

## Growth of single crystals from metallic fluxes

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### ABSTRACT

Our experience with the growth of a wide variety of intermetallic compounds from molten fluxes is reviewed. Common problems associated with this method of sample growth are discussed, as are problems and advantages of particular fluxes.

### § 1. INTRODUCTION

The availability of single crystals is vital for many classes of experimental measurements. Not only is this the case for measurement of most tensor properties, but this is also the case when it is necessary to eliminate effects caused by grain boundaries in polycrystalline samples. Single-crystal growth out of metal fluxes is particularly advantageous because it requires no specialized equipment and allows for relatively low growth temperatures. Some of the disadvantages are that the crystals can be too small for certain experiments (such as inelastic neutron scattering) and that there is always the possibility of either flux substitution for constituent elements of the desired material or macroscopic flux inclusions in the grown crystals.

In this paper we review the crystal growth technique used in our laboratory to obtain single crystals of intermetallic materials from metallic fluxes, with emphasis on the details of specific dilutions and temperatures required for growth of a wide range of materials. This paper follows an earlier paper by Fisk and Remeika (1989) and extends rather than reiterates the material covered in that work.

The next section discusses the basic technique for growing single crystals from metallic fluxes. Following this we examine details of several exemplary growths and finally discuss aspects of specific fluxes.

### § 2. EXPERIMENTAL TECHNIQUES

There are several general techniques for the growth of single crystals from metallic fluxes. The basic criteria that distinguish one from another are either the required operating temperatures or the method of extracting the crystals from the flux. For temperatures below 1200°C, sealing of the crucible in a quartz ampule is advantageous, since it provides a protective environment for the sample growth, contains volatile materials and, as will be discussed below, allows for an extremely simple removal of the crystals from the flux via centrifugal force: spinning off the flux. For temperatures over 1200°C or volumes greater than 5 ml, sealing the materials in quartz is no longer practical, and protective atmospheres must be provided in other ways. Even so, molten flux can, in some cases, still be removed via spinning, if the spinning temperature is below 900°C, the highest practical temperature, in our opinion, for spinning in an unheated centrifuge.

The most common method of maintaining the proper crystal growth environment is to seal the materials into a quartz ampoule. The starting materials are placed in a crucible inert to the melt, with materials having the higher melting temperatures on the bottom. As the low-melting materials melt they flow over the higher-melting materials and start incorporating them into the melt. The crucible itself is placed in a sealed evacuated quartz ampoule and slightly elevated off the bottom of the tube by shards of quartz. This is to avoid cracking the quartz tube as a result of differential expansion between the tube and the crucible. Finally, there is a plug of quartz wool above the crucible that acts as the filter during flux removal. After the crystals are grown, but at temperatures still above the melting point of the flux, the ampoule is taken out of the furnace, inverted in the cup of a centrifuge and quickly spun. This forces the still-liquid flux through the quartz wool and leaves the crystals in the crucible. If there is reason to believe that there may be a seeding problem caused by the presence of the quartz wool dust, then the crystals can be grown in the ampoule without the wool and subsequently sealed in another tube with quartz wool and heated to the desired spin-off temperature.

Another method of removing crystals from the flux involves chemically etching the solid flux away from the crystals, but this places a stringent requirement on the etchant; it must attack the flux much more quickly than it does the crystals. This is the case for many Al flux growths, since Al can be eaten away by NaOH solution, which often does not attack the desired materials. Other examples where this works are the cases of the  $R_2Pt_4Ga_8$ -Ga,  $CeCu_2Ge_2$ -In and  $YbCu_2Si_2$ -In growths. The Ga and In can be eaten by concentrated HCl which does not attack the crystals. Unfortunately, it is often the case that the solvents that will attack the flux also attack the crystals with an equal or greater enthusiasm. This is the case with  $RSb$ -Ga growths. Etching away the flux can also sometimes be achieved through electrolytic erosion.

