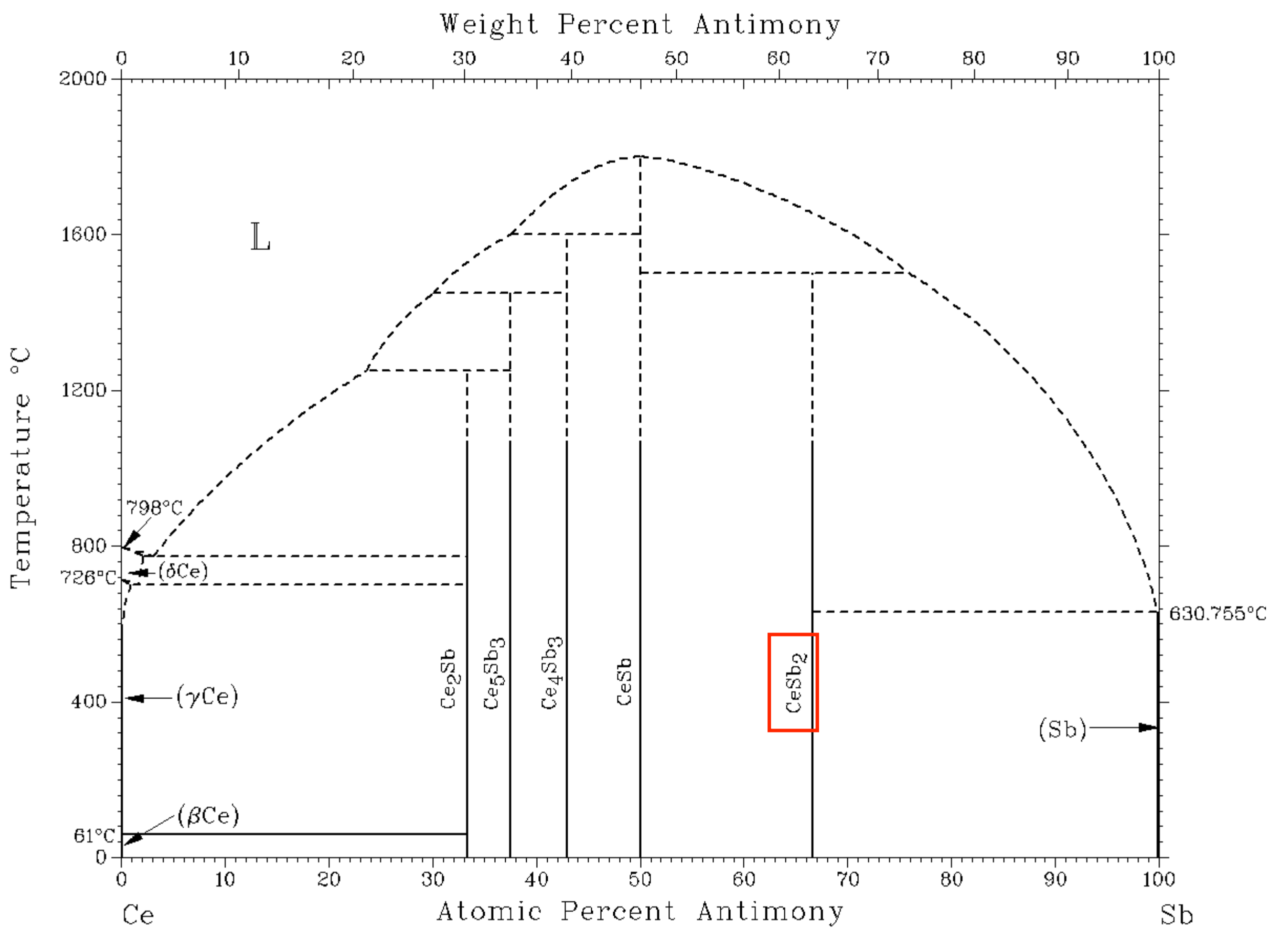
Best solvent



Place Al:Si = 60:40 into Al_2O_3

❑ What are some examples?

(2) How to make $CeSb_2$?   Melts incongruently



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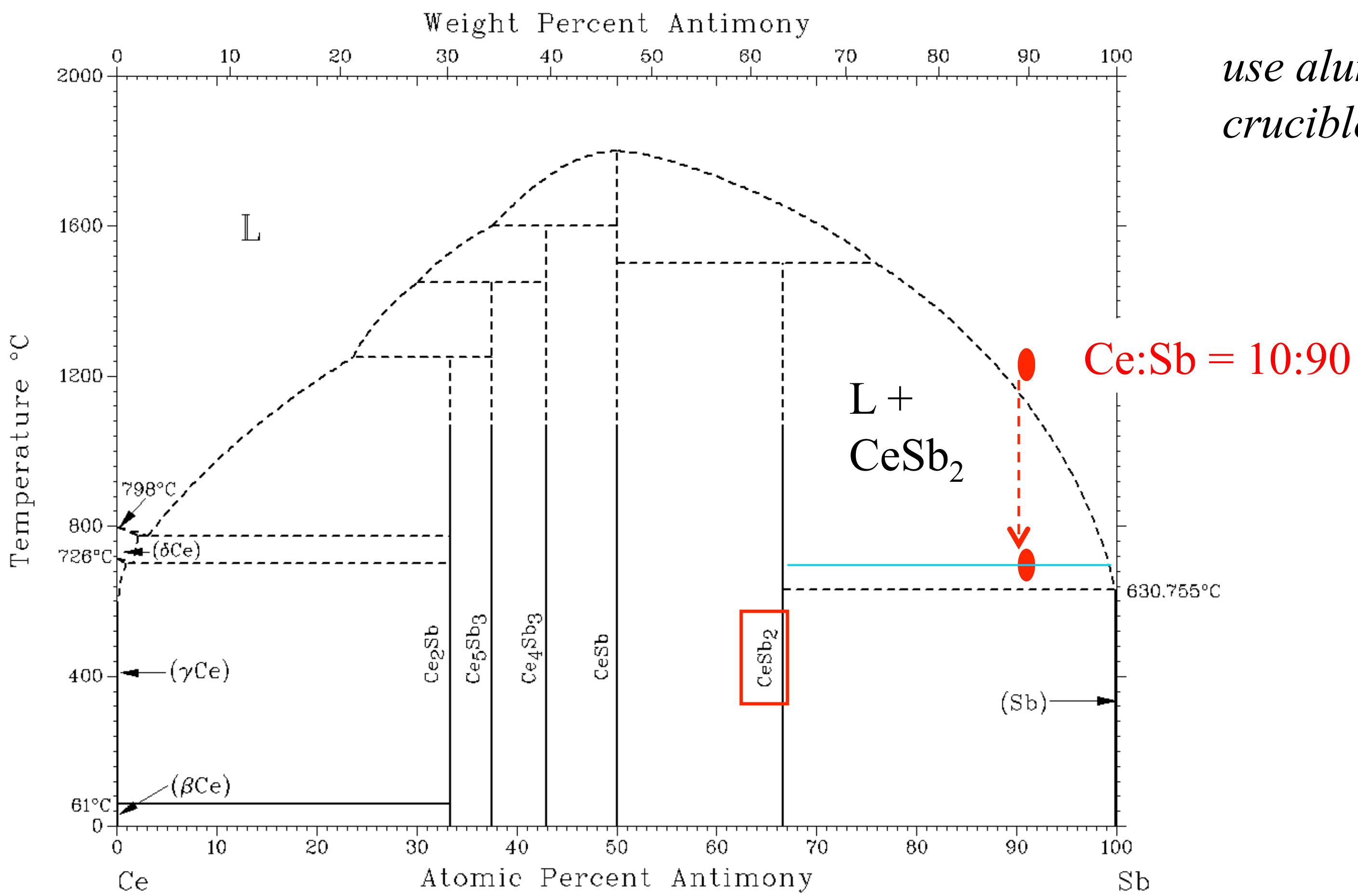
❑ What are some examples?

