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

GROWTH

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Physics 590 B
Jan 12 & 14 2009
The periodic table is a palette, it is a well stocked pantry, it is the menu to choose your meal from, it is the ultimate puzzle box, it is the end all of DIY projects. It is the basis set that we have to work with.
If you know how to cook, you have the freedom to create the meal that appeals to you.

(Not southern Indian tonight, what about northern Italian, or how about a Japanese hybrid/variant?)
If you know how to design, discovery, and grow samples you have the freedom to create the sample that will allow you to pursue the science that appeals to you.

(Enough local moment physics for a while, let’s look at some hybridization effects or superconductivity.)

Let’s get started then....

(i) Why do we want to grow single crystals?

(ii) How do we grow single crystals?
Why single crystals? (part I)

1. Anisotropic properties
2. No grain boundaries
3. Purity

i.e. to measure the intrinsic physical properties you must use single-crystals
Why single crystals?  (part II)

BECAUSE THEY ARE PRETTY!!!
This talk will draw heavily from these four papers

**Growth of single crystals from metallic fluxes**

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High-temperature solution growth of intermetallic single crystals and quasicrystals
Paul C. Canfield*, Ian R. Fisher

Differential thermal analysis and solution growth of intermetallic compounds
Y. Janssenab,* M. Angsta K.W. Dennisb, R.W. McCallum, P.C. Canfielda,c

Small sealed Ta crucible for thermal analysis of volatile metallic samples
Y. Janssenab,* M. Angsta, K.W. Dennisb, R.W. McCallum, P.C. Canfielda,c
New Materials development / single crystal growth is often done with very modest equipment.
The spaces are small, and there can be a delivery room-like atmosphere. Crystal growth, like birth, can be messy. It is a fantastic, exciting, and addictive experience, *(spontaneous symmetry breaking at its best)*.

*Let’s see how this works*
First you need an idea....

We will come back to this step in a later lecture.

Next, you should check some phase diagrams to see what might work....

Most of the diagrams I will show come from these books.
Binary phase diagrams are fundamentally like maps: they show the extent of liquid and solid.

Let’s develop a little vocabulary.
Eutectic points: minima in liquid regions

Solution growth requires readily accessible liquid regions.

Often these are found in eutectic valleys.
Deep Eutectics offer tempting liquid regions for growth.
Congruently melting compounds transform from a homogeneous solid to a homogeneous liquid at melting point.

Congruently melting compounds can be made by a wide variety of growth techniques that simply melt and solidify samples of fixed composition.
As we cool through the liquid, we ultimately cool enough to hit the liquidus-line for AgBa. At this temperature AgBa starts crystallizing and the remaining liquid becomes more Ba rich. The sample is no longer homogeneous and instead contains a solid of one stoichiometry and a liquid of another, changing stoichiometry.
Incongruently melting compounds undergo a paritectic decomposition into a mixed solid and liquid phase, only to form a homogeneous liquid at higher temperatures.

If you cool a liquid with composition AgBa, it will first form Ag$_2$Ba as the remaining liquid becomes more Ba rich and only forms AgBa below the paritectic temperature of 560°C.

AgBa and Ag$_2$Ba$_3$ decompose paritectically (melt incongruently).
Ag$_5$Ba can form with a variety of compositions and even have a single crystal with a spread of stoichiometries.

Ag$_2$Ba, AgBa and Ag$_2$Ba$_3$ are shown to have no width of formation and are called "line" compounds.
Crystal growth of CeSb$_2$?

This is all nice in theory....But how do we REALLY DO THIS???

*WITH OUR HAND AND BODIES NOT SOME MENTAL EXERCISE*

CeSb$_2$ is incongruently melting at a relatively high temperature. An attempt to cool a melt of CeSb$_2$ would end up with a mixed phase and lots of mess (high vapor pressures).

On the other hand there is a very open line of primary solidification. Grow CeSb$_2$ out of a “self flux” of excess Sb.
As a rule of thumb, if we are below ~12 % R we can use Al$_2$O$_3$ crucibles.

We need to seal the crucible in a silica tube to contain and protect the growth.

Shown below are two 2 ml crucibles and a snugly fitting silica tube.
Place the Ce and Sb into the growth crucibles.

Put quartz wool into the catch crucible.

