LABORATORY COURSE IN

Inorganic Materials Synthesis

KJM5100

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Bente Gilbu Tilset

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Basics about the laboratory course

PURPOSE

The purpose of the lab course is to obtain practical experience in preparation 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 in 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!
1a: 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 flusyyre 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 flusyyre-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 brannslukningsapparat, nøddusj, førstehjelpsutstyr og telefon finnes.

9) "Tommelfingerregel" for førstehjelp ved skader:
   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 beskrivelserne 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 longer 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.

EXERCISE

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.

PREPARATION OF InSb:

Fig. 1: Closing an ampoule.

This is the first part of Exercise 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) Sketch the hydrogen torch and describe how to open, use and close down the system.
5) Give a step-by-step description of how to use a vacuum 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?
1b: Preparation of AuAl₂ using sealed ampoule.

AuAl₂ (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 AuAl₂. Then add a small surplus of Al (ca. 1%)

![Fig. 1. The Al-Au phase diagram.](image)

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 SiO₂ and be oxidized to Al₂O₃. 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 AuAl₂ 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 due 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.
2: 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, \( k_0 = \frac{C_j^S}{C_j^L} \), 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)? Are 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.
Preparation and Properties of an Aqueous Ferrofluid

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Introduction

Imagine the production and applications of a liquid that can be controlled by a magnetic field. Creating a strongly magnetic liquid is not as easy as melting a strongly magnetic solid, since magnetic solids lose much of their magnetism above what is known as the Curie temperature, as thermal energy overwhelms the tendency of their electrons to align in magnetic domains (regions of similarly oriented electron spins). The Curie temperature is well below the melting point for known magnetic materials (1–3). Ferrofluids, which are colloidal suspensions of magnetic material in a liquid medium, are an example of a liquid that responds to an external magnetic field. The coupling of liquid and magnetic behavior means that the liquid’s location may be manipulated by an applied magnetic field.

Ferrofluids were first developed and classified in the 1960s by Stephen Pappell at NASA as a method for controlling fluids in space (4). NASA initially used them as rotating shaft seals in satellites, and they now serve the same purpose in a wide variety of machines, ranging from centrifuges to computer hard disk drives (1, 2). They are incorporated into the voice coil gap of loudspeakers for damping undesired vibrations and for cooling. Ferrofluids have also been used in the separation of metals from ores by taking advantage of a density change that appears in the fluid under application of a magnetic field. One South African company has even been utilizing ferrofluids to separate diamonds from beach sand (5). In medicine, a ferrofluidic actuator has been proposed for an implantable artificial heart (1). This actuator would be driven simply by applying an external magnetic field. It is possible to attach drugs to the surface of the magnetic particles and use magnetic fields to hold the drug at the site where it is needed (3). Aqueous magnetic fluids have successfully oriented biological assemblies such as the tobacco mosaic virus, enabling information concerning the helical structure of the virus to be obtained (6).

Recently, ferrofluids have been utilized in conjunction with microcontact printing and capillary filling to fabricate patterned structures of magnetic materials on the micron scale (7). The ability to produce patterns of ultrafine magnetic particles has important technological applications, since the information density on tapes, for example, is inversely proportional to the size of the particles. Research has been conducted exploring the use of ferrofluids as magnetic inks for ink jet printing (2). Magnetic inks are currently used in printing United States paper currency, as can be demonstrated by the attraction of a genuine dollar bill to a strong magnet (Fig. 1) (8).

Background

There are two major steps in synthesizing a ferrofluid.

The first is to make the magnetic nanoparticles (~100 Å diameter) that will be dispersed in the colloidal suspension. These particles must be chemically stable in the liquid carrier. The magnetic particles in ferrofluid are generally magnetite, Fe₃O₄, although other magnetic particles have been used. The second synthetic step is the dispersion of the magnetic particles into a carrier liquid by utilizing a surfactant to create a colloidal suspension. Surfactants are dispersion agents for particles in a liquid that work by adhering to the particles and creating a net repulsion between them (steric and/or coulombic), raising the energy required for the particles to agglomerate, and stabilizing the colloid (Fig. 2) (3). Aqueous-, oil-, and liquid-metal-based (mercury; gallium