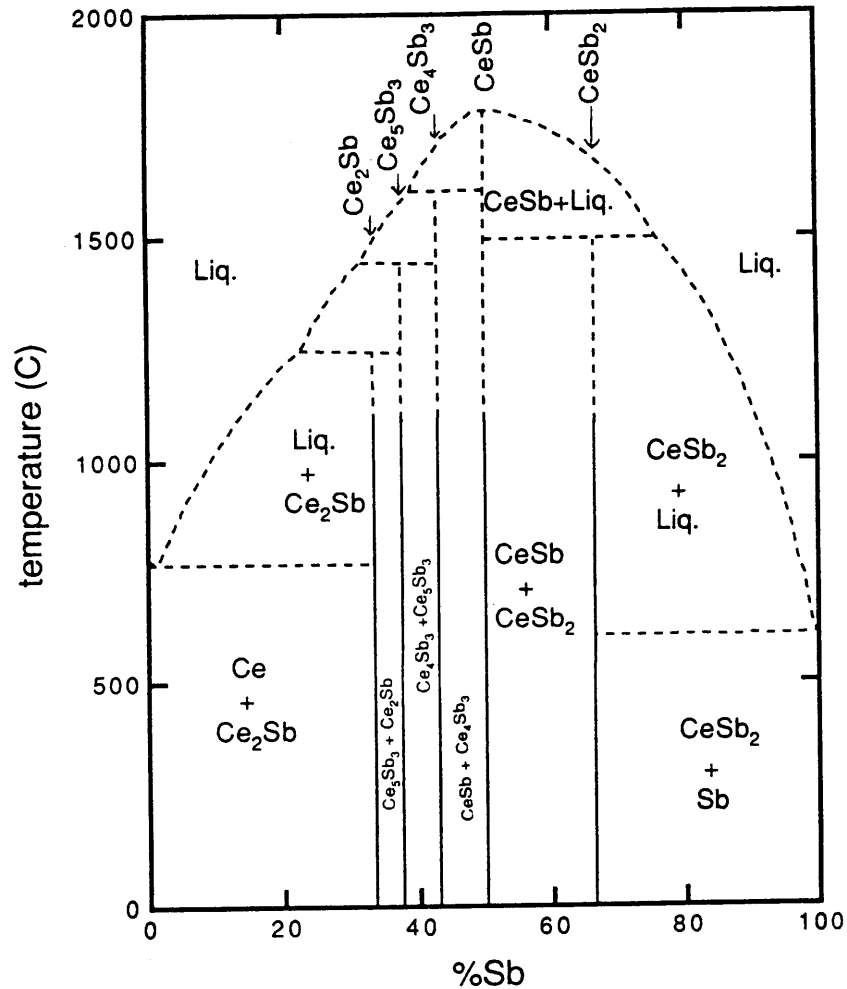
Finally, there is always the option of mechanically removing the crystals from the solidified flux. This is not the preferred route, since it is time consuming. In this paper we shall concentrate primarily on the materials that can be removed either via spinning off the flux or by chemical etching.

### §3. CASE STUDIES

In this section we shall discuss several materials in detail. These specific materials are chosen not because of particular physical properties, but because their growths illustrate specific features and problems worthy of comment. Figures 1 and 2 are the binary phase diagrams for Ce-Sb and Ce-Bi respectively. These are both based on data from Moffat's (1981) binary phase diagrams. This is the most recent of four collections of binary phase diagram data. The earlier references are Hansen (1958), Elliott (1965) and Shunk (1969). Phase diagram data referred to in this paper come from one of these four sources.

In fig. 1 there are three compounds that we shall focus on:  $CeSb_2$ ,  $CeSb$  and  $Ce_2Sb$ .  $CeSb_2$  cannot be synthesized by simply cooling a stoichiometric mix of Ce and Sb since it does not melt congruently.  $CeSb_2$  can, on the other hand, be grown out of excess Sb. For example, 10 at.% Ce in 90 at.% Sb heated to  $1175^\circ C$  and slowly cooled to  $750^\circ C$  will allow the formation of large ( $1\text{ cm}^2 \times 0.2\text{ cm}$ ) plates. At  $750^\circ C$  the sealed ampoule is taken from the furnace and the remaining liquid (over 98 at.% Sb) is spun off in the centrifuge. One aspect of the material (and related compounds such as  $CeBi_2$  and  $YbBi_2$ ) that is noteworthy is that, even with cooling rates as high as  $30^\circ C\text{ h}^{-1}$  (i.e. an overnight growth), high-quality crystals result as witnessed by residual resistivity ratios

