LABORATORY COURSE IN

Inorganic Material Synthesis

KJM5100

2006

Bente Gilbu Tilset

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Innholdsfortegnelse

Basics about the laboratory course

PURPOSE

The purpose of the lab course is to obtain practical experience in freparation and synthesis of inorganic materials. The course should give an improved understanding of some of the synthesis methods which are covered by the theoretical part of the curriculum. Furthermore, it is important that the students obtain experience in using synthesis equipment, learn good laboratory praxis and safe handling of chemicals.

SAFETY

In this laboratory course, poisonous chemicals, pressurized gasses, vacuum systems and high temperature are used. This means that there is a possibility for injuries to one self or others if the safety procedures are not followed. Information on general safety procedures will be given on the first laboratory class. Breaking of these procedures may lead to being expelled from the course. Specific elements of danger in the exercises are given in the laboratory handbook. If you are ion doubt, PLEASE ASK!

PREPARATION AND EXECUTION OF THE EXERCISES

Students are expected to meet prepared for the laboratory exercises. This includes reading the description of the exercise and understanding the theory connected to the exercise. As there is only a limited amount of equipment available, a rotary schedule will be set up. This means that in some instances one will have to perform exercises, where the theory has not yet been treated at class. However, student should prepare themselves by reading that part of the theory which is necessary for the exercise.

The laboratory work is time consuming and in several of the exercises, the reaction time is counted in days. It is therefore important to plan ahead, and for instance run two exercises in parallel. This will in most cases be planned by the laboratory responsible. Due to the limited amount of equipment, parallel exercises must be confirmed with the laboratory responsible. In some cases it is necessary to be present and watch over a reaction with a duration of several hours. It will then be a good idea to use the time for reports or reading.

The produces materials will be characterized using various methods. As characterization is not the prime topic of this course, most of the data will be collected by the laboratory responsible.

The exercises are continuously under development. Suggestions for improvements both in technique and descriptions will be received with thanks.

THE JOURNAL

A journal must be delivered for each exercise. The intention of the journal is to practise writing laboratory reports, describing the experiments, observations and results. The journal should include:

- The aim of the exercise
- A short account of the theory involved.
- A description of the practical work with the exercise and the equipment used. Note all relevant observations. The weighed amount of the used chemicals must be included. Note also failed experiments, if any.
- Results. All intermediate and final products should be described. Chemical equations for all reaction steps must be included. Note colours and colour changes.
- The questions in the laboratory manual must be answered.

NB! Please formulate the description using your own words in stead of copying the manual.
REMEMBER. You are writing the journals for your own benefit, and not to please the teachers!

Safety, instrumentation and glasswork.

This is an introduction to the laboratory course. The aim is to go through the safety rules at the laboratory, demonstrate equipment and instrumentation which will be used and to learn the use of gas regulators, pumps and the hydrogen torch. The properties of two types of glass will be investigated and InSb will be prepared.

SAFETY RULES

1. Everybody present at the laboratory must use protective eyeglasses. Additional safety equipment will be necessary for some of the exercises. Please respect the rules and guidelines given in the laboratory manual or by the laboratory responsible.
2. Laboratory coat must be used.
3. In this course hazardous acids e.g. hydrochloric acid, chromium-sulphuric acid and aqua regina mixed with hydrofluoric acid for washing glass equipment. Always use undamaged gloves (inflate them in order to check for leaks). Check that a 5% calcium gluconate or a 0.1M CaCl2 solution is present for treating injuries due to hydrofluoric acid.
4. Never taste the chemicals and avoid inhaling fumes from volatile compounds or gases.
5. Use the fume hoods. They give some protection against explosions, implosions and toxic gases. Remember to run ventilation at maximum and close the opening when using the fume hood. Please remember to set the ventilation at the lowest effect and close the opening after use.
6. Eating or drinking is not allowed in the laboratory.
7. It is not allowed to work in the laboratory without the laboratory responsible being present.
8. Make sure that you know the location of fire extinguishers, emergency shower, first aid kit and telephone.
9. Guidelines for preliminary first aid upon injuries:
    i. When ingesting or inhaling poisonous substances (solids, liquids or gasses): Provide fresh air. Drink water.
    ii. Eye injuries: Flush with water from an eye wash bottle.
    iii. Cuts: Rinse with water. Stop the bleeding.
    iv. Burns: Flush with cold water (recommended ca. 16˚C).
10. All injuries must be reported to the laboratory responsible, who will evaluate the need for further action.