Figure 1. Magnetic inks are printed onto paper money for identification purposes. When a strong magnet is brought near a dollar bill (A), the bill is attracted to the magnet (B).
alloys) ferrofluids have been developed with the proper choice of surfactant (1). The magnetic properties of magnetite that make it a desirable component of ferrofluids are derived from its crystal structure. Magnetite crystallizes in the inverse spinel structure above 120 K (9). The inverse spinel structure consists of oxide ions in a cubic close-packed arrangement. Iron(II) ions occupy 1/4 of the octahedral holes, and the iron(III) ions are equally divided between 1/8 of the tetrahedral holes and 1/4 of the octahedral holes. Electron spins of iron(III) ions in octahedral holes are aligned antiparallel to those in tetrahedral holes; therefore, no net magnetization is observed from these ions. The iron(II) ions, however, tend to align their spins parallel with those of iron(III) ions in adjacent octahedral sites, leading to a net magnetization. This arrangement of antiparallel spins throughout the solid that do not completely cancel is referred to as ferrimagnetism. Ferrofluids are actually superparamagnetic, meaning that a ferrofluid reacts to a magnetic field in the same way as a ferromagnetic or ferrimagnetic solid, but magnetizes and demagnetizes more rapidly because in a ferrofluid the magnetic domains are the same size as the actual particles. Manganese and cobalt ferrites, MnFe$_2$O$_4$ and CoFe$_2$O$_4$, respectively, also have the inverse spinel structure and have been used in the preparation of ferrofluids (10). The layer sequences for a conventional cubic unit cell and for a smaller tetragonal unit cell for magnetite are shown in Figure 3. The Fe$_{32}$O$_{64}$ cubic unit cell and the Fe$_{12}$O$_{32}$ tetragonal unit cell both have the same empirical formula, Fe$_3$O$_4$. Construction directions using the ICE Solid-State Model Kit (11) are included in the Supplemental Material.

A cubic unit cell built with the kit is shown in Figure 4. For magnetite to remain in suspension, its particle diameters need to be on the order of 10 nm (100 Å) (2, 4b). At room temperature, the thermal energy of these colloidal particles is of the same order of magnitude as the gravitational and magnetic attraction, $\sim 4 \times 10^{-21}$ J, and therefore the particles remain suspended. The original ferrofluids developed at NASA used finely divided magnetite, prepared by grinding in a ball mill for several weeks to obtain particles of an appropriate colloidal size. Carrier liquid, surfactant and a dispersant were added during the grinding process to prevent agglomeration of the nanoparticles. In an alternative procedure, as used in this paper, magnetite is synthesized in solution and precipitated as nanoparticles (2, 3).

Overview

This paper presents an easy, economical method for preparing a ferrofluid that can be used in high school or college science or engineering courses.1 This ferrofluid may be prepared in less than 2 h. The synthesis is based on reacting iron(II) and iron(III) ions in an aqueous ammonia solution to form magnetite, Fe$_3$O$_4$, as shown in eq 1.

$$2\text{FeCl}_3 + \text{FeCl}_2 + 8\text{NH}_3 + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 8\text{NH}_4\text{Cl} \quad (1)$$

The magnetite is mixed with aqueous tetramethylammonium hydroxide, (CH$_3$)$_4$NOH, solution. This surfactant can surround the magnetite particles with hydroxide anions and tetramethylammonium cations (12) to create electrostatic interparticle repulsion in an aqueous environment (Fig. 2).
This paper also includes a method for applying a ferrofluid-resistant coating to objects and describes a dramatic classroom demonstration of the attraction of ferrofluid to magnets.

**Synthesis**

**Safety**

**CAUTION:** Gloves and goggles must be worn at all times. Hydrochloric acid and aqueous ammonia are corrosive and should be handled with care. FeCl₂ is toxic, corrosive, and a mutagen. FeCl₃ is corrosive. Tetramethylammonium hydroxide is a strong base that is corrosive and flammable. Caution must be exercised when handling any of these materials. Wash immediately with water in case of skin contact.

Ferrofluids can be messy. This particular ferrofluid will permanently stain almost any fabric and it has a high pH. It is also very difficult to remove from magnets.

**Special Materials Required**

Cow magnet (0.5 in. diameter x 3 in.), available from farm supply stores or from Edmund Scientific, Barrington, NJ.

Strong neodymium-iron-boron (Nd₂Fe₁₂B) magnet, available from Edmund Scientific, Barrington, NJ, or Magnet Sales and Manufacturing Company, Culver City, CA.

Benchtop centrifuge, such as an International Clinical Centrifuge from the International Equipment Company, Boston, MA.

2.0 M FeCl₂ in 2 M HCl (39.76 g of FeCl₂·4H₂O in 100 mL of 2 M HCl).

1.0 M FeCl₃ in 2 M HCl (67.58 g of FeCl₃·6H₂O or 40.55 g of FeCl₃ in 250 mL of 2 M HCl).

0.7 M aqueous NH₃ (48 mL of concentrated aqueous NH₃ diluted to 1 L with H₂O).

25% aqueous (CH₃)₄NOH solution, available from Aldrich, Milwaukee, WI.

NOTE: Stoichiometry of the reaction is important. The solids are hygroscopic and previously unopened reagents will work better. It is absolutely essential that there is no undissolved material in the solutions. Prepare the iron chloride solutions by adding the solid iron chlorides to the 2 M HCl solution. The acidic conditions prevent formation of iron hydroxides. The iron(II) solution is susceptible to air oxidation and should be used within a week of preparation. Both the ammonia and (CH₃)₄NOH solutions should also be free of undissolved solids.

NOTE: We have also found that we can synthesize high-quality ferrofluid using 1 M tetra-n-butylammonium hydroxide, also available from Aldrich, in place of tetramethylammonium hydroxide. The ferrofluid spikes are about the same size for both surfactants, but tetramethylammonium hydroxide is less expensive.