Place the growth crucibles and catch crucibles into the silica tubing.
Place quartz wool on top of the crucibles

Use the $\text{H}_2\text{-O}_2$ torch to neck down the silica
Evacuate the silica and seal off the ampoules

Clean off any finger prints, grease, etc.

Place ampoules into furnace
Program the temperature – time profile and let the thermodynamics take place

When growth is done, pour off the excess liquid.  
(a = 10-1000 g is better than a = 1 g = 9.8 m/s$^2$)
Flux growth (slow cooling of a melt)

Basic idea: slow cool into 2-phase region

eg: $\text{CeSb}_2 / \text{Sb}$

- self flux
- $\text{Ce}_{0.05}\text{Sb}_{0.95}$
- $1190 \, ^\circ\text{C} \rightarrow 700 \, ^\circ\text{C}$
What about growth of the congruently melting compound, CeSb?

This is tricky if done just out of the binary: very high temperatures and lots of defects (due to vapor pressure and entropy).

Can this be grown out of extra elements in manner similar to growing a salt out of water?

This question is the essence of flux growth.
When I was first faced with this goal I simply tried several of the "usual suspects", i.e. low melting elements that offered good solubility for both Ce and Sb.

Sn worked best
There are only low melting compounds of Sn and Sb.
If the Ce is dilute in Sn, then we only worry about CeSn$_3$ at low temperatures.
3rd element flux  eg: CeSb / Sn

In this case we can think of this as a pseudo-binary cut through the Ce-Sb-Sn ternary phase diagram.

\[(\text{CeSb})_{0.05}\text{Sn}_{0.95}\]

1100 °C → 800 °C  (Spin at 800 to avoid the CeSn₃ 2nd phase)
M(H), M(T), ρ(H) and ρ(T) data can be used to assemble an H-T phase diagram of fantastic detail. We will study this more next lecture.

Complex field and temperature dependent magnetism can be found in CeSb, especially very high purity single crystals grown out of Sn in this method.
For the rest of this lecture we will review other examples of growth design and implementation. I will try to point out issues associated with:

Silica Softening---When using silica tubing you must respect $T \sim 1200 \text{ C}$

Vapor pressure (attack)

Crucible stability

But before that do be aware of:

Toxicity of compounds before reaction

Toxicity of compounds after reaction

Expense of it all...Quartz, crucibles, elements....
Let’s try to grow GdFe$_2$. This presents several problems. The first is the fact that both elements are relatively high melters. If we just put Gd and Fe in a crucible and heated to 1200 C they would not react (surface area of contact matters). An arc-melter can be used to pre-alloy the elements to allow growth below 1200 C.
Second problem:

Lots of Gd which attacks Al₂O₃ via the thermite reaction

Classic thermite reaction: \( \text{Fe}_2\text{O}_3 + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 + 2\text{Fe} + \Delta \text{ (heat)} \)

Or in this case, Gd reacts with Al₂O₃.....

\( \text{Al}_2\text{O}_3 + 2\text{Gd} \rightarrow \text{Gd}_2\text{O}_3 + 2\text{Al} + \Delta \text{ (heat)} \)

(Results in damaged/leaking crucible and contaminated and depleted melt.)
Lots of Gd which attacks $\text{Al}_2\text{O}_3$ via the thermite reaction.

We solved this by inventing a 3-cap Ta crucible.
Now for some ternary compounds.

RAgSb$_2$ to start

RAgSb$_2$ compounds can be grown out of excess Sb.

This is similar in spirit to growing CeSb$_2$ out of excess Sb: we are growing out of an excess of one of the constituent elements.
CeAgSb$_2$ (Ce$_{25}$Ag$_{25}$Sb$_{50}$) can be grown from a melt with initial stoichiometry of Ce$_4$Ag$_9$Sb$_{87}$

This growth can be place in Al$_2$O$_3$ and sealed in silica. Temperature profile is:

1200 C  120 hours  670 C
Now ternary growths out of eutectics: \( \text{RNi}_2\text{Ge}_2 \) and \( \text{RCu}_2\text{Ge}_2 \) series.

