

CHAPTER 2

SOLUTION GROWTH OF INTERMETALLIC SINGLE CRYSTALS: A BEGINNER'S GUIDE.

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Progress in experimental solid state physics, as well as in related disciplines, is often hampered by limited access to single crystals of novel materials. This lack of single crystalline samples constrains researchers to study or measure materials that are available rather than the materials that are most relevant to the questions at hand. The extreme example of this is the allegorical Ph.D. student who has to measure the one crystal that the advisor has on hand, regardless of the physical question to be probed. As part of the second Euroschool on complex metals I presented lectures on the design, discovery, growth and characterization of novel intermetallic compounds. In this paper I will focus on the basics of solution growth of novel compounds.

1. Introduction

The 2nd Annual European School in Material Science was held in Ljubljana, Slovenia from May 21 to 26, 2007. The focus of this summer school was the synthesis and properties of novel, bulk, intermetallic compounds. With this in mind I presented a series of four lectures on growth (first lecture) and characterization (second lecture) of novel compounds with an emphasis on the tuning of magnetism (the third lecture) and superconductivity (the fourth lecture). These lectures were based on my past twenty (or so) years of experience in the broad field of design, discovery, growth, characterization and understanding of novel materials. Whereas we have published literally hundreds of papers on the characterization (and hopefully added to the understanding) of a wide

number of materials ranging from local moment magnetism,¹⁻⁴ to quasicrystals⁵⁻¹⁰ and spinglasses¹¹⁻¹⁴ and from superconductors¹⁵⁻²² to heavy fermions,²³⁻²⁸ we have only published a small number of papers that explicitly outline how we synthesize the vast majority of these compounds: by solution growth.²⁹⁻³² This paper is an attempt to augment and compliment these technical, solution growth papers. I will try to outline, in a step by step fashion, how to plan a solution growth, how to assemble a growth and, near the end of the growth, how to decant the remaining solution from the crystals that (hopefully) have grown. This paper is meant to provide a novice with some concrete instructions and examples.

Before beginning with the details it is vitally important to make one point clear. Solution growth of intermetallic compounds is not a sterile, theoretical exercise; it involves the use of element and compounds with varying degrees of toxicity; it involves the use of sharp and very hot tools; it involves the use of high temperature furnaces. Before starting a program of research that involves the solution growth of intermetallics you should consult your local safety office and make sure that they advise and approve of your plans. Even in my laboratory, a lab that has over two decades of collective experience with solution growth, when we try a new variant or a new flux, we examine the procedure, discuss possible problems and make sure that we are proceeding in as safe a manner as possible. The growth of materials in this manner is not difficult, but it does involve steps that demand respect and careful attention.

2. What do you need?

Solution growth of intermetallic compounds requires a solution, something to hold it in, something to provide a protective environment, and something to provide a controllable temperature. In addition, a decanting device is often very useful too. Let's review each of these "needs" in turn.

If you want to grow CeSb out of a Sn flux, then you clearly need some Ce, Sb and Sn.²⁹ Often growth labs will have a collection of various high purity (and even lesser purity) elements and compounds on

hand for use. Like a well stocked liquor cabinet, you save the “good stuff” (in this case the really high purity stuff) for special occasions, such as when you have already optimized a growth using less pure (cheaper) stuff.

A comment on purity is appropriate at this point. Be very careful to understand what the purity of your starting materials is. It is important to know what you are using and what different purity numbers mean. For example, many chemical retailers will provide purities on a “metals basis”. This is (unfortunately) often a very deceptive number and provides a classic example of “caveat emptor”. Metals basis purity only considers other metals as impurities. Nickel with 5% iron would have a metals basis purity of 95% (so far so good). On the other hand nickel with 5% oxygen in it (e.g. in the form of a nickel oxide) and 0.5% iron would have a metals basis purity of 99.5%. The oxygen is not counted at all. Worse yet is the case of oxides. I have purchased VO_2 that was sold as 5-9's (i.e. 99.999%) purity that contained 10% V_2O_5 . The chemical retailer was not lying, but this is an ugly way of making a mixed phase material appear to be purer than it is.