**Procedure**

Combine 1.0 mL of stock FeCl₂ solution and 4.0 mL of stock FeCl₃ solution. Place a magnetic stirring bar in the flask and begin stirring vigorously. Add dropwise by pipet or buret 50 mL of 0.7 M aqueous NH₃ solution into the flask. We have found that the slow rate of addition is critical, and a pipet or buret is a convenient means of slowing the addition rate. Magnetite, a black precipitate, will form immediately. Stir throughout the addition of the ammonia solution. Cease stirring and allow the precipitate to settle (5–10 min), then decant and dispose of most of the liquid. Stir the remaining solution and centrifuge the solution for 1 min at 1000 rpm. (In general, at least 15–20 mL of liquid should be centrifuged in order to obtain an adequate amount of solid magnetite for preparing a ferrofluid sample; one or more centrifuge tubes can be used for this step, depending on the centrifuge available.) Decant the supernatant after centrifugation.

**Figure 4.** Model of the cubic unit cell of Fe₃O₄, built with the ICE Solid State Model Kit (11).

**Figure 5.** The final ferrofluid preparation step. Remove the magnetite from both ends of the stirring bar by grasping the bar in the center, touching each end in turn to the weighing boat above the strong magnet, and rotating the stirring bar until all of the magnetite adheres to the weighing boat through attraction to the strong magnet beneath the boat.
The dark, sludgelike solid at the bottom of the tube is magnetite. Divide 8 mL of 25% tetramethylammonium hydroxide ((CH₃)₄NOH) solution among however many centrifuge tubes were used during the centrifugation and stir with a thin glass rod until the solid is completely suspended in the liquid. Pour the contents of all of the tubes into a vacuum filtration flask, add a magnetic stirring bar, and stopper the flask. Magnetically stir the solution under aspirator vacuum for 30 min to remove excess ammonia from the solution. After stirring, slowly pour the liquid into a beaker. The magnetic stirring bar that remains in the filtration flask should be covered with a black sludge, which may or may not exhibit spikes at the ends of the magnet. Gently pour the stirring bar and attached sludge into a plastic weighing boat. Remember that ferrofluids are messy and can easily and permanently stain any fabric. Carefully and slowly hold a strong, block-shaped magnet (preferably a Nd₂Fe₁₂B magnet—see above for suppliers) up to the bottom of the plastic weighing boat, keeping it underneath the weighing boat. Using gloved fingers, grasp and rotate the stirring bar about its axis to remove the magnetite adhering to it by allowing the magnetite to be more strongly attracted to the stronger magnet held beneath the weighing boat (Fig. 5). Make sure the magnetite is removed from both ends of the stirring bar. Pull the now-clean magnetic stirring bar out of the weighing boat, being careful not to let it slip back into the weighing boat, where it could cause splashing. With the strong magnet still underneath the weighing boat, pour off any excess water. Finally, carefully remove the strong magnet from the bottom of the weighing boat.

Hold a cow magnet up to the bottom of the weighing boat to check whether the ferrofluid forms spikes in the presence of a moderate magnetic field (Fig. 6) (a more detailed description of ferrofluid spiking is given in the Results and Discussion section). If the fluid does not spike, or the spikes are small, remove the cow magnet, add one drop of distilled water, stir well with the glass rod, and again check for spiking with the cow magnet. If spikes are still not seen, try adding one or two more drops of water. It should not take more than a few drops to obtain a good spiking effect. If too much water is added, the ferrofluid will become too dilute and will not spike. If the ferrofluid is too dilute, hold the strong magnet under the weighing boat, then tilt the weighing boat so that the excess liquid runs off.

Results and Discussion

A fascinating physical property of a ferrofluid is the unusual distortion that the fluid experiences when exposed to a magnetic field. When a high-quality ferrofluid is brought into contact with a moderate magnetic field, such as that from a cow magnet, it develops spikes on its surface (Fig. 6). These spikes, which may adopt a close-packed hexagonal pattern, are due to surface instability of the suspended particles. The surface instability associated with the ferrofluid causes small waves to be constantly present on the surface of the liquid (2). When a magnetic field is applied, the amplitude of the waves increases until they begin to form peaks. If the magnetic force is large enough to dominate the forces of surface tension and gravity, the spikes appear. The spikes increase in size as the magnetic field is increased. By far, this is the easiest and most fascinating test for a high-quality ferrofluid. However, if the magnetic field becomes too great, the magnetic particles will reversibly precipitate from the solution (3). The synthetic procedure described above can be carried out with varying mole ratios of FeCl₂ to FeCl₃ in order to demonstrate the effect of stoichiometry. About 250 pairs of undergraduates in an introductory chemistry lab performed the synthesis with varying ratios of the precursor iron chloride solutions. There was time during the three-hour lab period for the students to perform the synthesis with the 2:1 iron(III)/iron(II) stoichiometric ratio that is known to work, as well as a second synthesis using a different stoichiometric ratio. A graph of the percent of successful syntheses (ferrofluids that spiked) as a function of precursor solution ratios for the pooled student data is shown in Figure 7. An alternate format for the lab is to assign
different stoichiometric ratios to different groups of students at the beginning of the lab. After the first synthesis is complete, the resulting fluids can be checked for spiking with a magnet. The stoichiometric ratio that results in the “best” ferrofluid (the one that responds most dramatically to a magnet) can then be assigned to the entire class for a second ferrofluid synthesis, allowing everyone to prepare a high-quality ferrofluid.