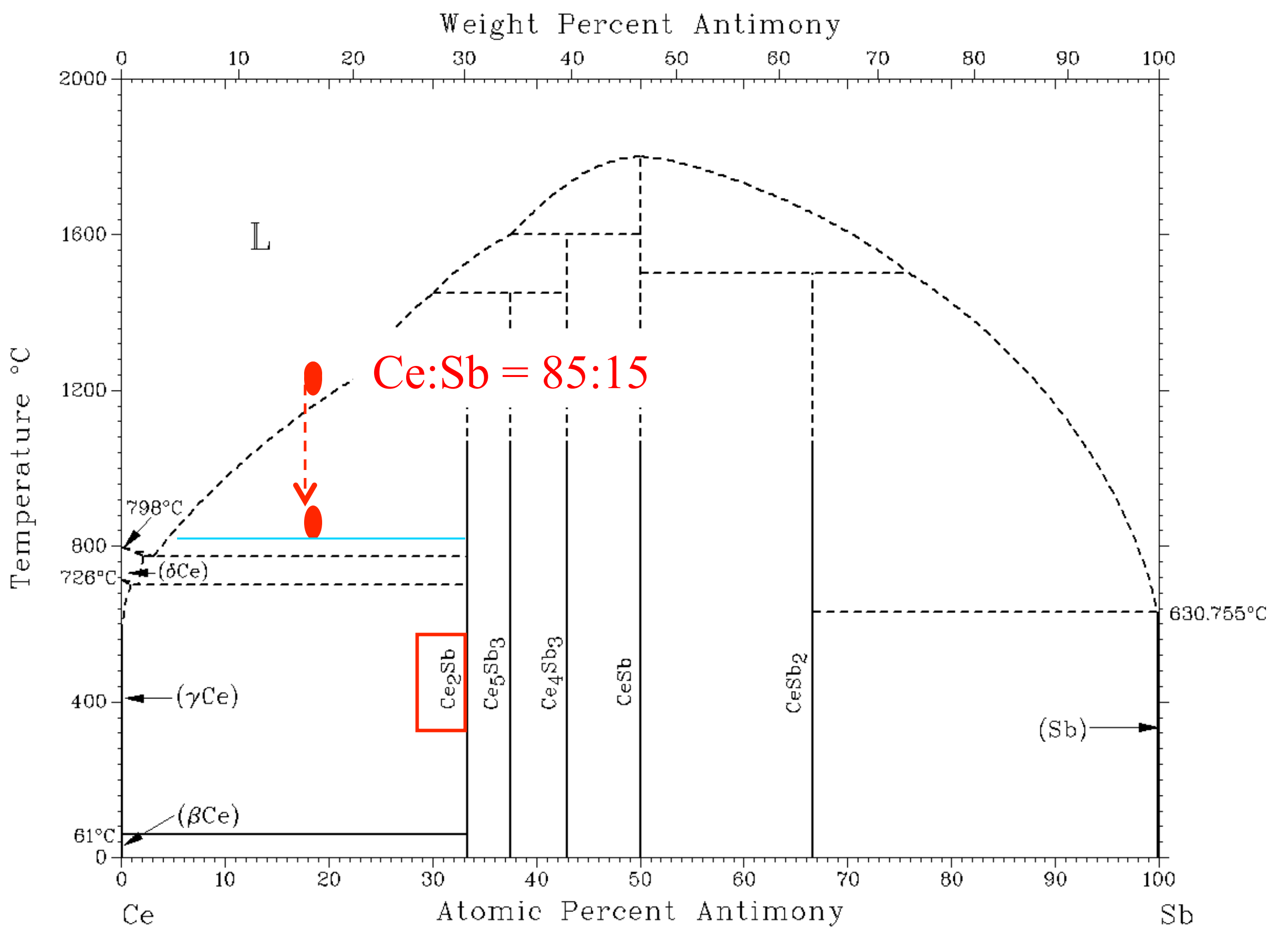
(2) How to make $CeSb_2$? Melts incongruently

use alumina crucible



❑ What are some examples?

(3) How to make Ce_2Sb? Melts incongruently

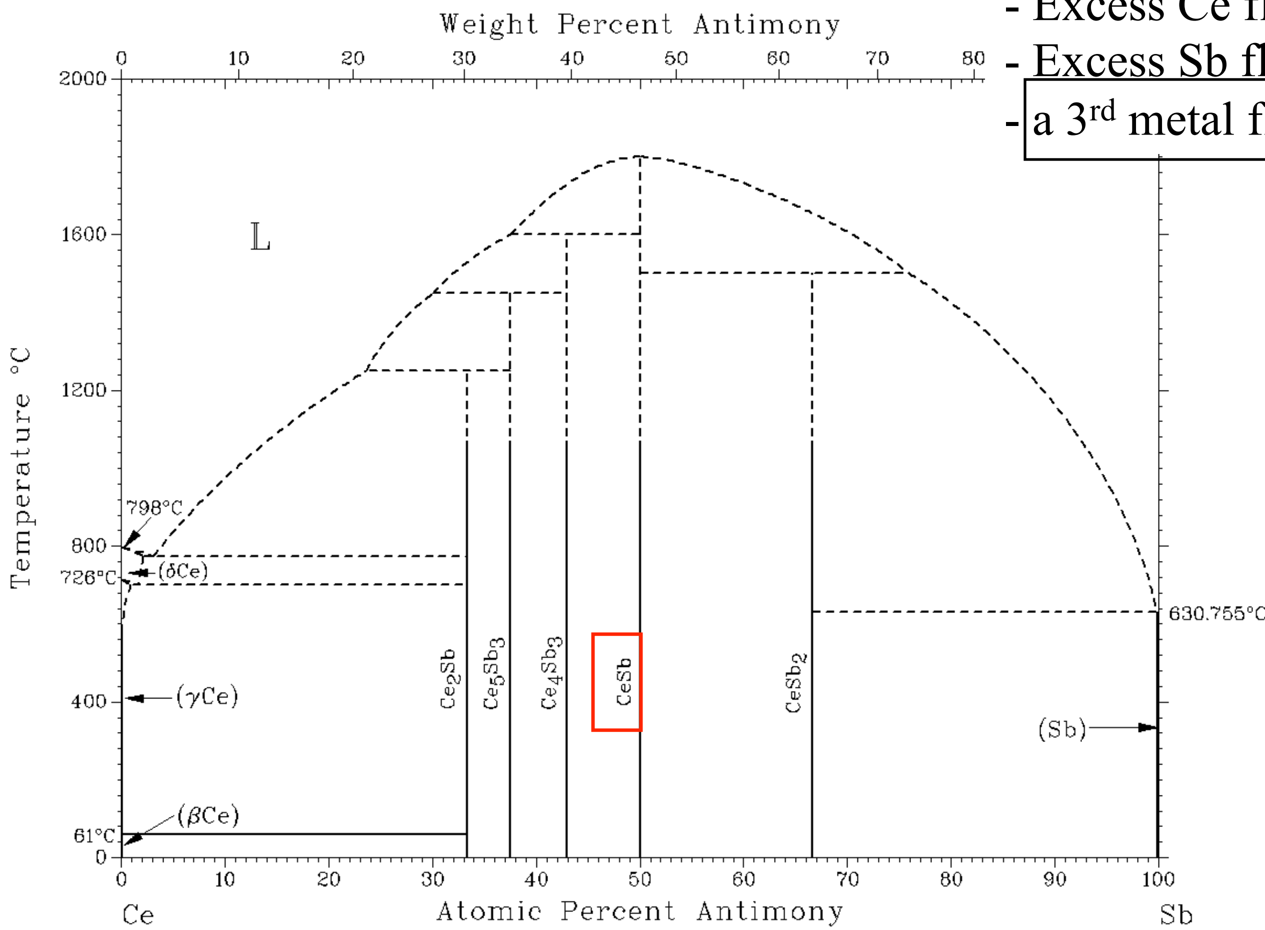


use Ta crucible

❑ What are some examples?

(4) How to make CeSb? Melts congruently at 1820 °C

- Melt growth technique
- Excess Ce flux
- Excess Sb flux
- a 3rd metal flux?