Please work in a calm and composed manner. **Think** before acting. Read and follow the instructions and procedures given when using the equipment. This is especially important when working with gasses under pressure or with vacuum lines. **ASK** if you are uncertain.

På norsk:
SIKKERHETSREGLER

1) Alle som oppholder seg på laboratoriet skal benytte vernebriller. Ekstra verneutstyr vil være påkrevet til enkelte øvelser. Følg påbud gitt i veiledningsheftet eller av labveileder.

2) Labfrakk skal brukes.

3) I dette kurset benyttes bl.a. saltsyre, krom-svovelsyre og kongevann iblandet flussyre til vask av utstyr. Bruk hele hansker (blås dem opp for å sjekke at det ikke finnes hull) og sjekk at en 5% kalsiumglukonat eller 0,1 M $CaCl_2$ løsning er tilgjengelig for behandling av eventuelle flussyre-skader.

4) Smak aldri på kjemikaliene og unngå å inhalere damp fra flyktige forbindelser og giftige gasser.

5) Bruk avtrekkskap - det beskytter både mot eksplosjoner, implosjoner og giftige gasser. Husk å sette viften på fullt og trekke ned vinduet når skapet er i bruk, og å sette den på laveste effekt og trekke ned vinduet etter bruk.

6) Det er ikke tillatt å spise eller drikke på laboratoriet.

7) Det er ikke lov å arbeide i laboratoriet uten tilsyn av labveileder.

8) Sørg for å vite hvor brannslukkningsapparat, nøddusj, førstehjelpsutstyr og telefon finnes.

9) "Tommelfingerregel" for førstehjelp ved skader:
    i) Har man fått i seg noe giftig (fast, flytende eller gassformig): Sørg for frisk luft. Drikk vann.
    ii) Øyeskader: Skyll med vann fra øyevaskeflaske.
    iii) Kutt: Rens eventuelt med vann. Stopp blødningen.
    iv) Brannsår: Skyll med kaldt vann. (anbefalt ~16°C)

10) Ved skader skal man gi beskjed til labveileder, som skal vurdere behov for ytterligere tiltak.

La alt arbeide foregå i rolige former. **Tenk** før du gjør noe! Les og følg beskrivelsene av prosedyrer ved bruk av forskjellige typer utstyr. Dette er spesielt viktig i omgang med gasser under trykk og ved bruk av vakuumlinjer. **Spør** hvis det er noe du er usikker på.

EQUIPMENT

A common tour will be arranged to allow everybody to be acquainted with the different type of equipment present at the laboratory. Also the locations for activities such as weighing and washing will be presented.
In the course a number of different furnaces will be used. There will be an introduction to the use of temperature regulators and to the construction and function of thermocouples, which are used for temperature measurement.
Thermocouples may show different response after construction. They have to be calibrated in order to determine absolute temperature. This may be done toward a standard thermocouple or by measuring the voltage (response) at several known temperatures (e.g. from melting points or phase transitions). The procedure of calibrating a thermocouple will be presented.
When using furnaces, it is important to know the temperature gradients present. This is especially important when it is not possible to place the thermocouple at the exact same place as the sample, or when several samples are distributed in the furnace. Temperature profiles for some of the furnaces used will be shown.

Temperature regulation will vary between the furnaces used. A simple way is to apply constant voltage and follow the temperature using a thermocouple. This may be used in order to obtain a certain temperature without needing to control it over a longet period of time.
However, on most furnaces the temperature will be regulated using PID temperature controllers with zero point compensation. The function of a PID controller will be demonstrated (Appendix 1). Also programmable temperature controllers will be used, allowing heating rates, holding times and cooling rates (to some degree) to be controlled. Also here a PID type control is involved. The programmable regulator is used when controlled heating/cooling is required, or when complex heating profiles are needed in a synthesis.