Fig. 1

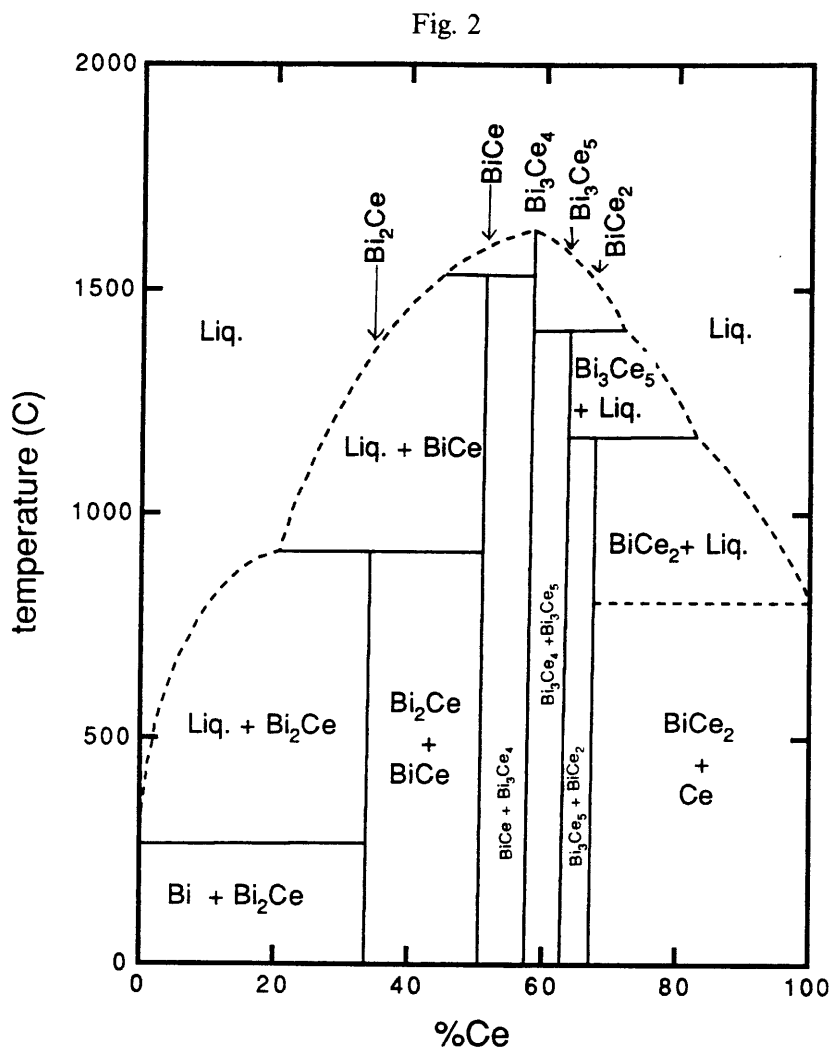


The Ce-Sb binary phase diagram. (After Moffatt (1981).)

between 4 and 300 K as large as 200. By examination of fig. 2 it can be seen that a similar procedure will work with  $\text{CeBi}_2$ .

$\text{Ce}_2\text{Sb}$  can be grown in a similar manner out of excess Ce. 10–15 at.% Sb in Ce is heated to  $1175^\circ\text{C}$  and cooled to  $900^\circ\text{C}$ . The melt has to be placed into a Ta crucible since the alumina crucible used in the case of  $\text{CeSb}_2$  would be attacked by the primarily Ce melt. At  $900^\circ\text{C}$ , liquid can be spun off, but because of its aggressive nature the liquid attacks the quartz ampoule, sometimes causing it to lose its vacuum. Instead of just quartz wool on top of the crucible it is possible to add some alumina powder or an inverted alumina crucible. These can catch most of the spun-off liquid, protecting the walls of the quartz ampoule during the spin-off and cool-down to room temperature. As in the last case, examination of fig. 2 will show that  $\text{Ce}_2\text{Bi}$  can be grown in a similar manner.