The structure of the synthesized magnetite particles can be identified by X-ray powder diffraction. The average particle diameter for the crystalline precipitate can be determined by Scherrer’s formula, eq 2, using the half-widths of the most intense X-ray diffraction peaks (3, 13).

\[ t = \frac{(0.9 \lambda)}{(B \cos \theta_B)} \]  (2)

In this formula, \( t \) is the particle diameter in Å, \( \lambda \) is the wavelength of the X-ray radiation in Å, \( \theta_B \) is the Bragg angle of the peak, and \( B \) is the peak broadening. Peak broadening is a measure of the size of the nanoparticles with respect to reference particles. The reference particles must have a crystal thickness greater than ~2000 Å, which gives relatively narrow peaks (Fig. 8A). A commercially manufactured sample of magnetite has particles that are sufficiently large to serve as a reference. The peaks for the colloidal sample are typically broader (Fig. 8B). The peak broadening, the difference between the sample and reference peak widths, is given by the Warren formula (eq 3) (14).

\[ B^2 = B^2_{\text{colloid sample}} - B^2_{\text{bulk material}} \]  (3)

\( B \) is the peak width (in radians) that is measured at half the maximum peak intensity. The data for the bulk material may be obtained from JCPDS files (15) or from a diffraction pattern of commercial \( \text{Fe}_3\text{O}_4 \) (available from Aldrich, Milwaukee, WI) having an average crystal size greater than ~2000 Å (13). Using the peak at \( 2\theta = 35.6^\circ \) (Miller indices, (311)), the average size of magnetite particles synthesized by the method described in this paper is ~14 nm. These magnetite particles are small enough to sustain a colloidal suspension, and a good ferrofluid can be produced.

A Ferrofluid-Resistant Coating

Many water- and oil-based ferrofluids tend to stain (sometimes permanently) materials with which they come into contact. This procedure outlines a method to affix a ferrofluid-resistant coating to a container. (The container should be able to withstand temperatures in the range of 120–180 °C.) Scotchgard Fabric Protector FC-247 is a concentrated aqueous suspension of fluoroaliphatic resin; it can be obtained from 3M Specialty Chemicals Division, St. Paul, MN. Avoid eye and prolonged skin contact with this suspension. Thoroughly coat the surface of the container that will contact the ferrofluid with the Scotchgard: rotate the vessel or use a spray-bottle to evenly coat it, then pour out the excess liquid. (The excess can be poured back into its storage bottle to be reused.) Allow the container to dry for approximately an hour in open air, then place it in a 120–180 °C oven for 30 min. Let the vessel cool to room temperature before allowing ferrofluid to contact the treated surface. We have found this coating to resist wetting and staining by ferrofluid for a period of several weeks. This coating can be removed by soaking in hot soapy water or a KOH/isopropanol base bath. Scotchgard fabric protector, sold in spray cans, provides a more limited resistance to ferrofluid.
The “Leaping Ferrofluid” Demonstration

The following describes a demonstration (Fig. 9) that uses magnets to force a ferrofluid to leap into the air, providing a dramatic demonstration of the effects of magnetic fields on ferrofluid. Using a cork borer, bore a hole slightly smaller than the diameter of an 18 ×130-mm test tube (~17 mm) in a #13 rubber stopper, then push the test tube through the hole until the stopper is about a third of the way from the bottom of the tube. This stopper will prevent ferrofluid from following the magnets all the way up the test tube. Attach a 3-fingered clamp near the bottom of a ring stand and place the test tube vertically in the clamp, leaving about 3 cm clearance under the end of the test tube. Stack small strong magnets so the poles are at the ends of the stack. Nd$_2$Fe$_{12}$B magnets, such as those available from Edmund Scientific Corporation, Barrington, NJ, or Magnet Sales and Manufacturing Company, Culver City, CA, work well, as long as they are sufficiently small to fit easily into the test tube. Tie the end of the string around one of the magnets.

Place the tied magnet on one end of the stack, using broken magnet pieces (broken with a hammer) as spacers to give more stability to the gap caused by the string (Fig. 10). Attach a ring clamp near the top of the stand, thread the string through a one-hole #1 rubber stopper that will be placed in the open end of the test tube (small side of the stopper toward the magnets) and through the ring clamp ring, and tie the other end to a ~100-g weight. The weight should be slightly heavier than the magnets, so that when it is released it will hold the magnets in the “up” position, away from the ferrofluid that will be placed below the test tube. Tie the end of the string around one of the magnets.