Once the composition of the solution is known the next step is to decide how to hold it. Generally this is done in a crucible. The most common crucible for intermetallic growth is high density, sintered Al_2O_3 . (In a similar manner the most common crucible for oxide growths is pure Pt.) The choice of crucible is generally one determined by cost and stability. Al_2O_3 is stable against attack from many of the low melting elements that are used as solutions: Al, Cu, Zn, Ga, Ge, In, Sn, Sb, Pb, and Bi. On the other hand thermite-like reactions are a problem with solutions that are sufficiently concentrated in rare earth metals, Mg, or some transition metals (such as Ti, Hf and Zr). These metals can form a more stable oxide and sometimes release Al into the melt. In these cases other crucibles such as yttria, zirconia, or elemental Ta have to be used.³⁰⁻³² For this article only the use of Al_2O_3 will be discussed. As a rule of thumb, about ten atomic percent of rare earth can be added to one of the low melting elements listed above and held in an Al_2O_3 crucible without attack (up to ~1200 °C). Lesser amounts of other reactive elements can also be held in Al_2O_3 , sometimes at lower temperatures.

The solution, sitting in the crucible usually needs to be protected from the air; from possible reaction with oxygen, nitrogen, etc. This is most easily done by sealing the crucible into an amorphous silica ampoule. This requires a hydrogen-oxygen blow torch, a well ventilated glass bench, and a pumping station for evacuating and back filling the ampoule before sealing.

The growth then needs to be heated and cooled in a controlled manner. This is usually done with a furnace that has a programmable temperature controller. Generally a furnace that can go as high as (or higher than) 1200 °C is needed. If the furnace available only reaches 1000 °C, then this precludes growths that require higher temperatures. Generally heating is done rather fast (100 °C / hour) and cooling is done in steps and rather slowly (1 – 10 °C / hour or slower). A temperature controller with multiple steps is convenient, but not required. Generally the furnace should be one that can be opened rapidly and allow for the removal of the hot ampoule at the end of the growth.

Once the growth cycle is completed it is often very convenient to decant the remaining solution from the crystals that have (hopefully) grown. If the excess liquid is not removed, it will solidify around the crystals and will have to be removed by chemical and / or mechanical means once the growth is at room temperature. Decanting of the still hot growth requires a lab centrifuge with metal cups to hold the ampoule.

So then, to answer the question, “what is needed?”: the elements or compounds that will comprise the initial solution; a crucible to hold the melt; a quartz bench to form and evacuate the ampoule that protects the melt from air; a programmable furnace; and a centrifuge for decanting off the excess solution at the end of the growth.

3. Planning the growth

The first step in planning a growth is to have an idea. This is often the hardest step in the process. The best way around this difficulty is to follow the advice of Linus Pauling, who said, “The way to get good ideas is to get lots of ideas and throw the bad ones away.”

Once a specific compound has been determined to be of interest, or a specific compositional phase space has been identified as promising, then

it is useful to see if any information exists about it in the form of phase diagrams. For simplicity we can examine the schematic phase diagram shown in figure 1a. If the compound AB_2 is to be grown, then, given that it is a paratectically melting compound, methods that utilize cooling of a stoichiometric (or near stoichiometric) melt of AB_2 will not give single phase AB_2 . This means that methods such as arc melting, Bridgeman growth, or zone refining can yield a mixture of AB, AB_2 , and B. AB_2 can, though, be readily grown via the cooling of a solution rich in B. As long as the initial melt composition is more B-rich than that of the composition of the liquid at the paratectic temperature (P on diagram), then the primary solidification (on cooling) will be AB_2 .