EXCERCISE

The first practical exercises involve use of gas regulators (reduction valves) for gas cylinders, regulation of the hydrogen torch and the vacuum pump.
When melting of glass in the hydrogen torch, dark glasses must be worn in order to protect the eyes. Important: **When the pump is being shut off, the tube must be open,** so that the pump is exposed to ambient pressure and not to vacuum or low pressure in order to avoid pump oil being sucked into places where it should not be. The laboratory responsible will demonstrate how to operate the equipment, and then the students must familiarize themselves with the equipment. This is important, as similar equipment will be used throughout the course. Remember that incorrect operation may lead to accidents.

WORKING WITH GLASS

Open the hydrogen and oxygen valves as shown and ignite the hydrogen torch. A Pyrex and a quartz glass tube must be melted at the midpoints to make ampoules. Note how the glasses work/feel in the hot flame. Try to quench both types of glass in cold water.
One half of the quartz glass tube must be narrowed down in the centre in order to make an ampoule, Figure 1. Use the vacuum pump to evacuate the ampoule before closing it in the hydrogen torch (Figure 1). Before and after closing the ampoule the vacuum must be tested using a vacuum tester. The laboratory responsible will explain how this works.
After using the hydrogen torch, the gasses must be closed, and the pump shut down.

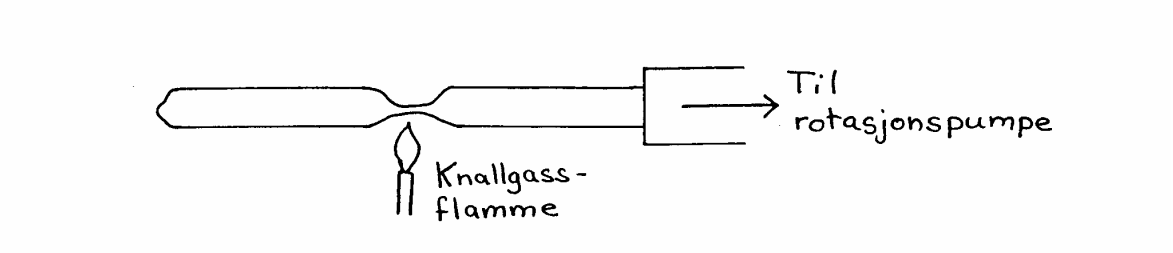

Fig. 1: Closing an ampoule.

PREPARATION OF InSb:

This is the first part of Excercise 2 ”Closed ampoule technique and zone melting of InSb.” Therefore you should familiarize yourself with that exercise before continuing. First In and Sb should be weighed into a glass ampoule which must be evacuated and sealed off. Then In and Sb must be fused together, forming InSb, along with a small amount of eutectic InSn + Sb. Follow the description in exercise 2.

QUESTIONS TO THE REPORT

1) How does a thermocouple work and how would you proceed to calibrate it?
2) Which kind of thermocouples are usually used, and why?
3) Give a short account of PID control of furnaces.
4) Scetch the hydrogen torch and describe how to open, use and close down the system
5) Give a step-by-step desciption of how to use a vaccum pump (rotary pump) when evacuating and sealing an ampoule. Remember that the pump must be shut down after use.
6) Why is the ampoule narrowed down before evacuating and closing the ampoule?
7) Give a short account of the function of the vacuum tester.

8) Describe how Pyrex and quartz glass behave in the hydrogen torch and upon quenching,
9) Which temperature would you used for preparing InSb, and why?

Preparation of $AuAl_2$ using sealed ampoule.

$AuAl_2$ (Norwegian: purpurpest) is prepared using a sealed ampoule. The purpose of this exercise is to practice using the hydrogen torch and to learn about synthesis of intermetallic compounds.