Place the magnets in the test tube and fill the tube with mineral oil to about 2 cm from the top. The viscous oil decreases the descent rate of the magnets, preventing splashing of the ferrofluid from the external walls of the glass tube. Apply silicone caulk to the mouth of the tube and to the sides of the small stopper, then insert the stopper and cure for 24 h. A watch glass with a small amount of ferrofluid (a few milliliters of either a commercial oil-based ferrofluid from Ferrofluidics Corporation, Nashua, NH, or the water-based ferrofluid synthesized using the procedure given in this paper) can then be placed under the test tube. An option to prevent staining and to aid draining of ferrofluid off of the tube is to treat the contact surface of the test tube (that below the large rubber stopper) and of the watch glass with Scotchgard (see above).

When the weight is lifted, lowering the magnets through the oil, the ferrofluid leaps to the surface of the test tube, displaying its dramatic spiking (Fig. 11). When the weight is lowered, the magnets are raised, pulling the ferrofluid along with them until they are prevented from following any farther by the

[Diagram of the demonstration setup]

Figure 9. Construction of the “leaping ferrofluid” demonstration.

Figure 10. Construction of the magnet stack used in the “leaping ferrofluid”

Figure 11. The leaping ferrofluid demonstration. (A) The magnets are in the raised position. (B) The magnets are in the lowered position. (C) Ferrofluid spiking at the end of the test tube, which occurs when the magnets are in the lowered position.
barrier of the large rubber stopper. At this point the ferrofluid drains off the test tube back into the watch glass. If the ferrofluid does not leap to the magnets, the test tube should be moved closer to the ferrofluid. The demonstration may be repeated many times successively and presented in a large lecture hall using a video camera.

Conclusion
Ferrofluids are fascinating materials. They are easy to synthesize and the preparative procedures illustrate a wide variety of chemical and physical concepts, including stoichiometry, crystal structure, colloidal properties, oxidation states, and magnetism. The small size of the particles also provides a means for introducing nanoscale materials and preparation. The synthesis and properties of ferrofluids would fit into the curriculum of many types of introductory science and engineering laboratory courses.

Acknowledgments
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Notes
WSupplementary materials for this article are available on JCE Online at http://jchemed.chem.wisc.edu/Journal/issues/1999/Jul/abs943.html and can be downloaded from this site. ffsup is a Microsoft Word 6.0 document of instructions for building the solid state model of the magnetite structure and the student laboratory synthesis of ferrofluid. Images and movies of these and other experiments are available at the Materials Research Science and Engineering Center Education and Outreach Web site, http://mrsec.wisc.edu/edetc/. 1. A classroom kit (The Ferrofluidic Adventure Science Kit) is available from Ferrofluidics Corp., 40 Simon St., Nashua NH 03061; phone: 603/883-9800; fax: 603/883-2308; www.ferrofluidics.com. 2. Experimental conditions for powder diffraction: Scintag PAD V diffractometer, Scitag Inc., Cupertino, CA; X-ray source: λ=1.540562 Å (Cu α1KLIII); steptime: 0.600 s; stepwidth: θ=0.020°, 2θ=0.040°; 2θ range: 20–70°; scan rate: 20/min

Literature Cited
5. Ogden, F. The Last Book You’ll Ever Read; MacFarlane, Walter, and Ross: Toronto, 1993; p 206.
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Preparation of manganese oxide thin film using the ALCVD (ALD) technique

Manganese oxides

Manganese forms a number of oxides with varying oxygen content, MnO–Mn$_2$O$_7$, where each of the oxides in addition has several crystalline modifications (polymorphs). Manganese oxides are mainly semiconductors and the conductivity increase with increasing oxidation state.

MnO$_2$ has shown good properties as a protecting and conducting layer on Ta$_2$O$_5$ in some capacitors. MnO$_2$ is thermodynamically unstable at ambient conditions, and must therefore be prepared under special conditions. MnO$_2$ is also of interest in the battery industry because one of the polymorphs is used extensively as counter electrode in most batteries. Mn$_3$O$_4$ and Mn$_2$O$_3$ are of interest e.g. for energy storage. One of the recently investigated properties of manganese oxides is the electrochromic properties. This means that colour or optical absorption in a film of the material may change by applying an electrical field. Manganese oxides, and especially MnO$_2$, are also well suited as catalysts in a number of reactions involving hydrocarbon oxidation.

The ALCVD (ALD) method

ALCVD (Atomic Layer Chemical vapour Deposition) or ALD (Atomic Layer Deposition) is a type of CVD technique. In “ordinary” CVD the reactant gases are brought together into the reaction chamber. In this way a high growth rate is obtained, but at the same time the possibility of uncontrolled growth and gas phase reactions increases. In ALCVD each gas is pulsed separately into the chamber, followed by a flushing step using inert gas.