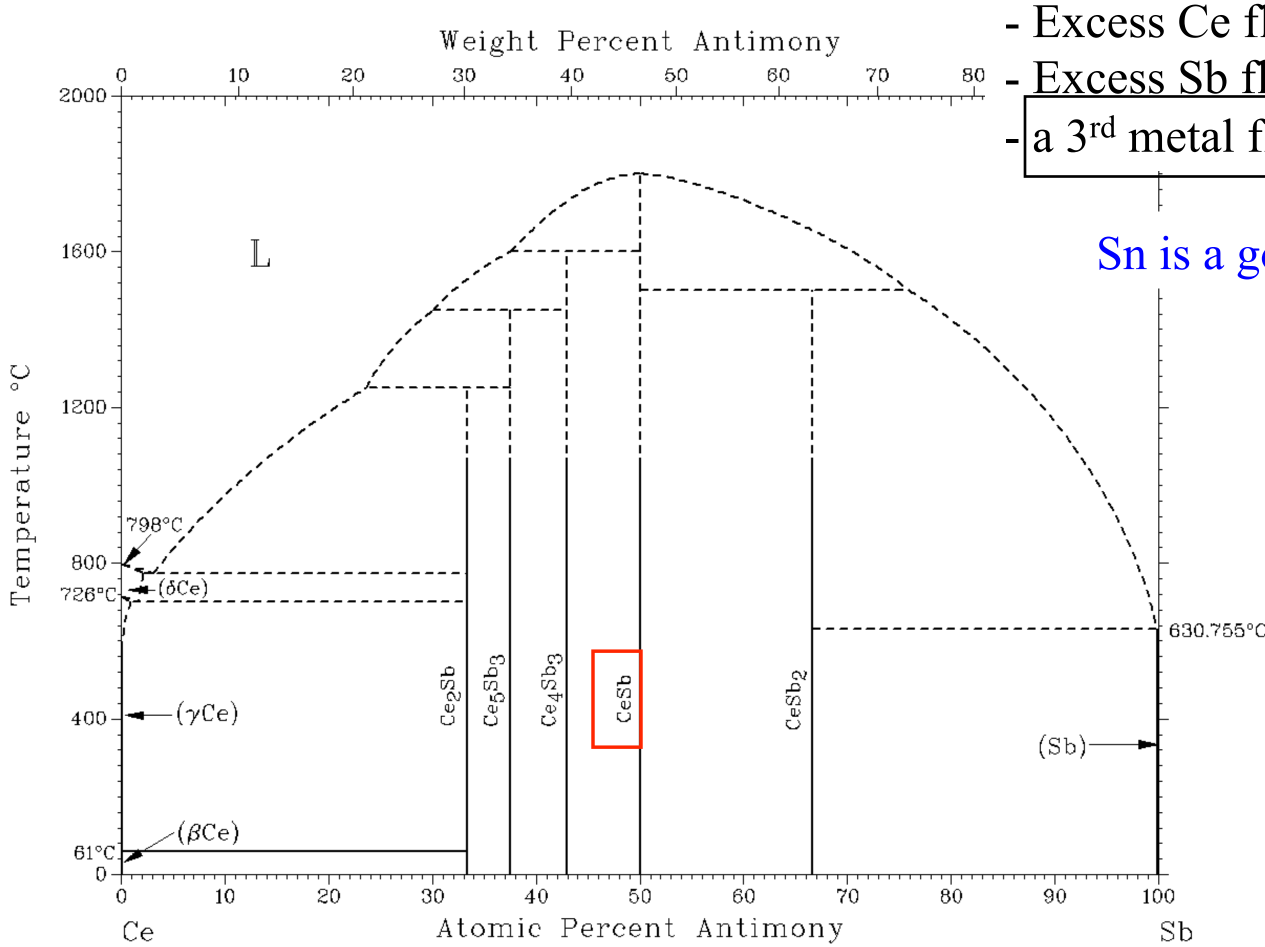


❑ What are some examples?

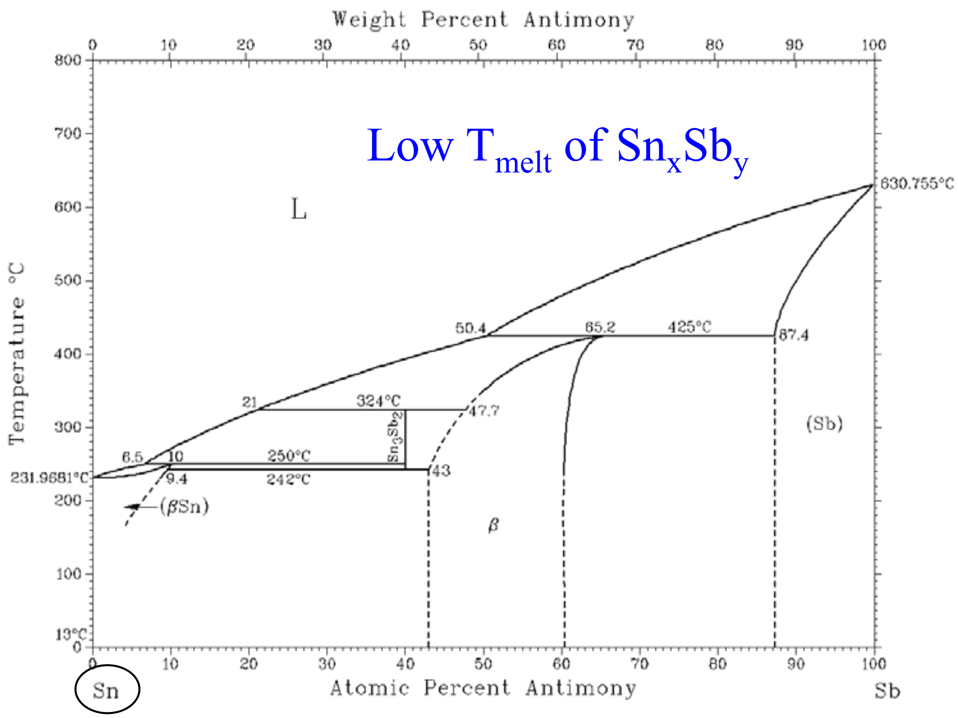
(4) How to make CeSb?   Melts congruently at 1820 °C

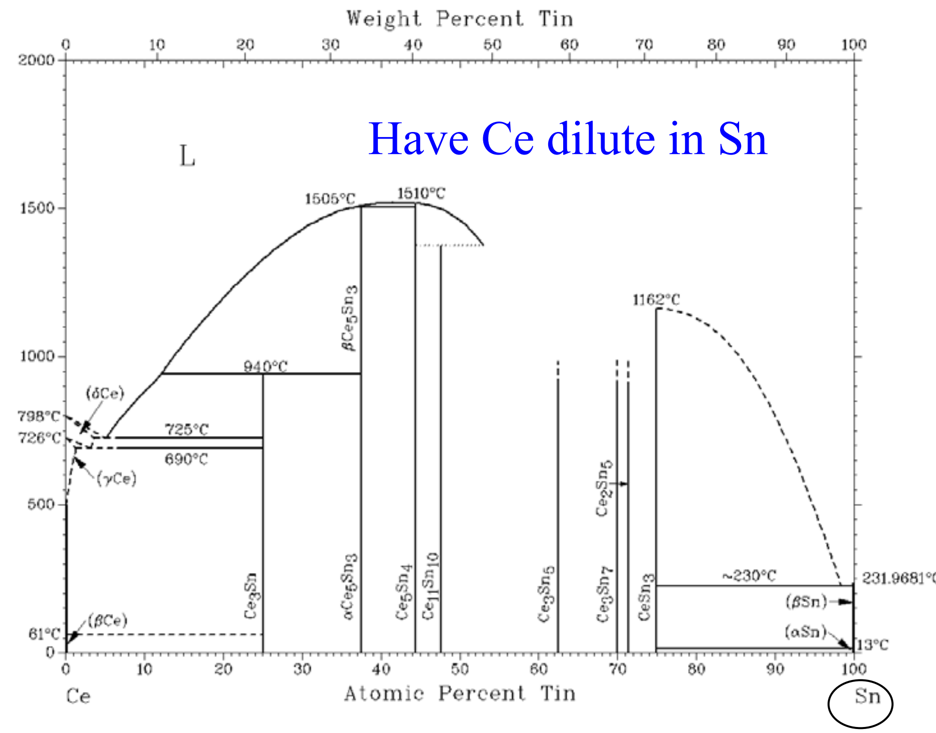
- Melt growth technique
- Excess Ce flux
- Excess Sb flux
- a 3rd metal flux?