Both the Ge-Cu and the Ge-Ni binaries have low, broad eutectic valleys.
Ce<sub>0.05</sub>Cu<sub>0.475</sub>Ge<sub>0.475</sub> is placed in an Al<sub>2</sub>O<sub>3</sub> crucible, sealed in a quartz ampule and heated to 1190°C. The ampule is cooled to 825°C over 200 h and then the excess liquid is decanted. The resulting crystal
CeCu$_2$Ge$_2$ ($m = 2 \text{ g}$)

Grown in a 5 ml Al$_2$O$_3$ crucible, sealed in silica

1190 C \hspace{2cm} 200 \text{ hours} \hspace{2cm} 825 C
RAgGe can be grown out of a Ag-Ge rich melt. In this case the starting melt reflects the Ag-Ge eutectic composition.
Crystals of RAgGe have allowed for the study of anisotropic metamagnetism as well as the discovery of new quantum critical properties in YbAgGe.

Melt stoichiometry: $\text{Yb}_{10}\text{Ag}_{68}\text{Ge}_{22}$

$1100 \text{ C} \quad 100 \text{ hr} \quad 850 \text{ C}$
Here is a 1992 summary of binary and ternary samples that I had grown out of binary, ternary and quaternary melts.

This is a very powerful technique for exploratory growth. Over a decade my group has made over 6000 growths similar to the ones I have been describing.

<table>
<thead>
<tr>
<th>Crystals</th>
<th>Flux</th>
<th>Dilution* (at.%)</th>
<th>Temperature (°C)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>RB₄</td>
<td>Al</td>
<td>R, 0.2</td>
<td>1450–700</td>
<td>R ≡ Sm, Gd–Lu, also U, Th</td>
</tr>
<tr>
<td>YbAlB₄</td>
<td>Al</td>
<td>Yb, 1.0</td>
<td>1450–700</td>
<td>R ≡ La–Eu, Yb, Ca, Ba, Sr, Nb, Am</td>
</tr>
<tr>
<td>RB₆</td>
<td>Al</td>
<td>R, 0.2</td>
<td>1450–700</td>
<td>R ≡ La–Lu, Y, U, Th BeO crucible</td>
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<tr>
<td>RBe₁₃</td>
<td>Al</td>
<td>R, 5.0</td>
<td>1250–700</td>
<td>R ≡ La–Lu, Y, U, Th BeO crucible</td>
</tr>
<tr>
<td>RA₁₃</td>
<td>Al</td>
<td>Yb, 0</td>
<td>1200–660</td>
<td>R ≡ Yb, Lu, Y, Sc</td>
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<tr>
<td>TiB₂</td>
<td>Al</td>
<td>Ti, 2.0</td>
<td>1440–800</td>
<td>No spin, NaOH etch</td>
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<tr>
<td>CeSi₂₋ₓ</td>
<td>Al</td>
<td>Ce, 5.0</td>
<td>1150–800</td>
<td>No spin, NaOH etch</td>
</tr>
<tr>
<td>UAl₃</td>
<td>Bi</td>
<td>U, 2.0</td>
<td>1150–700</td>
<td>BeO crucible</td>
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<tr>
<td>UPt₃</td>
<td>Bi</td>
<td>U, 7.0</td>
<td>1250–800</td>
<td>BeO crucible</td>
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<tr>
<td>YPd</td>
<td>Bi</td>
<td>Y, 10</td>
<td>1175–600</td>
<td>BeO crucible</td>
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<tr>
<td>RBiPt</td>
<td>Bi</td>
<td>Ho, 6.0; Yb, 10; Lu, 3.0</td>
<td>1150–500</td>
<td>R ≡ Nd–Lu</td>
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<tr>
<td>R₂Bi₄Pt₃</td>
<td>Bi</td>
<td>Ce, 13</td>
<td>1150–500</td>
<td>R ≡ La–Pr</td>
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<tr>
<td>RB₁₂</td>
<td>Bi</td>
<td>Ce, 10</td>
<td>800–400</td>
<td>R ≡ La, Ce, Pr, Yb</td>
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<tr>
<td>R₂Bi</td>
<td>Ce</td>
<td>Bi, 15</td>
<td>1150–900</td>
<td>R ≡ La, Ce, Ta crucible</td>
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<td>Ce₂Sb</td>
<td>Ce</td>
<td>Sb, 12</td>
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<td>CeFe₂</td>
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<td>1100–700</td>
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<tr>
<td>R₂Pt₄Ga₈</td>
<td>Ga</td>
<td>Ce, 1.0</td>
<td>1100–500</td>
<td>R ≡ La–Nd, Sm, Gd, etc.</td>
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<tr>
<td>CeCu₂Ge₂</td>
<td>In</td>
<td>Ce, 3.0</td>
<td>1175–750</td>
<td>Plates 2 mm × 2 mm × 0.2 mm</td>
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<tr>
<td>CeNi₃Ge₂</td>
<td>In</td>
<td>Ce, 3.0</td>
<td>1175–700</td>
<td>Plates 2 mm × 2 mm × 0.2 mm</td>
</tr>
<tr>
<td>YbCu₂Si₂</td>
<td>In</td>
<td>Yb, 4.0</td>
<td>1150–600</td>
<td>Plates 2 mm × 2 mm × 0.2 mm</td>
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<tr>
<td>RPb₃</td>
<td>Pb</td>
<td>Ce, 10</td>
<td>1100–800</td>
<td>R ≡ La, Ce</td>
</tr>
<tr>
<td>RPhPb</td>
<td>Pb</td>
<td>Ce, 7.0</td>
<td>1150–500</td>
<td>R ≡ La, Ce</td>
</tr>
<tr>
<td>RBiPt</td>
<td>Pb</td>
<td>Ce, 7.0</td>
<td>1150–500</td>
<td>R ≡ La, Ce, Pr</td>
</tr>
<tr>
<td>YbCu₂Si₂</td>
<td>Sn</td>
<td>Yb, 3.0</td>
<td>1150–700</td>
<td>R ≡ La, Ce, Pr</td>
</tr>
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<td>TiNiSn</td>
<td>Sn</td>
<td>Ti, 9.0</td>
<td>1150–600</td>
<td>Pyramidal</td>
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<tr>
<td>MnSnNi</td>
<td>Sn</td>
<td>Mn, 10</td>
<td>1150–450</td>
<td>Pyramidal</td>
</tr>
<tr>
<td>RSb</td>
<td>Sn</td>
<td>Ce, 5.0</td>
<td>1150–750</td>
<td>R ≡ La–Nd</td>
</tr>
<tr>
<td>RSb₂</td>
<td>Sb</td>
<td>Ce, 10</td>
<td>1175–750</td>
<td>R ≡ La, Ce</td>
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<tr>
<td>U₃Sb₂Pt₃</td>
<td>Sb</td>
<td>U, 8.0</td>
<td>1150–750</td>
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<tr>
<td>PtSb₂</td>
<td>Sb</td>
<td>Pt, 10</td>
<td>1150–750</td>
<td></td>
</tr>
</tbody>
</table>