When a chamber is filled with gas a layer of molecules will be deposited on all surfaces of the chamber. These molecules may be physically or chemically adsorbed on the surface. (Fig. 1a)

![Figure 1](image)

**Figure. 1.** The various steps in a ALCVD cycle. A) Pulsing of reactant X. B) Flushing using an inert gas in order to remove the molecules in the gas phase. C) pulsing with reactant Y, which reacts on the surface. D) flushing by inert gas.
The difference between physical and chemical adsorption depends on the strength of the interactions between the molecules and the surface. If the molecules are bound to the surface only by van der Waals interactions, then it would be considered as physisorption (up to ca. 40 kJ/mole). This type of adsorption has no activation energy attached. If the adsorption involves stronger bonds, i.e. ionic or covalent bonds, it is considered as chemisorption. This type of adsorption often involves rearrangement of the adsorbed molecules, and includes activation energy. This case is often considered as a reaction of the molecules with the surface. In most cases of chemical adsorption this will only involve the first layer attached to the surface. Subsequent layers will be physically adsorbed.

During an ALCVD pulse the substrate (and all other accessible surface) will be coated by a layer of molecules, which should be chemically adsorbed. After a certain pulse length the chamber is flushed by an inert gas, Fig. 1B. This will remove all reactive molecules in the gas phase, and is the flushing step is long enough, all physically adsorbed molecules will be removed as well. The result is a chemically adsorbed layer. In the next step a pulse of a different reactant will be introduced, which will react chemically with the previously adsorbed layer, Fig. 1C. In this manner the film is grown layer by layer, Fig 1D.

As the method is very precise and “binary”, it is ideal for preparing thin films, which cover large areas and has an even coating over edges and steps. If this is compared with “ordinary” CVD the possibility of gas phase reactions is eliminated. This prevents formation and deposition of particles which may ruin the film. In ALCVD the point is that the precursor should not decompose. This is often the opposite as for CVD where some processes utilize thermal decomposition of the precursor in stead of chemical reactions. This limits the possibility of direct transfer of CVD processes to ALCVD, but increases the possibility of controlled growth. In a CVD process reactants are needed which will react with each other, without being so reactive that gas phase reactions occur. The ALCVD process, on the other hand, may use more reactive precursors than the CVD process.

The exercise
In this exercise a manganese oxide will be prepared by ALCVD technique. The purpose of the exercise is to obtain some experience with metalorganic synthesis, to work with purity considerations and to work with large up-to-date equipment. In addition, experience using a sublimator for purification of compounds will be obtained.

Experimental
Chemicals used in the exercise

<table>
<thead>
<tr>
<th>Chemicals</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>KMnO₄</td>
<td>methanol</td>
</tr>
<tr>
<td>MnCl₂·4H₂O</td>
<td>trichloroethylene</td>
</tr>
<tr>
<td>2,2,6,6-tetramethyl-3,5-heptadione (thd)</td>
<td>acetone</td>
</tr>
<tr>
<td>NH₃</td>
<td></td>
</tr>
</tbody>
</table>
The precursor

The first step is to prepare the precursor, Mn(thd)$_3$. The precursor is prepared by a Lewis acid/base reaction where electron pairs from thd are used for complexing electron poor Mn. thd is a $\beta$-ketone; the enole form is therefore fairly stable and may also react as an acid (as shown below). We will attempt to make the acid form a complex with Mn$^{3+}$.

\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{H} \\
\text{O} \\
\text{O} \\
\end{array}
\quad \rightarrow
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{H}^- \\
\text{H}^+ \\
\end{array}
\]

As there are no easily accessible and stable Mn(III) salts, we have to prepare a solution which contains a formal mean oxidation state of manganese of 3. This is done by mixing the appropriate amounts of MnCl$_2\times$4H$_2$O and KMnO$_4$.

- Write a reaction between MnCl$_2\times$4H$_2$O and KMnO$_4$ and calculate how much of each is needed to prepare 0.01 mole Mn(thd)$_3$.

Weigh these amounts separately. MnCl$_2$ is first dissolved in 50 ml. methanol in a 100 ml beaker. KMnO$_4$ is dissolved in 10 ml. water and added to the Mn$^{2+}$ solution. Let it stand covered under stirring in ca. 15 minutes.

In the mean time the calculated amount of thd is measured in a graduated cylinder. (Do not waste any of the thd, as it is very expensive!) Also prepare ca. 100 ml of a 2.5M aqueous solution of NH$_3$.

Arrange the beaker with the manganese solution, pH electrode and magnetic stirrer as shown in the figure below. Mix the reactants simultaneously and dropwise while keeping the pH between 6 and 7. This is very important, so please be careful! Start by adjusting the pH in the solution using NH$_3$.

[Diagram of the reaction setup]

Mixing thd and ammonia while maintaining pH between 6 and 7.
When all the has been added stirring is continued over-night. When the solution has been stirred over night it is suction filtered in the appropriate glass sinter filter, used only for this compound. The brown precipitate is washed at least twice with a 50% solution of methanol in water, the solution should be cold. (If in doubt, please ask the laboratory responsible.) Distribute the washed precipitate onto a large watch glass and dry it in a vacuum furnace. Set the vacuum furnace to ca. 60°C and let it stand over night. When the product is dry it must be purified by sublimation. The laboratory responsible will demonstrate how the sublimation equipment works. The principle of the sublimator is described below.