Consider the Al-Au phase diagram (below). Weigh stoichiometric amounts of Au and Al for synthesis of $AuAl_2$. Then add a small surplus of Al (ca. 1%)

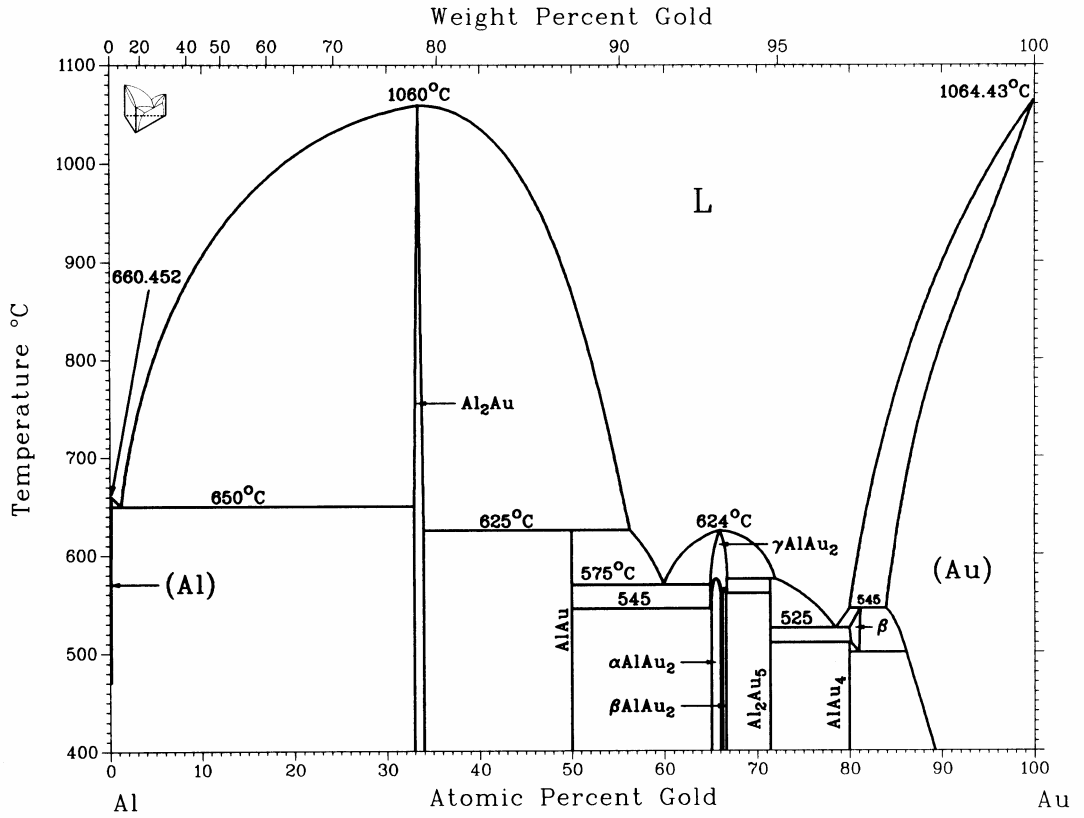

Fig. 1. The Al-Au phase diagram.

Transfer the metals to a quartz ampoule and melt it closed using vacuum in the ampoule, similar to the InSb exercise. After checking the vacuum in the ampoule, the sample is melted in the ampoule using the hydrogen torch. Use the largest available nozzle, and grip the ampoule with pliers.

Attempt to melt the mixture as fast as possible. Aluminium has a strong affinity toward oxygen, and it is beneficial to react the metals before the oxide film on aluminium becomes too thick. Even when there is vacuum in the ampoule some

oxygen and water will be present, which will react with aluminium, Furthermore, Al may react with SiO_2 and be oxidized to Al_2O_3. An alternative would be to use ampoule linings or containers of alumina or graphite. However, if the sample is heated fast enough most of the aluminium will react with gold to $AuAl_2$ before aluminium is oxidized to any significant extend.

Start by heating the tong and surrounding area. This is to avoid formation of a cold zone around the tong, which may cause the melt to freeze it this point during the subsequent mixing.

Then heat the sample intensely and observe the colour changes. If the reaction is exothermic the intensity of emitted light should increase when the reaction occur dur to the heat released. This is an indication that the reaction has occurred.

When the sample is melted, it is mixed by holding the ampoule with the tong and knocking it repeatedly against the edge of the laboratory bench.