A potential cooling curve is shown as a dotted line in Fig. 1a. This line represents the temperature dependent composition of the liquid phase as the growth cools. Between temperatures T_1 and T_2 the liquid stoichiometry does not change. Once $T < T_2$, though, crystalline AB_2 starts to form and the remaining solution becomes increasingly B-rich. In general it is desirable to stop cooling the growth at some temperature T_3 that is greater than the eutectic temperature so that the excess solution can be decanted off. In general a binary phase diagram is not known precisely and reported versions of any given binary phase diagrams can differ from each other (sometimes significantly). Since rapid cooling through T_2 can cause multiple nucleation and dendritic growth (neither of which are conducive to the growth of large, well formed single crystals) slow cooling of the melt should begin at some temperature above T_2 . For the growth of AB_2 a possible growth cycle could consist of heating to T_1 , dwelling at T_1 for several hours to allow for homogenization of the melt, dropping to $T_2 + 50$ °C in an hour or two and then cooling from $T_2 + 50$ °C down to T_3 over 50 -100 hours. At T_3 the growth could then be taken out of the furnace and decanted.

The compound AB can be grown from a stoichiometric melt, at least in theory, but in many cases the temperatures associated with the primary solidification (the temperatures above the paratectic temperature on the B-rich side and the eutectic temperature on the A-rich side) can be too high. Given that the growths that will be discussed in this introductory paper will be sealed in amorphous silica (see ^{30, 33} for higher temperature growths and how to handle them) it should be noted that the

maximum temperature that can be used during the growth procedure is very close to 1200°C. Amorphous silica softens and loses its structural integrity for temperatures significantly above 1200°C and either collapses or explodes (depending on the internal pressure at that temperature). In cases like this it can be useful to find a third element (or combination of elements) to act as a flux: a solution that has a lower temperature surface of primary solidification of the compound AB. This is shown as a schematic, pseudo-binary, phase diagram in Fig. 1b. In such a case a small amount of elements A and B can be added to a lot of element C. The cooling curve, with temperatures T_1 , T_2 , and T_3 is operationally the same as that discussed above for Fig. 1a. In this case, finding a viable element C can be the tricky part since data on ternary (or higher) phase diagrams can be very limited or simply non-existent. A real example of growths using phase diagrams like those shown in Fig. 1 is the growth of CeSb_2 and Ce_2Sb out of excess Sb and Ce respectively and the growth of CeSb out of Sn as a third element.²⁹

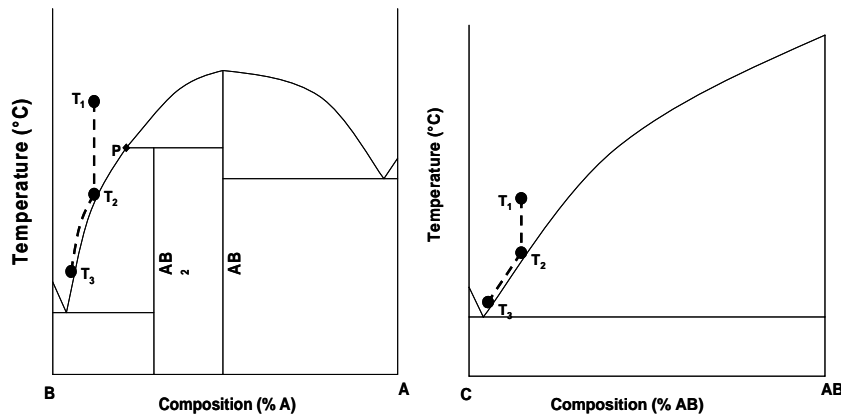


Fig. 1a (left panel): Schematic binary phase diagram for the A – B system. The dotted curve represents a possible cooling curve and the associated composition of the solution. Point P indicates the composition of the liquid / solid line at the paratectic temperature.
 Fig. 1b (right panel): Schematic pseudo-binary phase diagram for the C – AB system. The dotted curve represents a possible cooling curve and the associated composition of the solution.

Whether based on consultations of phase diagrams, previous growths,

experience and / or intuition, a growth starts with the determination of an initial composition of the melt and a heating and cooling profile. These can (and usually are) be adjusted in subsequent growths based on information extracted from earlier attempts. Ultimately, if a growth is successful, a growth can be optimized and a standard composition and temperature profile can be used to grow it repeatedly and reliably.