Sn is a good choice



• Sn is a low-melting element that offered good solubility for both Sb and Ce





e.g. Try Ce:Sb:Sn = 5:5:95

1100 °C

800 °C

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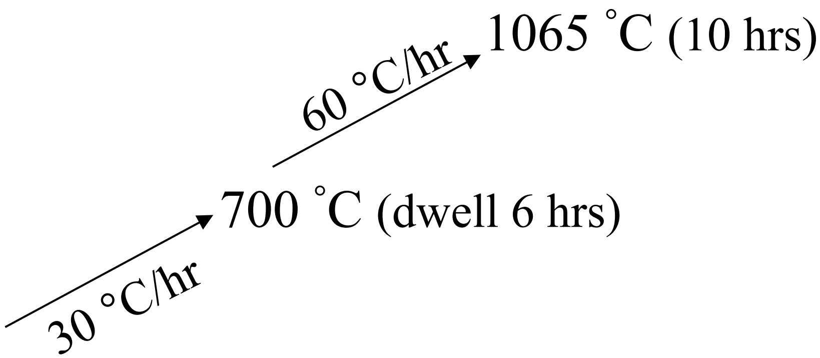
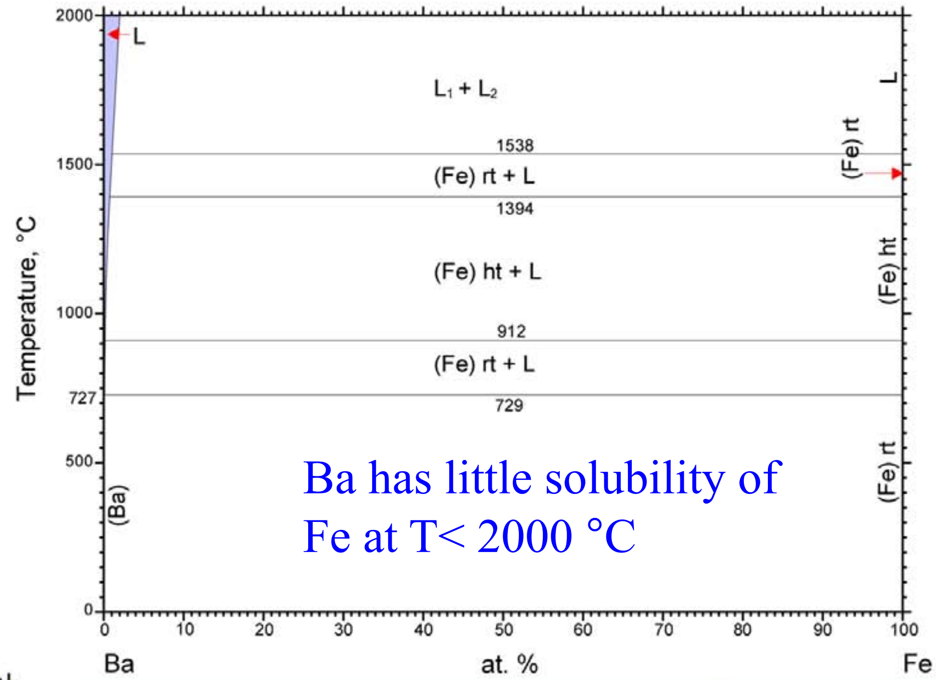
❑ What are some of my research examples?

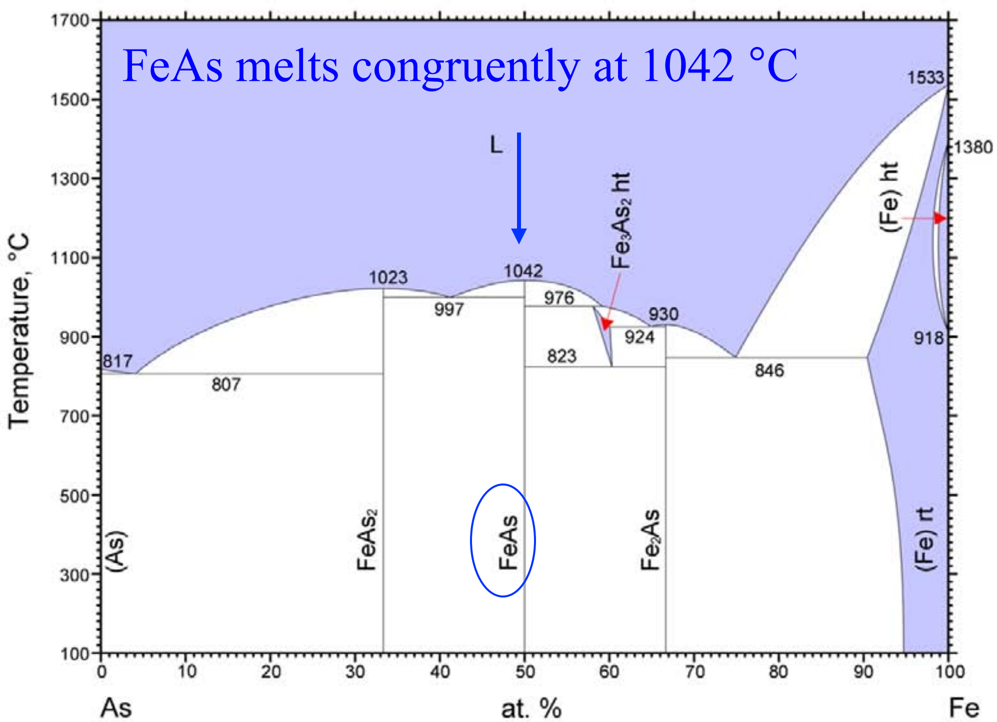
Growth of $BaFe_2As_2$

- Ternary phase diagram not known
- Arsenic has a high vapor pressure (~600 °C, 1 atm)
- Look for binary phase diagrams: Ba-Fe, Fe-As, Ba-As

1st, make FeAs







No Atomic % Diagram for Ba-As

2^{nd}, put $Ba(FeAs)_5$ in alumina crucible, in silica

350 °C/hr

1180°C (dwell 15 hrs)

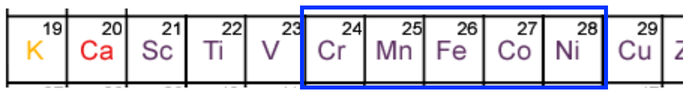
2 °C/hr

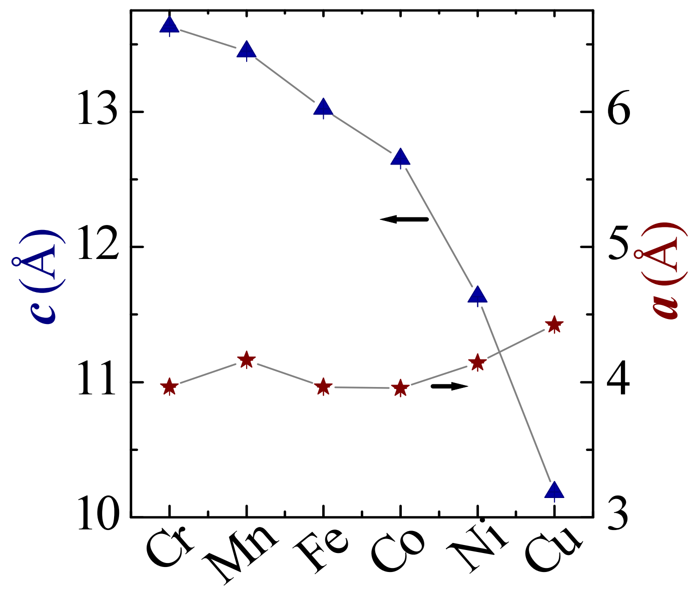
1090°C

AT_2As_2
(A = Ca, Sr, Ba;
T = Cr, Mn, Fe, Co, Ni)

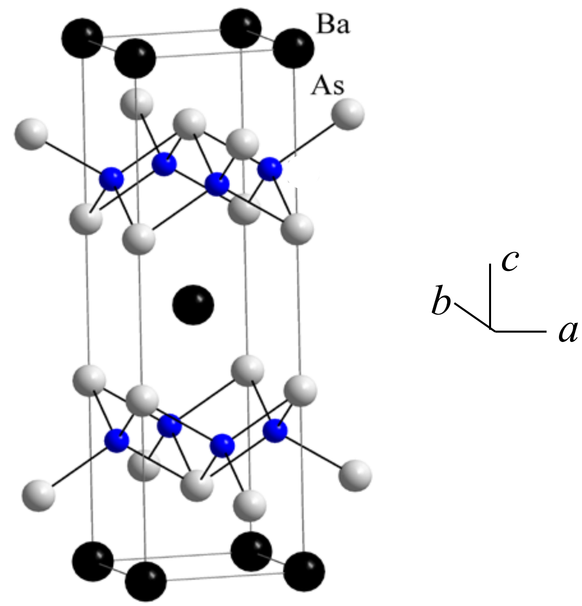
Phys. Rev. Lett. **101,** 117004 (2008).
Physica C **469**, 350 (2009).