$\text{CeSb}$  is the only congruently melting compound in the Ce-Sb phase diagram. It is also the highest-melting compound and can only be grown out of excess Ce or Sb at temperatures well above  $1400^\circ\text{C}$ . This makes it very hard to grow single crystals via the same methods that were used for the  $\text{CeSb}_2$  and the  $\text{Ce}_2\text{Sb}$ . By trying a variety of third metals as fluxes, we found that the  $\text{CeSb}$  (as well as several other light-rare-earth antimonides) could be grown out of Sn. By placing Ce:Sb:Sn in an atomic ratio of 5:5:95 (5 at.% Ce with respect to the Sn with the Sb implicitly following the Ce) in a



The Bi-Ce binary phase diagram. (After Moffatt (1981).)

crucible and heating to 1150°C followed by a cooling to 750°C, single crystals of CeSb were grown. There were, of course, small amounts of Sn still trapped on the surfaces and between twins, but for many purposes (in this case photoemission) this is a tractable problem. The reason that the crystals were spun off at the relatively high temperature of 750°C instead of much lower temperatures that Sn flux will allow is that at lower temperatures an unwanted second phase started to come out of the melt: CeSn<sub>3</sub>. This is evident from the Ce-Sn binary phase diagram. For 5 at.% Ce in 95 at.% Sn, CeSn<sub>3</sub> starts to come out of the melt at roughly 750°C.

We now turn to the growths of a variety of ternary rare-earth-Pt-Bi compounds. The ternary phase diagram for the rare-earth-Pt-Bi system apparently changes between Pr and Nd. For La, Ce and Pr, R<sub>3</sub>Bi<sub>4</sub>Pt<sub>3</sub> (the Y<sub>3</sub>Sb<sub>4</sub>Au<sub>3</sub> structure) comes out of the excess Bi, while for Nd→Lu the RBiPt (the AgAsMg structure) crystallizes (R ≡ rare-earth element). There is no rare earth for which both phases grow out of excess Bi. (We have been able to grow the lighter RBiPt compounds out of Pb flux, however). It is worth noting that a similar situation arises in the binary RAl systems. For the lighter rare earths, RAl<sub>3</sub> cannot be grown out of the melt owing to the prominence of the R<sub>3</sub>Al<sub>11</sub>, but after Sm this phase becomes far less stable and the RAl<sub>3</sub> compounds can then be grown out of excess Al. The existence of an unwanted phase that is more stable than the phase that is desired can often scuttle a growth attempt.

Two other examples of this can be found in some of our attempts to grow  $\text{Ce}_3\text{Sb}_4\text{Pt}_3$  and  $\text{YbSbPt}$  out of excess Sb; in each case the parasitic phase  $\text{CeSb}_2$  or  $\text{PtSb}_2$  respectively was the only phase that crystallized. In both of these examples the difference between the cases of excess Bi and excess Sb can easily be understood by an examination of the Sb–Ce and Bi–Ce or Sb–Pt and Bi–Pt binary phase diagrams. The  $\text{CeBi}_2$  peritectic temperature is at  $910^\circ\text{C}$  while the peritectic temperature for  $\text{CeSb}_2$  is over  $1200^\circ\text{C}$ . Similarly,  $\text{PtBi}_2$  has a peritectic at  $660^\circ\text{C}$  while  $\text{PtSb}_2$  melts congruently at  $1225^\circ\text{C}$ . The fact that the Sb compounds have greater stabilities than their Bi counterparts is a likely explanation for why they prevent the growths of  $\text{YbSbPt}$  and  $\text{Ce}_3\text{Sb}_4\text{Pt}_3$  from excess Sb.

#### §4. REVIEW OF METALLIC FLUXES

The table lists a wide variety of materials that we have grown using the metal-flux technique. The materials are grouped according to the flux used to grow them. In this section we shall review some of the particular problems and advantages associated with each of these fluxes.