3. Assembling the growth

Once the growth has been planned it is time to get into the lab and actually assemble it. At this point we will start using the materials described in passing above. Figure 2 is a picture of a length of amorphous silica tubing that has been sealed and flattened on one end and two 2 ml Al_2O_3 crucibles. These will be used to provide a growth environment.

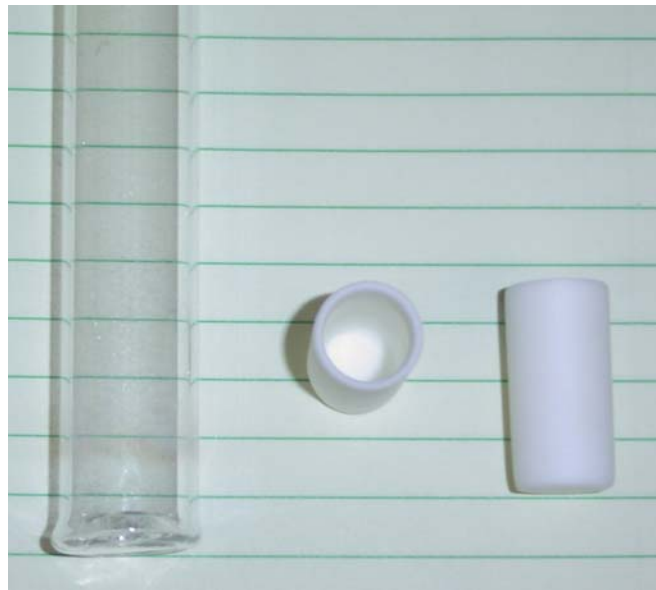


Fig. 2: Silica tube (sealed and flattened on bottom) and two 2ml Al_2O_3 crucibles.

Figure 3 shows the crucibles with some of the elemental metals placed inside.



Fig. 3: Al_2O_3 crucibles being packed with elemental metals for growth of RAl_3 compound (elemental Al shown).

Generally it is best to have higher melting elements or alloys surrounded by lower melting ones, as shown schematically in Fig. 4a. Once the growth crucible is assembled, the “catch” crucible can be packed with silica wool (Fig. 4a, b). The purpose of this crucible is to immobilize the excess liquid at the end of the growth the silica wool helps to separate the crystals from this excess fluid. If there were no silica wool, or if there is an inadequate amount, then some of the crystals can move over to the catch side and still be embedded in the ultimately solidified, excess liquid. In some cases the growth can be assembled without a catch crucible and the silica wool can simply be placed on top of the growth crucible. In such cases, though, there can be chemical attack between the solution and the silica tube or, if the solution expands upon cooling, the tip of the ampoule will crack and shatter as the plug of decanted solution solidifies. Both of these cases can lead to a loss of inert environment while the crystals are still hot and often leads to surface oxidations (or worse).

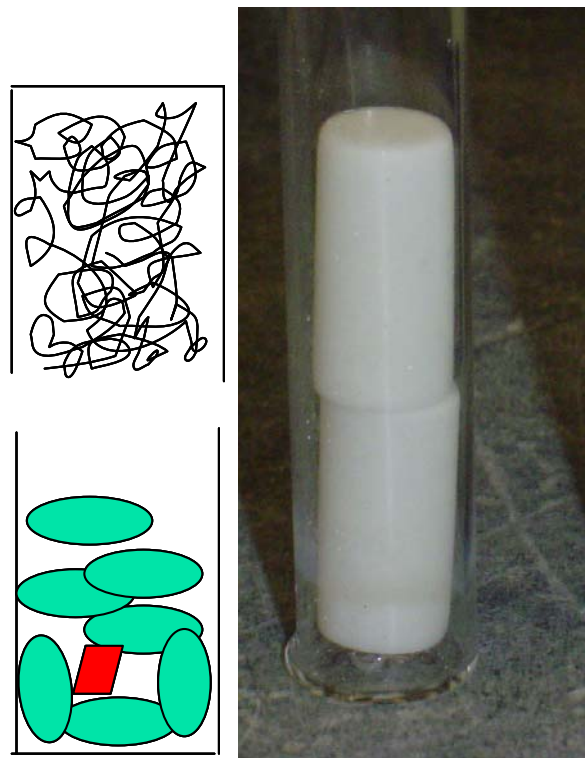


Fig. 4: (a-left panel) Schematic diagram of growth and catch crucibles. The smaller, parallelogram, shape indicates a higher melting element and larger, elliptical, shapes represent the lower melting element. The upper crucible is packed with silica wool to provide a filtering and immobilization of the excess liquid at the end of growth cycle, during the decanting step. (b- right panel) Picture of growth and catch crucibles in silica tube.