* All materials in this table are dissolved in the flux stoichiometrically. The values shown for dilution are the amounts of one of the crystal components with respect to the flux.
To finish we can examine a few more ternary growths. These are *highly complex* compounds that are actually simple to grow, pointing out that just because *humans* consider them complex does not imply anything about their free energy or nucleation rate.

After this detour into “forbidden” symmetries we will finish with the growth of a refractory quaternary and some calorimetry.
In 1997 we became interested in growing RMgZn quasicrystals (to study their magnetic properties). All prior samples had been poly-grain and poly-phase.

At that point it was appreciated that this curious phase was stable.

It was also appreciated that they were incongruently melting.

Additionally, in 1997 it was reported that they had an exposed surface of solidification!

At this point you should know what this means!!!
Single grain $R_9Mg_{34}Zn_{57}$ via solution growth


Fig. 1. The temperature profile used to prepare single-grain quasicrystalline $R$–Mg–Zn from the ternary melt ($R = Y$, Er, Ho, Dy and Tb). Note that the time axis is not to scale. The inset shows a schematic diagram of the Ta device used for the growth and separation of the samples from the ternary melt.


Fig. 1. (a) Schematic pseudo-binary cut of the Y–Mg–Zn phase diagram approximately along the $Y_xMg_{60-3x}Zn_{40+2x}$ line (based on Ref. [2]). Vertical arrow represents initial melt with composition $Y_3Mg_{51}Zn_{46}$. Note: neither axis is to scale. Inset: photograph of HoMgZn single grain over mm scale.