BaT_2As_2





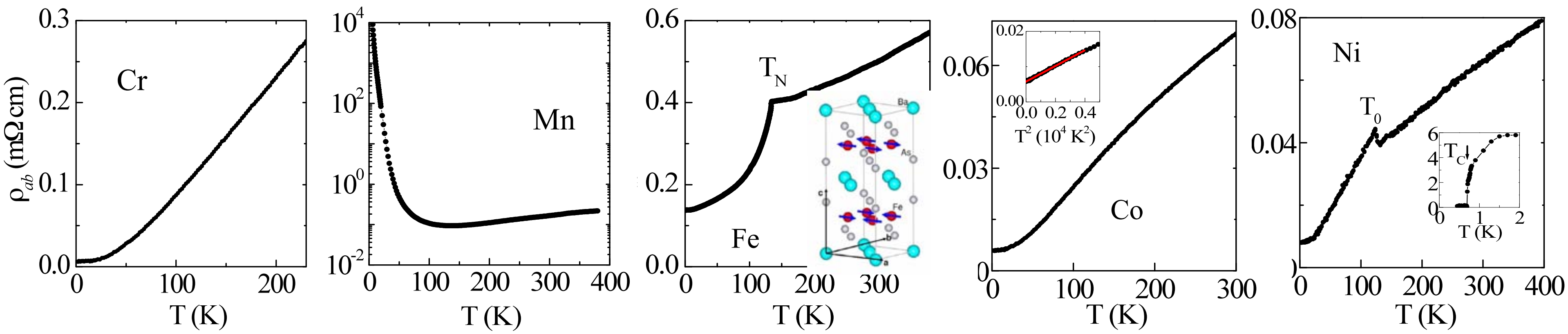
~ 7.4 % volume collapse

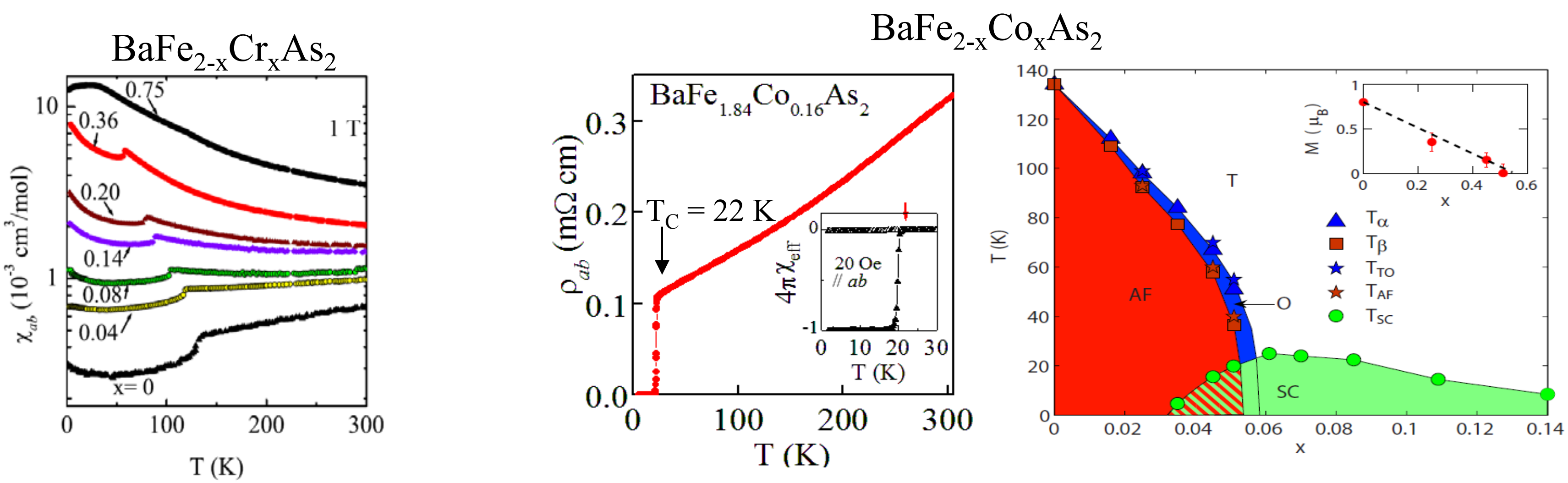


*I*4/*mmm*

Z. Naturforsch. B 36 (1981), 1668.

Ba$T_2$$As_2$

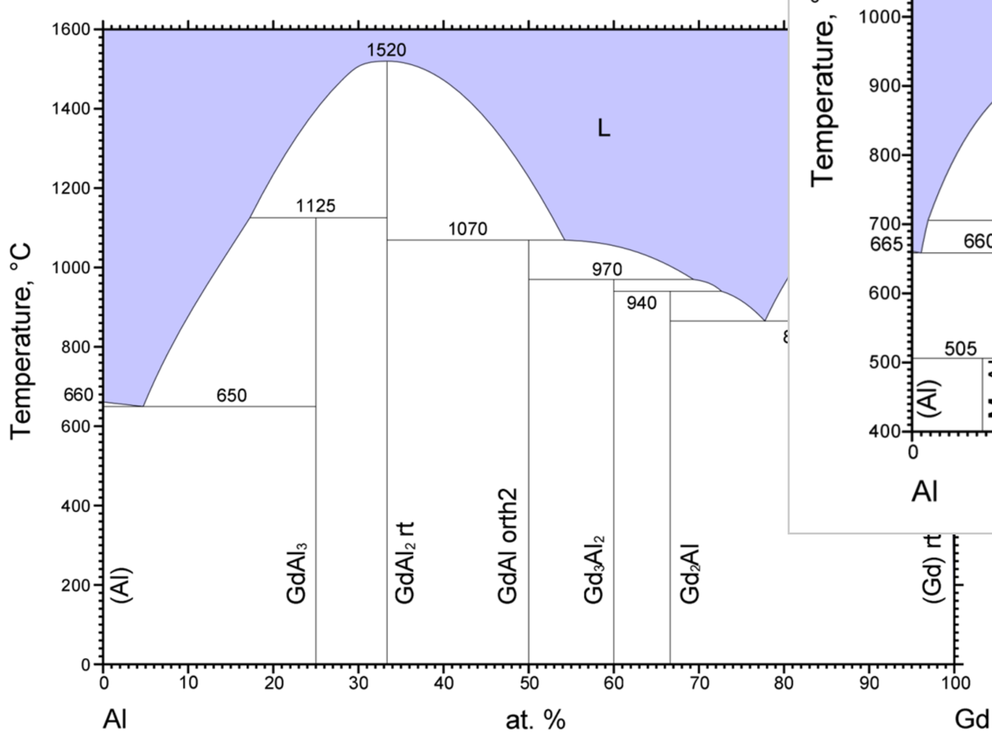


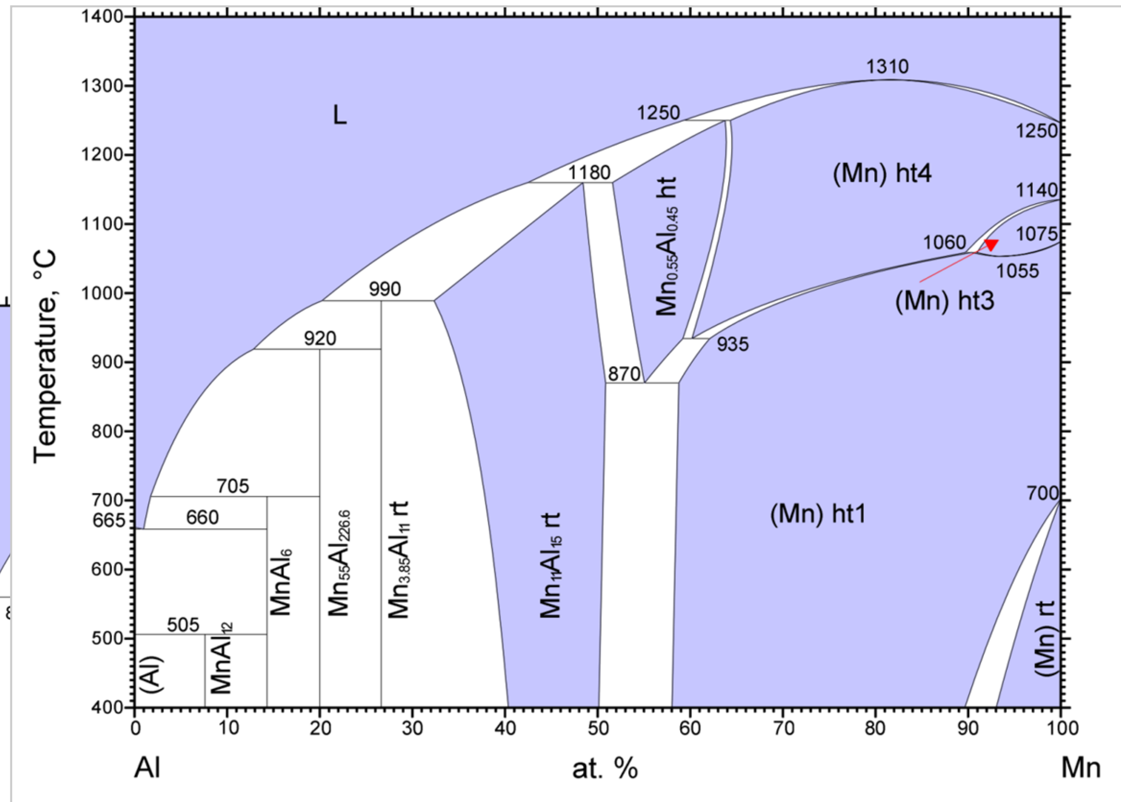


Phys. Rev. Lett. **101,** 117004 (2008).
Phys. Rev. B **79**, 024512; 094429; 224524; 144523 (2009).
Physica C **469**, 350 (2009).