Figure 5 shows the silica tube after necking. The growth and catch crucibles are easily seen as well as a plug of silica wool on top of the catch crucible. This wool acts as a cushioning device that prevents the crucibles from slamming into the sealed tip of the tube and shattering it during the decanting step. It is important that during the necking step the silica tube is softened (by the hydrogen-oxygen blow torch) and allowed to collapse with minimal pulling. This allows for necks that are thick walled. If the tubing is pulled and thinned, then the seal can be weak or

the silica can suddenly bubble inward and shatter as the neck is heated up for the seal.



Fig. 5: Growth ampoules after necking, but before sealing. Note the silica wool above the catch crucibles

The necked tubes are attached to a pumping system, evacuated and back filled with an inert gas (argon is often used). Depending upon the growth, the ampoules can be sealed in partial vacuums ranging from less than a torr up to $\frac{1}{4}$ atmosphere or higher. Often partial pressures of Ar that will result in near ambient pressure at the maximum growth temperature are used when the melt contains elements that have vapor pressures in excess of 0.1 atmosphere or when the solution contains elements that are both volatile and reactive with the silica tubing (such as Al). Once the ampoule has been pumped and flushed (usually three or more times) and back filled to the desired pressure of Ar, it is sealed off

with the hydrogen / oxygen torch. The sealed ampoule is then placed in a larger Al_2O_3 crucible for mechanical support, as shown in Fig. 6. The ampoule should be cleaned with a mild organic solvent, such as ethanol, to remove grease / finger prints, which can, at elevated temperatures, lead to attack on the silica.



Fig. 6: Sealed growth ampoules in 50 ml Al_2O_3 crucibles for mechanical support. Note: in this image, the growth and catch crucibles are hidden by the 50 ml, support crucibles.

4. Running the growth

At this point the sealed ampoules can be placed into the furnace (Figs. 7 and 8). This is done by donning the thermally insulating gloves and using the tongs shown in Fig. 8. In addition a face visor is always used to protect the face and neck. These furnaces are heated by two banks of SiC heaters, one on top and one underneath the hearth plate that the ampoules are supported by. If the solution contains extremely volatile elements (e.g. Zn) then the ampoules can be raised up toward the upper bank of heating elements. This helps to prevent re-condensation of the solvent on top of the silica wool by making the top of the ampoule slightly hotter than the bottom.



Fig. 7: Two growth ampoules in box furnace. Furnaces such as this can easily hold up to 10 growth ampoules and allow for rapid sampling of phase space



Fig. 8: 1500 °C, SiC heater element, box furnace used for solution growth. Power supply / temperature controller shown on right. High temperature gloves (on top of temperature controller) as well as tongs (on top and underneath of temperature controller) also shown.

Once the ampoules are in the furnace the temperature profile can be programmed into the temperature controller and recorded into the lab notebook. In general heating to the maximum temperature can be achieved within a few hours. A dwell, of several hours, at maximum

temperature is often used so as to encourage complete dissolution and mixing of the solution. Cooling of the solution can take from as little as 5 hours to as long as several hundreds of hours, depending upon the specific growth. Exploratory growths are generally fast whereas highly optimized growths are, in general much slower. A temperature controller that allows for the input of hours between temperature set points, rather than cooling rate, is preferable since this, de facto, can allow for almost any arbitrary and small cooling rate. For example, if the melt is to be cooled from 575 °C to 510 °C in 100 hours this is trivial to program if hours to cool is input, but awkward if the rate has to be input. With the usual 0.1 °C / hour resolution this requires a choice between 0.6 °C/hour (108.3 hours) or 0.7 °C/hour (92.8 hours). After the slow cooling is complete the furnace should be programmed to dwell at the final temperature for a long time so that there is no possibility of the furnace shutting off before the growth is removed.