##### 4.1. Al

Growths out of Al as a flux cannot be sealed into quartz ampoules as a general rule, since even Al vapour attacks the quartz, leading to a loss of the protective atmosphere. This can sometimes be avoided by very fast growths, or the use of some inert atmosphere in the ampoule to dilute the Al vapour. For this reason, Al growths must be made under an independent protective atmosphere such as a vertical-tube furnace with an inert gas flowing through it as described by Fisk and Remeika (1989). Although the growth cannot be performed in a quartz ampoule, the cooled crucible with the grown samples and solidified Al can subsequently be sealed into a quartz tube and heated above  $660^\circ\text{C}$  to melt the Al. This allows for the removal of flux via spin-off. Although the sealed ampoule will be attacked by the molten Al, it usually will hold vacuum long enough for the sample to be sufficiently cooled to resist any great amount of oxidation. In cases where this is not practical or simply not desired, the Al flux can be chemically removed by reacting it with NaOH solution.

##### 4.2. Bi

Bi as a flux has many advantages. It has a low melting point and fails to form high-temperature binary compounds with a number of metallic elements that can act as unwanted second phases.

##### 4.3. Ce

Although Ce is not generally considered a good flux for intermetallic growth, it does offer several noteworthy features. Because of the relatively low melting temperature of Ce, it can be used to grow Ce-rich materials such as  $\text{Ce}_2\text{Bi}$  and  $\text{Ce}_2\text{Sb}$ . In addition to this, R–transition-metal binary phase diagrams often have quite low eutectic temperatures; Ce–Fe has an eutectic temperature of  $592^\circ\text{C}$  and Ce–Co has an even lower eutectic temperature of  $424^\circ\text{C}$ . Not only do these eutectics offer an easy growth avenue for  $\text{CeFe}_2$  and  $\text{CeCo}_2$ , but also they can be used as a flux to grow other compounds out of. (One example is the growth of  $\text{PrB}_4$  out of a Pr–Co eutectic).

Ce-rich growths cannot be made in alumina crucibles, but Ta crucibles are suitable in many instances. Although the Ce vapour does not attack the quartz ampoule enough

## Crystal growth from metallic flux.

Crystals	Flux	Dilution <sup>a</sup> (at.%)	Temperature (°C)	Comments
RB <sub>4</sub>	Al	R, 0.2	1450-700	R ≡ Sm, Gd-Lu, also U, Th
YbAlB <sub>4</sub>	Al	Yb, 1.0	1450-700	
RB <sub>6</sub>	Al	R, 0.2	1450-700	R ≡ La-Eu, Yb, Ca, Ba, Sr, Np, Am
RBe <sub>13</sub>	Al	R, 5.0	1250-700	R ≡ La-Lu, Y, U, Th BeO crucible
RAl <sub>3</sub>	Al	Yb, 0	1200-660	R ≡ Yb, Lu, Y, Sc
TiB <sub>2</sub>	Al	Ti, 2.0	1440-800	No spin, NaOH etch
CeSi <sub>2-x</sub>	Al	Ce, 5.0	1150-800	No spin, NaOH etch
UAl <sub>3</sub>	Bi	U, 2.0	1150-700	
UPt <sub>3</sub>	Bi	U, 7.0	1250-800	BeO crucible
YPd	Bi	Y, 10	1175-600	
RBiPt	Bi	Ho, 6.0; Yb, 10; Lu, 3.0	1150-500	R ≡ Nd-Lu
R <sub>3</sub> Bi <sub>4</sub> Pt <sub>3</sub>	Bi	Ce, 13	1150-500	R ≡ La-Pr
RBi <sub>2</sub>	Bi	Ce, 10	800-400	R ≡ La, Ce, Pr, Yb
R <sub>2</sub> Bi	Ce	Bi, 15	1150-900	R ≡ La, Ce, Ta crucible
Ce <sub>2</sub> Sb	Ce	Sb, 12	1150-900	Ta crucible
CeFe <sub>2</sub>	Ce	Fe, 45	1100-700	Ta crucible
RSb	Ga	Ce, 5.0	1150-650	R ≡ La-Nd
R <sub>2</sub> Pt <sub>4</sub> Ga <sub>8</sub>	Ga	Ce, 1.0	1100-500	R ≡ La-Nd, Sm, Gd, etc.
CeCu <sub>2</sub> Ge <sub>2</sub>	In	Ce, 3.0	1175-750	Plates 2 mm × 2 mm × 0.2 mm
CeNi <sub>2</sub> Ge <sub>2</sub>	In	Ce, 3.0	1175-700	Plates 2 mm × 2 mm × 0.2 mm
YbCu <sub>2</sub> Si <sub>2</sub>	In	Yb, 4.0	1150-600	Plates 2 mm × 2 mm × 0.2 mm
RPb <sub>3</sub>	Pb	Ce, 10	1100-800	R ≡ La, Ce
RPbPt	Pb	Ce, 7.0	1150-500	R ≡ La, Ce
RBiPt	Pb	Ce, 7.0	1150-500	R ≡ La, Ce, Pr
YbCu <sub>2</sub> Si <sub>2</sub>	Sn	Yb, 3.0	1150-700	R ≡ La, Ce, Pr
TiNiSn	Sn	Ti, 9.0	1150-600	Pyramidal
MnSnNi	Sn	Mn, 10	1150-450	Pyramidal
RSb	Sn	Ce, 5.0	1150-750	R ≡ La-Nd
RSb <sub>2</sub>	Sb	Ce, 10	1175-750	R ≡ La, Ce
U <sub>3</sub> Sb <sub>4</sub> Pt <sub>3</sub>	Sb	U, 8.0	1150-750	
PtSb <sub>2</sub>	Sb	Pt, 10	1150-750	