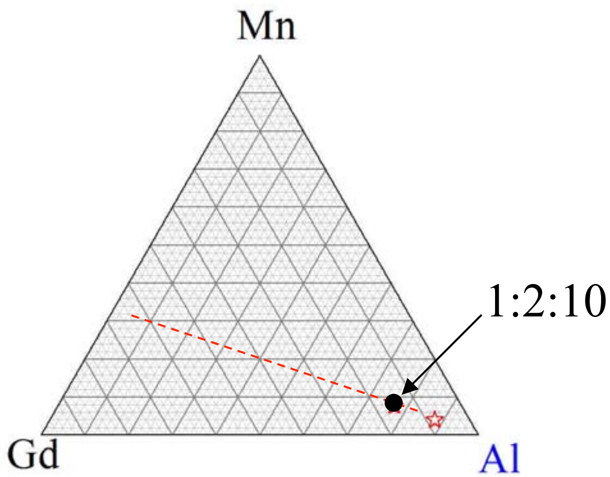
Growth of $GdMn_2Al_{10}$

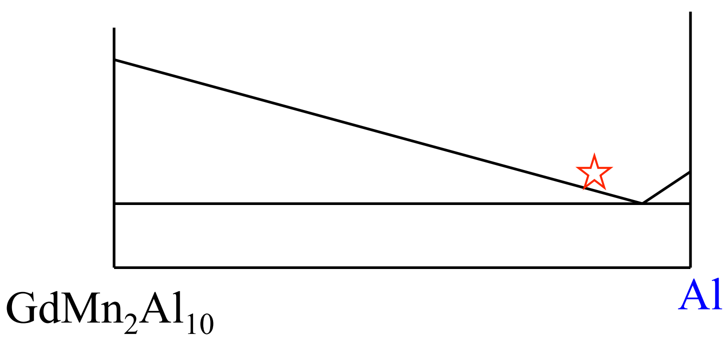
- Ternary phase diagram not known

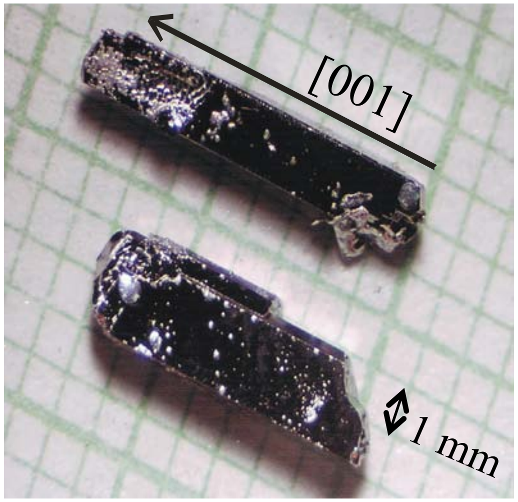




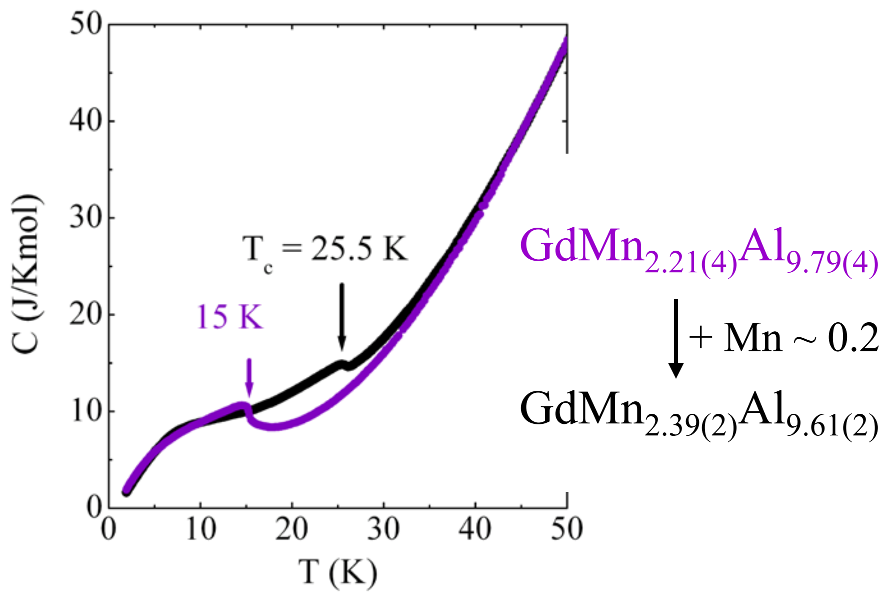
Try Gd:Mn:Al = 0.04: 0.08: 0.88 ☆

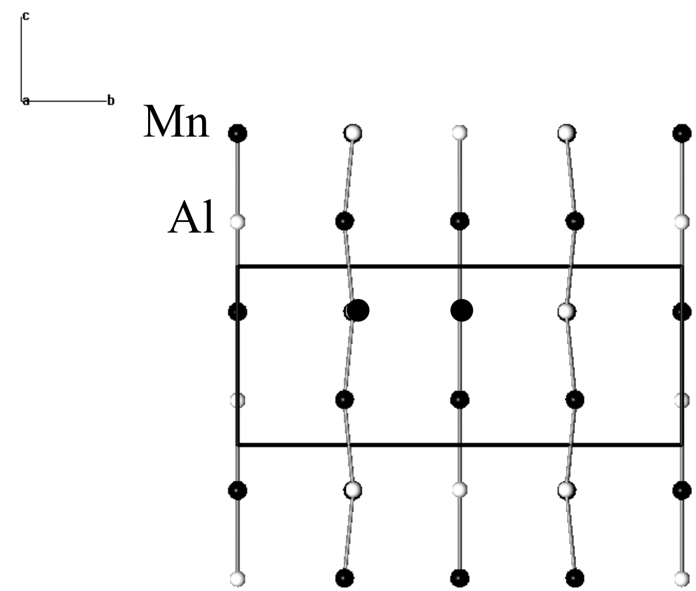






$GdMn_2Al_{10}$

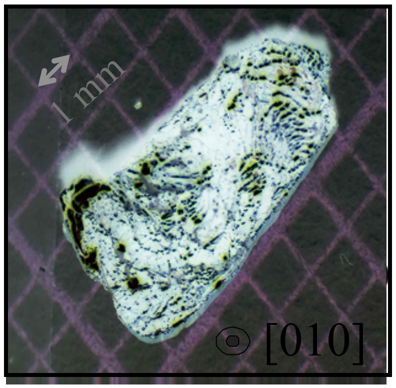


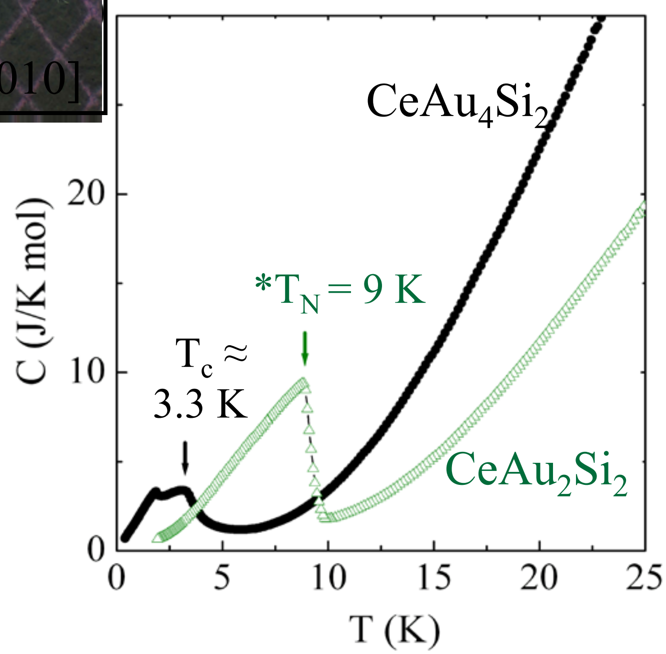


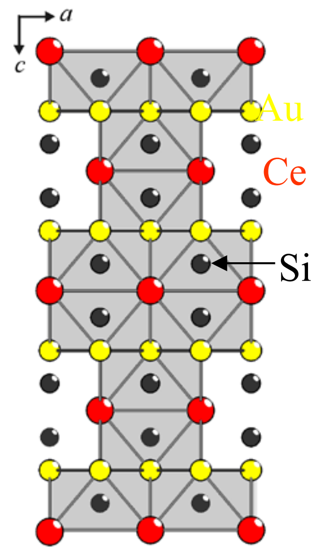
*P*4/*nmm*

Z. Naturforsch. **53b** (1998), 673.
Phys. Rev. B **76** (2007), 174419.