Growth was done out of a Mg rich solution in Ta 3-cap crucible due to extreme reactivity of Mg with Al$_2$O$_3$ and silica.
Solution grown single grain of $\text{R}_9\text{Mg}_{34}\text{Zn}_{57}$ revealing natural growth habit.

With samples like this we were able to clearly determine the intrinsic properties of this compounds.
Growth of decagonal $\text{Al}_{72}\text{Ni}_{11}\text{Co}_{17}$

Grown in 5 ml (or larger) $\text{Al}_2\text{O}_3$ with $\sim \frac{1}{4}$ atm. partial pressure Ar to mitigate effects of Al vapor pressure.
Growth of icosahedral $\text{Al}_{71}\text{Pd}_{21}\text{Mn}_8$

Grown in 5 ml (or larger) $\text{Al}_2\text{O}_3$ with $\sim \frac{1}{4}$ atm. partial pressure Ar to mitigate effects of Al vapor pressure.
Growth of icosahedral $\text{Al}_{71}\text{Pd}_{21}\text{Mn}_{8}$

This growth is a rare combination of a very low nucleation rate and an initial melt very close to the sample stoichiometry. This is why we can grow such large grains. It also led us to grow over a very narrow temperature range with very high yields.
Al$_{73}$Pd$_{18}$Re$_9$

Can have starting stoichiometry ranging from Al$_{78}$Pd$_{15}$Re$_7$ to Al$_{71}$Pd$_{22}$Re$_7$. Cool from 1100 to 900°C at rate of ~ 0.5°C/hr.

Single grain, single phase samples reveal standard, weak localization....NO “Insulating” behavior.
RNi$_2$B$_2$C: A quaternary growth out of self-flux eutectic

This is a tricky growth.

Refractory compound

It is incongruently melting

On the other hand, there is a nice eutectic in the B-Ni binary system....
This is a two step growth:

1) Under protective atmosphere heat to 1500 and cool slowly to 1200 and quench.

2) Seal in silica, reheat to 1200, soak and then decant.

Grown from equal masses of RNi$_2$B$_2$C and Ni$_2$B
RNi$_{2}$B$_{2}$C crystals grow as plate and can even by crucible limited....

(again, cryptomorphic disks)
Superconducting for $R = \text{Dy, Ho, Er, Tm, Lu, Y}$ - $T_C$ values ranging from 17 K – 6 K

Magnetic order for $R = \text{Gd, Tb, Dy, Ho, Er, Tm}$ - $T_N$ values ranging from 20 K to 1.5 K
In many cases attempts at ternary growths involve educated guesses. Very few ternary phase diagrams are known or established. This means that for many of the cases reviewed today we had to iterate in on an optimized stoichiometry and temperature profile from the initial, first guesses.

As in cooking, experience is beneficial. In the same way that you know nutmeg brings out flavor in a white sauce, it becomes clear that Sn or In are good solvents for Si and Ge based compounds.

On the other hand, once a stoichiometry has been chosen, we can simplify the determination of temperature profile by calorimetric measurements on small samples.
Calorimetric data can provide guidance as to the temperatures of the start and end of crystallization. This information is particularly important when primary solidification occurs over a very limited temperature range.
We have developed a method of encapsulated small samples of volatile and/or reactive melts for calorimetric measurements.

We tested this on a melt that was both reactive and volatile.
Growth of Pr$_7$Ni$_2$Si$_5$

Pr$_{50}$Ni$_{25}$Si$_{25}$ DTA

Heat flow (arb. units)

$T$ (°C)

600 700 800 900 1000 1100

5 hr  1190  2 hr  1190  2 hr  1100  50 hr  1000
Summary:

I hope that some of you now simply want to get into the lab a play around with growth.

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You are NOT limited to the four samples that your Professor found in a drawer.

All Physics does not have to be found in Si.

You can try to discover, design, and make crystals that will allow you to pursue the specific science that interest YOU.
That's All Folks
Acknowledgements

Orson Welles once said that making films was like being a small child with a very expensive paint box. In a similar manner searching for new materials and growing single crystals of a wide variety of compounds requires a adequate and flexible materials budget. We gratefully acknowledge the US Department of Energy, Office of Basic Energy Sciences. Their unflagging support has made all of this research possible.

Ames Laboratory is operated for the US Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. The work at Ames was supported by the Director of Energy Research, Office of Basic Energy Sciences.