The sublimator may be described as a vacuum furnace with a temperature controlled cold finger. The principle is to heat the compound to obtain a suitable vapour pressure and deposit it onto the cold finger. The finger should keep a temperature slightly below that of the furnace. Everything is kept under vacuum to increase the diffusion rates. The sublimation is initiated by setting the temperature of the finger relatively high and then increasing the temperature of the furnace while monitoring the pressure. The pressure should be below 0.2 mbar before the temperature is increased to the sublimation temperature. In this way water and high vapour pressure organic compounds will be removed from the sample. The final sublimation should be done slowly so that contaminants with a higher sublimation temperature are not carried with the sublimating compound. When a large part of the sample has sublimated, the temperature of the furnace may be increased while at the same time decreasing the temperature of the finger. (2-3°C). For the compound Mn(thd)$_3$ the finger and furnace may be set initially to 60°C. Then the temperature of the furnace may be slowly increased to 100°C while the temperature of the finger is lowered to 40°C. When the sublimation is over, the apparatus is taken apart and the purified sample is scraped off the finger. The sublimator must be cleaned thoroughly with acetone. The melting point of the sample is determined and noted. Weigh the final product and calculate the yield.

The precursor is now ready to be used. But before proceeding to the making of films, substrates must be washed.

Figure X. Sketch of the sublimator.
**Washing substrates**

Some substrates will be handed out by the laboratory responsible. Remember that any carelessness in the washing procedure and touching of the substrates will become very visible after growing the film…

The substrates are washed by first treating them with warm trichloroethylene, warm acetone and warm ethanol, each step for 5 minutes. Thereafter they are washed with a special soap and cotton on each side before being rinsed with plenty of spring water and finally distilled water. They are then dried as fast as possible by an air blower. It is important that the substrates do not dry in between each step as impurities may crystallize.

It is not the intention that you should run the ALCVD machine by yourself; the laboratory responsible will show you how this is done.

Ozone is the other reactant in the production of the manganese oxide films. Ozone is produced by electrical discharges in a chilled container. In this equipment the ozone is produced in a commercial ozone generator. The laboratory responsible will introduce you to the operation of this. It is important to remember that ozone is an environmental poison for humans so that all leakage must be avoided.

After producing the films, sketches should be made of the substrates and observations should be noted. The laboratory responsible will determine the thickness of the films using X-ray profilometry (reflectance).

**Questions to the exercise.**
- Mention some advantages and disadvantages of ALCVD compared to ”ordinary” CVD.
- How would you proceed when making thin films of TiN and TiO2?
- Point out the purpose of each step of the washing procedure.
5: Citrate-, and flux-methods for preparation of YBCO, YBa$_2$Cu$_3$O$_7$

In this exercise two exercises are run in parallel. YBa$_2$Cu$_3$O$_7$ is prepared in two different ways; powder is prepared by a citrate route and single crystals are made by flux growth.

The Material

YBa$_2$Cu$_3$O$_7$ was discovered in 1987 as the superconducting component in samples with bulk composition Y$_{1.2}$Ba$_{0.8}$CuO$_4$. This was the first known compound with a critical temperature ($T_c$) above 90K. This discovery accelerated the research into superconductors, both in attempts to prepare materials with higher critical temperature and in developing a theory for superconductivity. A great deal of effort is also put into development of application of the new high temperature superconductors. The high critical temperature made it possible to use liquid nitrogen as a coolant. This is much less expensive than liquid helium, which is in practical use today, but there are still obstacles to be overcome before high temperature superconducting ceramic can be used.

The crystal structure of the compound is shown in Figure 1a. It is orthorhombic and shows similarities to the perovskite structure. Compared with the ideal perovskite structure this compound has ordered oxygen vacancies in the atomic arrangement. In addition, Y and Ba are ordered on A-type positions. This results in a tripling of the unit cell in the $c$-direction relative to the cubic perovskite. Cu, which is situated at the B-type positions, take two different coordinations, square planar for Cu$_1$ and square pyramidal for Cu$_2$. In the ideal perovskite structure all B-type cations are octahedrally coordinated. In YBa$_2$Cu$_3$O$_7$ copper has an...
unusually high oxidation state (2.3). It is not possible to reach this high oxygen content except by annealing in oxygen at relatively low temperature. The oxygen content may be varied between 7.00 and 6.35 for the orthorhombic YBa$_2$Cu$_3$O$_{7-\delta}$ phase. By further reduction a phase transition to a closely related tetragonal structure (composition YBa$_2$Cu$_3$O$_{6+\delta}$) occur. $T_C$ decrease with decreasing oxygen content and is below 77K ($= T_{b,N_2}$) at 6.85. Further development of the materials has increased $T_C$ to around 160K.