There are several things to consider when making samples in the hydrogen torch:

- If you heat elements or compounds, which have a high vapour pressure at high temperature (e.g. S, Sb, As, P…) the ampoule may explode due to the internal pressure. Generally speaking, the ampoule may withstand an internal pressure of 10 bar. The way to proceed in these cases is to heat the reaction gently in steps, so that the reaction occurs at a relatively low temperature. (When using e.g. Pd metal it is important to remember that palladium may dissolve a large amount of hydrogen, which will be released upon heating, and may cause the ampoule to explode due to the high internal hydrogen pressure formed.)
- During heating the sample may expand more than the glass. This is of no importance when powdered or small pieces of the starting materials are used. (As long as the pieces are too small to span the ampoule and cause this to break.) However, when the sample is solid the difference in thermal expansion may cause the ampoule to break. Splinters may form, but generally breaking due to gas pressures are more dangerous. It is, however, important to consider whether the sample will react and burn in air when the ampoule cracks.

- When the ampoule containing a melt is removed from the flame it will start to solidify. During this process several thing may go wrong! Some melts wet the ampoule and the solid sticks to the wall, so that tension is formed during cooling. This may crack the ampoule, and may render repeated heating of this impossible, but it is usually not dangerous. If the melt solidify to a lump this will occur from the ampoule walls. When the sample is cooling, a void may form between the sample and the wall. If a melted phase is still present, this may run into the void. If the ampoule is reheated, the thermal expansion may again break the ampoule. This is even more likely to happen in a multiphase system where one phase crystallizes at a lower temperature than other.

The journal for this exercise is written together with the InSb exercise. Note all weights and observations.

Sealed ampoule and zone melting of InSb.

This exercise provides experience with the zone melting technique in addition to further training in working with quartz glass.

The material

InSb is of interest due to its semiconducting properties. The material takes the zincblende type crystal structure with a unit cell length of a = 6.48 Å. The bonds are mainly covalent with 5-10 % ionic character.
The compound is usually prepared by melting stoichiometric amounts of very pure In and Sb purified by zone melting. Further zone melting of the product is an efficient purification method as the solid solubility of a surplus of In or Sb is very limited. As seen from the phase diagram (Figure 1) the non-stoichiometry of InSb is very small. By zone melting it is also possible to control the amount of doping (donors and acceptors) and thereby the electronic properties of the compound.