5. Decanting

Decanting is often the step that many researchers over look when thinking about solution growth, especially decanting in a centrifuge. This, it turns out, is a very useful and, in many cases, vital step. Just inverting the growth ampoule in the furnace, and letting gravitational acceleration (9.8 m/s^2) pull at the remaining solution, is not enough to lead to significant separation of crystals from the solution. In many cases the metallic solution is quite viscous and, in addition there can often be a thin layer of crystals or slag on the meniscus that prevents or hinders fluid flow. Figure 9 shows the solution to these problems: a centrifuge equipped with a metal rotor and cups. A back of the envelope calculation shows that an ampoule spinning at 1000 rpm (slow for a lab centrifuge) with the sample volume about 10 cm from the axis of rotation provides a factor of 100 increase in the acceleration felt by the solution. This is more than enough to remove the excess solution, and in many cases actually produce mirrored growth facets on the exposed crystals (see Fig. 10).



Fig. 9: Centrifuge with brass rotor and cups. Refractory fiber is used at the bottom of the sample cup to provide cushioning. Small coins of the world (as part of our international growth effort) are used as counter weights.

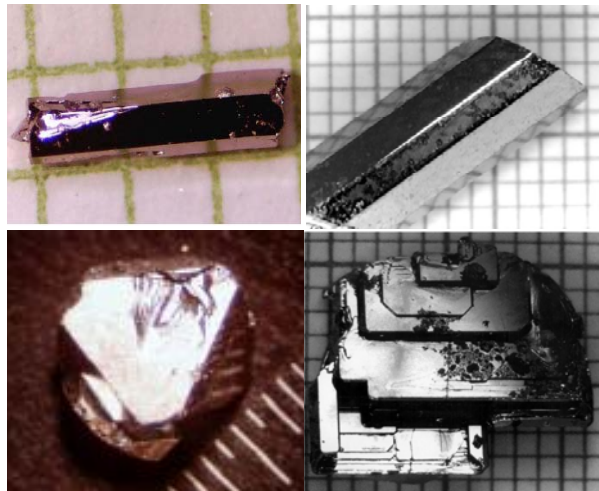


Fig. 10: Examples of crystals grown via solution growth as described in text. Upper left: YbAgGe (trigonal unit cell)²⁵; upper right: decagonal phase AlNiCo⁷; bottom left: YFe₂Zn₂₀ (cubic)²³; lower right: LaAgSb₂ (tetragonal).²

The decanting process is a dynamic one. The centrifuge, rotor and cups are at room temperature and the growth can be at temperatures as high as 1200 °C. This process works because the growth is inside of a crucible that is itself inside of a silica ampoule (in many cases and evacuated ampoule). If the ampoule is removed from the furnace in a prompt manner and quickly tipped into the cup of the centrifuge, then the excess liquid can be decanted off before it drops in temperature by more than 10 or 20 °C. To decant thermal gloves and a visor need to be worn and tongs are used to grab the 50 ml alumina crucible. The ampoule is then tipped into the centrifuge cup, the lid of the centrifuge is slammed shut, and the centrifuge is started. This whole process (from opening the furnace door to starting the centrifuge) should take no more than 5 seconds. The centrifuge need to run for less than 10 seconds since the decanting takes place in the first second or two of acceleration. Too much time with the centrifuge on actually increases the risk of breaking the ampoule and even deforming or breaking the crystals. Once the centrifuge rotors come to rest the ampoule can be removed and placed in a safe place to cool.