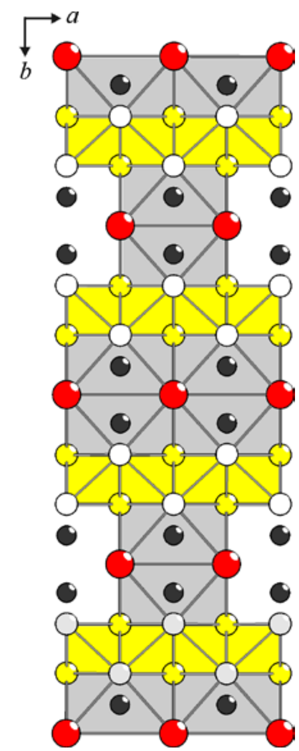
Growth of $CeAu_xSi_2$



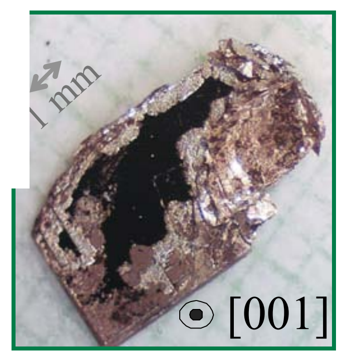




I4/mmm



Cmmm



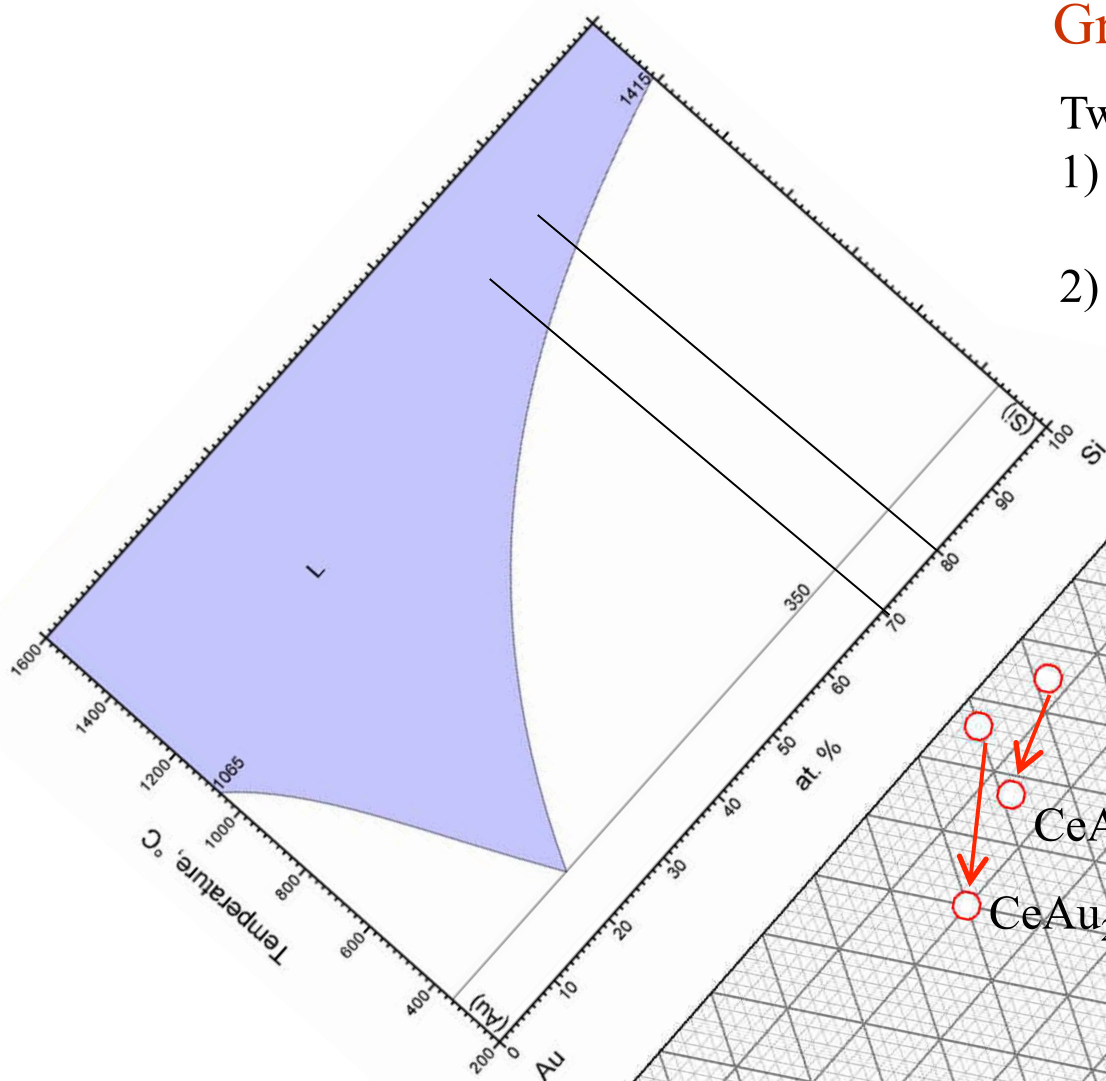
* T_N = 4 K, 8.1 K

Physica B, 378 (2006), 812

J. Magn. Mag. Mater 272-276 (2004), e405.

J. Solid State Chem. **181**, 282 (2008).

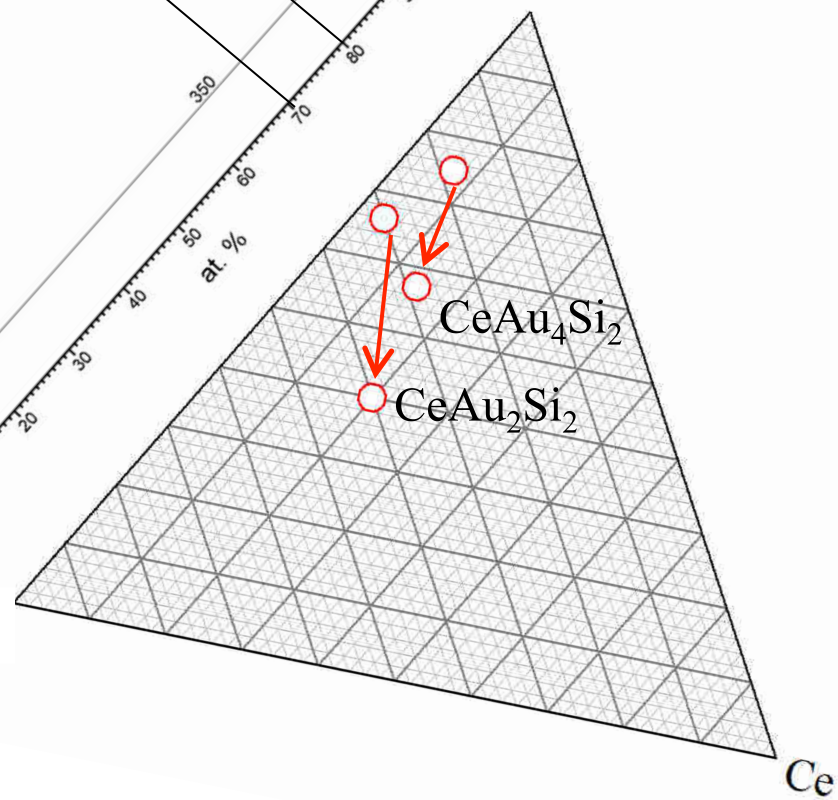
$CeAu_xSi_2$



Grown out of Au-Si eutectic

Two step growth:

1) First melt Au and Si together at ~ 1400 °C using an arc melt
2) Seal Ce and Au-Si in silica, soak & slow cool for crystal growth