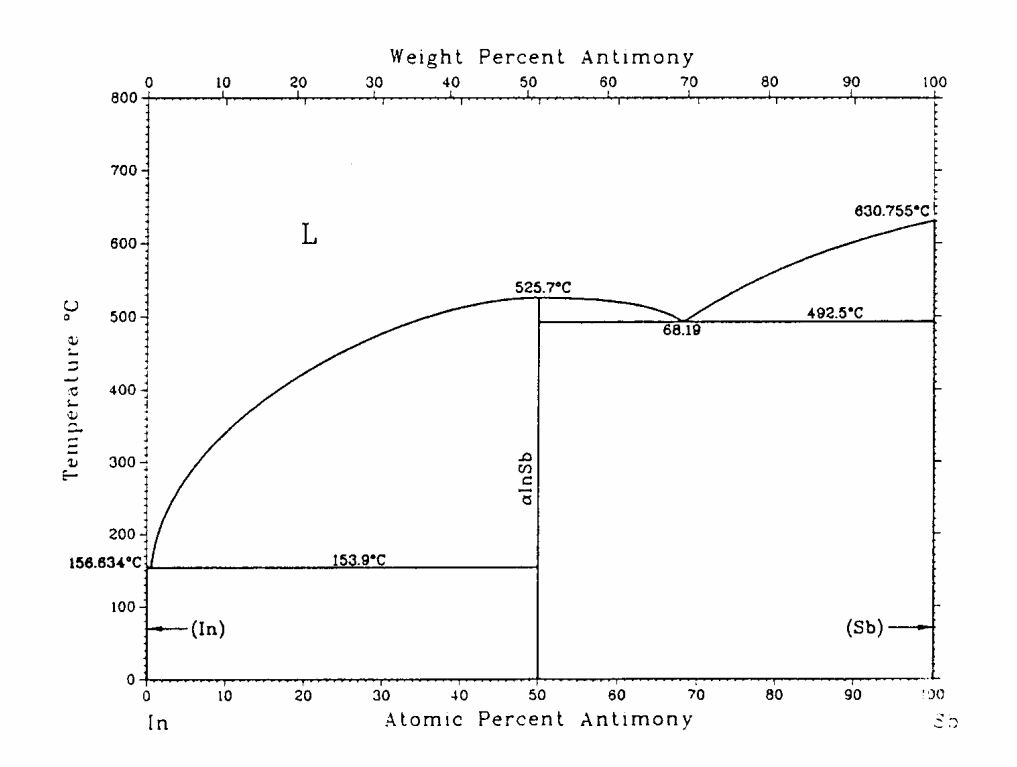

Fig. 1: The In-Sb phase diagram.

The methods

Reactions in evacuated and closed quartz glass ampoules are often used to prepare intermetallic compounds or alloys where e.g. formation of oxides must be suppressed. Quartz glass may be used safely up to ca. 1100˚C. At higher temperatures the oxygen diffusion through the glass becomes significant in addition to the initial softening of the material. In addition is important to note that some reagents such as Cr, Mn, Rh and Ge may react with quartz glass. In these circumstances inner crucibles, e.g. alumina or platinum, should be used in order to separate the reactants from the quartz glass.

Zone melting utilizes the fact that contaminants have different solubility in the solid and the melted phases. For a given contaminant it is possible to define and measure a distribution coefficient, $k0 = C_j^S/C_j^L$, where C_j^S and C_j^L are the equilibrium concentrations of component *j* in the solid and liquid phase, respectively. A more detailed description of zone melting, please refer to Appendix 2.

The exercise.

Starting materials:

- ✓ In
- ✓ Sb

Procedure:

Weigh carefully approx. 1 g (total In + Sb) so that a small surplus of Sb compared to the stoichiometric composition InSb. Transfer the metals to a quartz glass ampoule, which is then evacuated and sealed. Heat the ampoule and starting materials in flame until the metals melt. Tilt the ampoule from side to side a couple of times to ensure homogeneity in the melt. **(Be careful – This is very hot! Use tongs!)**

For the zone melting, the InSb sample is mixed with previously prepared samples in a long quartz glass ampoule, which is evacuated and sealed. The length of the ampoule should be considerably longer than the length of the liquid zone formed during zone melting. Melt the mixture over a flame and cool the ampoule horizontally, so that a rod is formed, with a length similar to the ampoule.

NOTE!: The laboratory responsible will demonstrate the use of the zone melting apparatus. Do not attempt to operate it on your own!

The ampoule is positioned in the zone melting apparatus and the voltage of the tube furnace and the zone heater are set at 200 and 80V, respectively. Temperature profiles of the zone are shown in the curves situated by the apparatus. When the temperature

has stabilized, the travelling speed of the zone is adjusted following directions from the laboratory responsible. Leave the zone melting apparatus running until the next day. Take out the ampoule, open in one end and observe the sample using a microscope. Note the length the zone travels in each run, the speed of the zone and the temperature of the zone and furnace. How many passes did the zone make?

Questions for the journal.

Characterization:

1. Describe the sample. Do you observe changes (before/after)? Aare there any differences between the first and last part of the sample (as seen in the direction the zone travelled)?
2. In the microscope you will look at prepared samples of InSb from different parts of a zone refined rod. Describe your observations. Comment on purity.
3. The prepared sample was run at the conditions: 200V on the tube furnace, 80V on the zone heater and speed ½, i.e. 3.97 cm/h. The zone passed the rod 8 times. What could be done to improve the purification process?

Comment:
When working with a doped sample (e.g. for p-n junctions) neither powder diffraction nor microscopy would be suitable analysis methods. This is due to the very low concentration of dopants, usually less than 10^{-4} mol dopants per mole InSb. Such doping levels would give no phase separation and would not result in any detectable changes in unit cell parameters.