6. Opening the growth and planning the next one

When the ampoule has cooled to close to room temperature it can be opened. Care should be used when opening it since it contains fibrous glass and once opened will also have shards of glass and, depending on the elements used, hazardous waste. Opening the ampoule in a well ventilated space similar to that was used for the glass work is a good way to minimize these risks. Often the growth ampoule will contain some, or all, of the well formed single crystals, with the remaining ones being caught on the top of the silica wool in the catch crucible. In many cases it is necessary to break open the growth crucible so as to extract the crystals that have nucleated off of the inner walls. In general the Al_2O_3 crucibles are not re-usable, so breaking them is not an unforgivable waste. (This is very different from the case of oxide growth out of Pt crucibles that are cleaned and reused for tens of growths.)

One of the bonuses of solution growth is that the crystals often manifest well developed (and even mirrored) facets. A few examples are

shown in Fig. 10. These are clearly examples of successful growths. Clearly, not every attempt is so successful. Below are a few “trouble shooting” comments. Much more detail and theoretical background can be found in texts on crystal growth.^{34,35}

Total spin: Called this because all of the material in the growth crucible is still liquid at the decanting temperature and therefore is “spun” to the catch crucible side. In terms of Fig. 1, this means that the spin temperature was above T_2 . Although this is irritating (the growth produced no crystals) it can actually be a very useful data point. It means that the starting temperature of the next growth can be reduced to a temperature close to the spin temperature that resulted in the total spin. This can lead to much lower cooling rates, since time is not being wasted in cooling through large expanses of the homogeneous liquid phase.

No spin: As suggested by the name, nothing leaves the growth crucible during the decanting (spinning) step. This usually means that the decanting temperature was too close to or below the local eutectic point. The simplest thing to do is repeat the growth and decant at a higher temperature. Often the growth and catch crucibles can simply be resealed into a new ampoule and used again. Note: if there has been some spin or if there has been some attack on the growth crucible, then this is not advisable since the stoichiometry of the initial melt has been changed in an unquantifiable manner.

Growth crucible cracked / ruptured: The growth crucible can be damaged due to a number of reasons. The most common is a thermite-type reaction, as described above. If this is suspected then either the amount of reactive metal in the melt needs to be reduced, or a different type of crucible needs to be used. Sometimes the elements placed in the growth crucible can react exothermally when they melt and mix. When this is the case, the energy released can shatter the crucible during the initial heating of the growth. If this is suspected, then a pre-melting of these elements (e.g. in an arc melter) will allow for the release of energy outside of the crucible. One example of this is Al and Pd. When they are melted together they release considerable energy (glow brightly) and shatter Al_2O_3 crucibles. On rare occasions the growing crystals become so large that they actually break the crucibles as they span the inner diameter. This is a “good” problem since it means that the crystals are

large. Often in this case the cracks are not large enough to cause any leaking of the melt.

Small and / or poorly formed crystals: This can happen for many different reasons. The most common one is associated with cooling too fast. It is important that the melt does not cool too rapidly through T_2 so raising the temperature at which slow cooling starts sometimes helps. On the other hand, reducing the cooling rate often is important as well. Essentially more time (i.e. a lower cooling rate) is the easiest, first adjustment to a growth when there is a need to improve crystal size or quality

Growth of a second phase: In some growths there can be well formed, larger crystals with smaller crystals of a different morphology on top. For example, crystals with a cubic morphology and linear dimension of 5 mm with little rods growing off of them at skew angles. This is a clear hint that during the cooling process a second phase (rods) started to grow at lower temperatures than the primary phase (cubes). The simplest way to try to avoid this is to repeat the growth with a higher decanting temperature (increase T_3).

7. Final remarks

This paper is meant to provide a detailed introduction to the mechanics of solution growth. It is meant to augment earlier papers on this technique²⁹⁻³³ while presenting new details that are often presumed to be “obvious” or “known”. Solution growth of novel materials is not limited to intermetallic compounds. Many of the same ideas are applicable to oxides, salts, and organic compounds.^{34, 35} This paper, as well as these references will hopefully provide the interested researcher with the information necessary to start using this powerful technique. In a century that will be faced with a myriad of technical challenges that will have to be addressed by the discovery and design of new materials with specific, complex properties, the more scientists that are engaged in the search for such compounds, the better humanities chances are of surviving to see the dawn of the 22nd century.

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