<sup>a</sup> 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 cause a loss of atmosphere during a normal growth, the liquid that is spun off will attack the ampoule. Generally this does not cause any damage to the crystals through loss of atmosphere during cooling.

#### 4.4. Ga

Ga is a very attractive flux owing to its exceedingly low melting point and vapour pressure. There are two major problems with it, however. One is that, even after spin-off, liquid Ga tends to wet the surfaces of the grown crystals. If a subsequent chemical etching can remove this without attacking the crystals, this is not a serious problem. The second, more serious problem is that, in the case of rare-earth compound growth, Ga often forms compounds with the solutes that preclude the desired material from growing. This can, in some cases, be an insurmountable problem.

#### 4.5. In

Indium has proven to be an excellent flux for a variety of  $\text{ThCr}_2\text{Si}_2$  materials. In addition to this, In does not seem to form inclusions in or wet to the materials grown out of it to a sufficient extent to short out the sample during a resistance against temperature measurement because of its superconducting ground state below 3.4 K.

#### 4.6. Pb and Sn

Pb and Sn are similar in two of their problems as fluxes. Both tend to coat the materials grown out of them which leads to a loss of resistance below their superconducting transition temperatures. Both of these fluxes also tend to form  $\text{RPb}_3$  and  $\text{RSn}_3$  second phases that can interfere with the growth of the desired material. This latter problem can often be avoided by spinning off the flux at temperatures above the formation of these second phases. In order to achieve suitable crystal size the use of a higher spin-off temperature can necessitate higher concentrations of the desired material in the melt.

#### 4.7. Sb

As mentioned above, Sb can be problematic as a flux owing to the stability of the Sb-rare-earth second phases that can form. This is primarily because the Sb itself is a relatively high melting element to use as a flux.

### § 5. DISCUSSION

What ultimately governs the choice of one flux over another will be whether the desired material grows. In some cases, such as when the desired material contains a potential flux as one of its constituents, one flux will present a greater chance of success than the others, but even in these cases finding the right flux can be problematic. Even when the growth of one member of a series (such as the  $\text{R}_3\text{Bi}_4\text{Pt}_3$  series) has been optimized, it is not uncommon to have difficulty with other members. Fundamentally what governs the growth of one phase rather than another out of a flux is their relative stabilities with respect to that flux. The data for determining this is not in general available for ternary and higher-component melts.

When faced with the growth of an unfamiliar material, what is often the most successful approach is to try a variety of small growths using several different fluxes and dilutions. In the case of CeSb, Pb, In, Ga and Sn were all tried, with Sn giving the best results. Although this lack of a precise method or recipe for growing single crystals from a flux might strike some as a large hurdle to surmount, it is precisely this imprecision and reliance on either intuition or luck that gives this technique so much of its charm and power. The accidental growth of second phases is more often the source of interesting and new materials than the intentional plotting of any specific course. The challenge for the researcher is to be able to recognize when the new phase is of interest.

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