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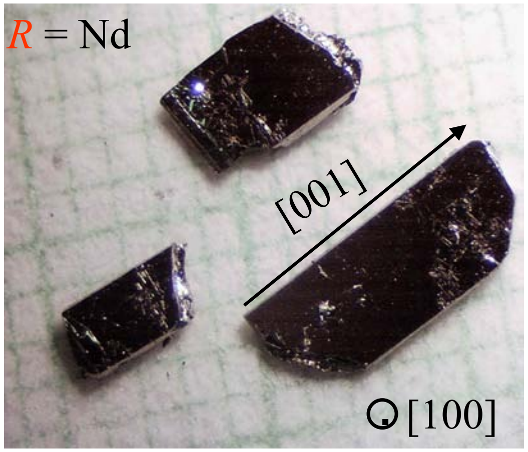
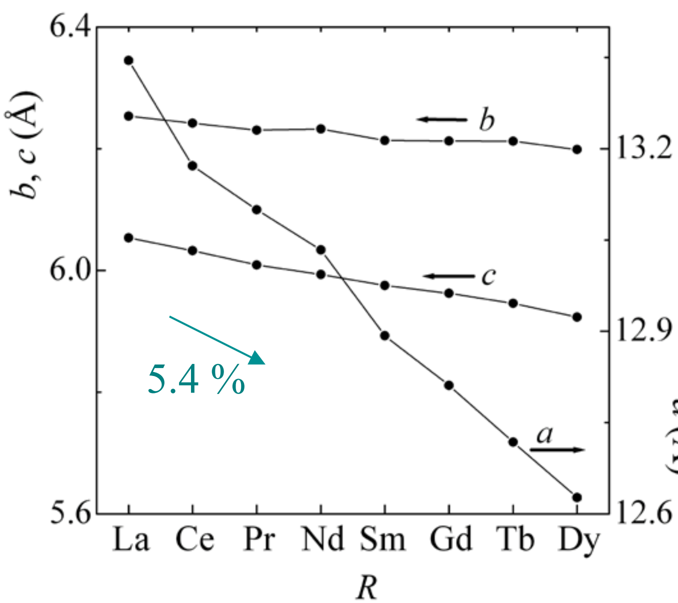
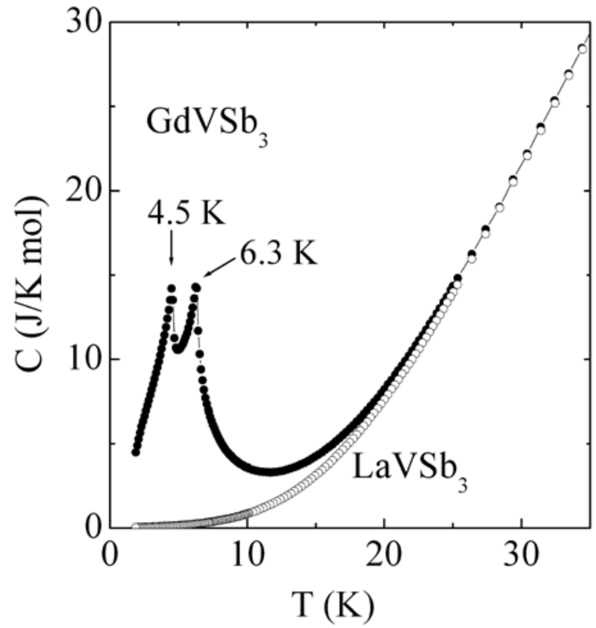
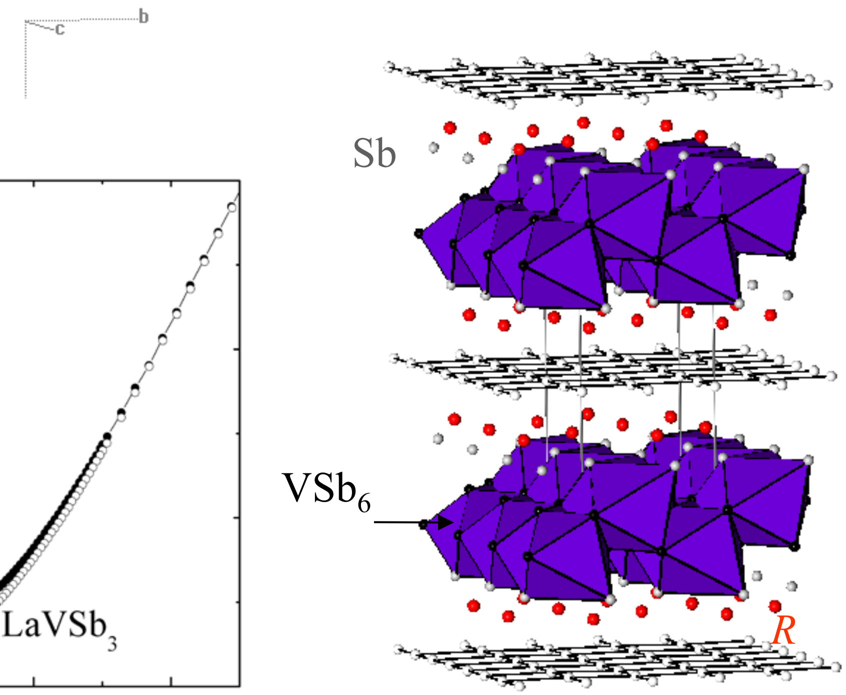
Growth of RVSb_3





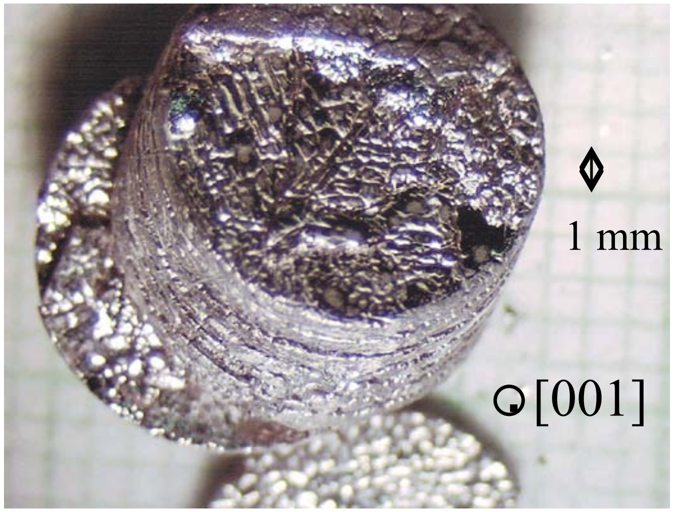




Pbcm

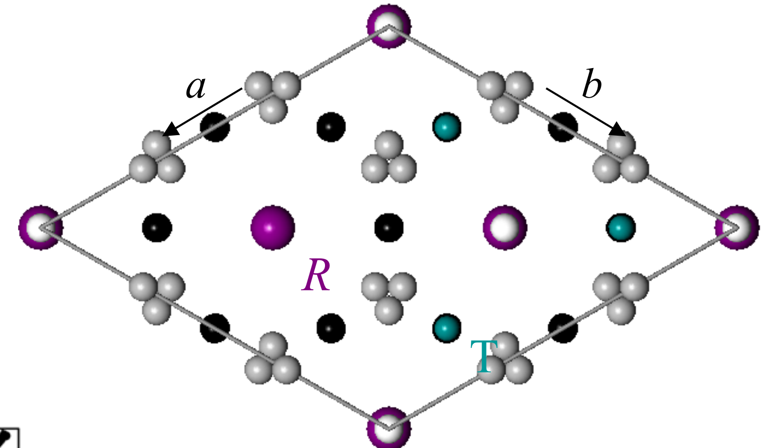
Phys. Rev. B, 65 (2001), 014421.
J. Magn. Mag. Mater. **320**, 120 (2008).

Growth of $R_2Co_3Zn_{14}$



R = Gd, T = Co

Initial melt of R:Co:Zn = 8:12:80; 6:11:83

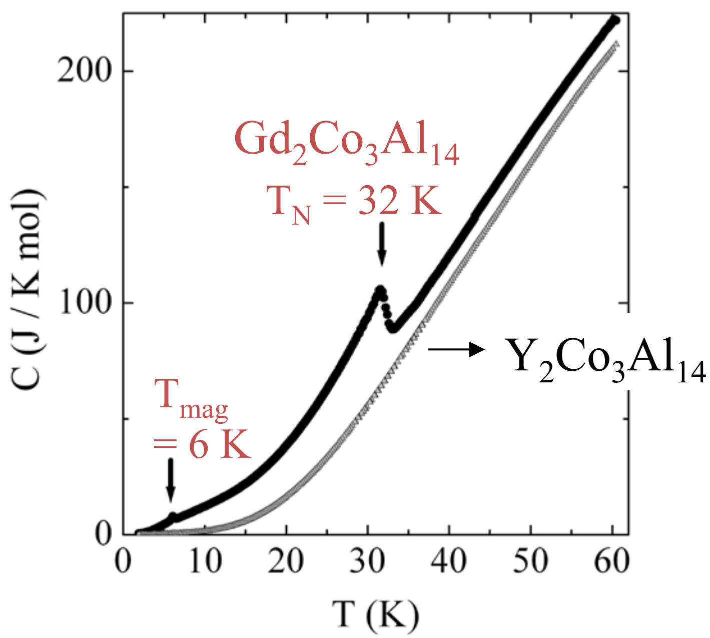


Zn1, Zn2,3

R-3*m*

Chem. Mater. **14** (2002), 2725.

J. Magn. Mag. Mater. **320**, (2008), 1035.



Concluding remarks:

- You can try to discover, and design that allow you to pursue the specific science that interest you.

- Although flux growth technique is less predictable than conventional crystal growth methods, the discovery of new materials may be made unexpectedly!

- Hope that you want to get in a synthesis lab and attempt crystal growth!