**The methods**

**The Citrate method** is a type of sol-gel method, where the homogeneous atomic distribution in a liquid phase is attempted maintained by polymerization of citric acid complexes. Citric acid is a tri-protonic carboxylic acid with the formula:

\[
\begin{align*}
&\text{H} \\
&\text{H - C - COOH} \\
&\text{H O - C - COOH - H}_2\text{O} \\
&\text{H - C - COOH} \\
&\text{H}
\end{align*}
\]

When different cations form complexes with the molten acid an intimate mixture of the ions on an atomic scale is obtained. During careful heat treatment in air of a solution of citric acid complexes polymerization and decomposition take place in parallel until a gel is formed. When the remaining water is removed from the gel a xerogel is obtained, which is an amorphous glass-like crust. Most of the organic content is removed by further heating of the the xerogel in air, usually at approx. 450°C. The desired oxide is formed by heat treatment above the decomposition temperature of the carbonate. (A more thorough description of the original development of the citrate method for preparation of YBa$_2$Cu$_3$O$_7$ can be found in: P. Karen and A. Kjekshus “Citrate-gel synthesis in the Y(O)-BA(O)-Cu(O) system”, *J. Amer. Ceram. Soc.*, 77 (1994) 547-552)

**Flux growth** involves growth of crystals from non-aqueous solutions at temperatures above room temperature. The components of the desired product are dissolved in a solvent, the flux. Thereafter the product is precipitated in a process analogous to crystallization from aqueous solutions. As with growth from aqueous solutions, crystals grow at temperatures lower than the melting point of the material. This is especially important when: 1) the desired phase is incongruently melting, 2) a phase transition takes place to another (unwanted) modification before melting or 3) decomposition rather than melting takes place. Flux growth is also beneficial when the phase has a high vapour pressure at the melting point or if the melting point is very high. A phase diagram for the solids present in the system Y-Ba-Cu-O at 900°C and 1 atm. O$_2$ is shown in Fig. 2. It is seen that YBa$_2$Cu$_3$O$_7$ (denoted 123 in Figs. 2 and 4) is in equilibrium
with CuO, Y$_2$BaCuO$_5$ (=211) and/or BaCuO$_2$, depending on the bulk composition of the sample. Closer studies have given the liquidus surface for the copper-rich part of the Y-Ba-Cu-O system as shown in Fig. 3. From this Figure it is seen which phases are obtained directly by cooling a melt with various compositions. We observe that only a relatively narrow composition-range will give YBa$_2$Cu$_3$O$_7$ as the primary precipitate. In order to obtain an impression of how the phase diagram looks in this area, a pseudo binary phase diagram for the section through the phases YBa$_2$Cu$_3$O$_7$ and Y$_2$BaCuO$_5$ is shown in Figure 4. This section is also indicated in Figures 2 and 3. We see that YBa$_2$Cu$_3$O$_7$ melts peritectically: YBa$_2$Cu$_3$O$_7$ $\rightarrow$ Y$_2$BaCuO$_5$ + melt, and that a narrow compositional range exists (marked with a double arrow) where YBa$_2$Cu$_3$O$_7$ may be precipitated directly from the liquid phase.

Figure 2: Subsolidus phase diagram for the system: Y-Ba-Cu-O at 900°C and 1 atm O$_2$.

Figure 3: The liquidus surface for the Cu-rich part of the Y-Ba-Cu-O system.
Sections which are approximately parallell to the one shown, display similar regions of precipitation of $\text{YBa}_2\text{Cu}_3\text{O}_7$, with varying width and temperature range. The lowest temperature at which the flux is still liquid is at e1 (see Fig. 3); an eutectic where $\text{YBa}_2\text{Cu}_3\text{O}_7$, $\text{BaCuO}_2$ and $\text{CuO}$ are in equilibrium with the liquid. This eutectic show similarities to the one found in the two-component system $\text{BaO-CuO}$, see Fig. 5, but it is shifted both regarding the compositional ratio between Ba and Cu and in temperature due to addition of $\text{Y}_2\text{O}_3$ and a different partial pressure of oxygen.

In order to obtain the largest possible yield of $\text{YBa}_2\text{Cu}_3\text{O}_7$, over a large temperature range, a bulk composition positioned on the full part of the line between $\text{YBa}_2\text{Cu}_3\text{O}_7$ and e1 should be used. When $\text{YBa}_2\text{Cu}_3\text{O}_7$ precipitates the composition of the melt is changed so that it at the end has a composition like the eutectic e1, where the lowest melting point in the Cu-rich part of the phase diagram is found. The cooling should be slow from a temperature above the

**Figure 4:** A section through the Y-Ba-Cu-O phase diagram in air ($P_{O_2}=0.21$ atm). L is the liquid phase

**Fig. 5:** The phase diagram for $\text{BaO-CuO}$ in an Ar-$O_2$ mixture, $P_{O_2}=0.21$ atm.
peritectic for YBa$_2$Cu$_3$O$_7$ (1015°C) and down to a temperature somewhat above the eutectic (890°C). Further cooling will result in a mixture of YBa$_2$Cu$_3$O$_7$, BaCuO$_2$ og CuO.

No matter which synthesis method is used, the last step is a heat treatment of the YBa$_2$Cu$_3$O$_7$ samples in an oxygen rich atmosphere in order to achieve the desired oxygen stoichiometry. In this step the crystals made by the flux method will crack due to the strain from varying oxygen content (and thereby variations in the unit cell dimensions) through the crystal.

**The exercise**

Starting materials:

- ✓ Y$_2$O$_3$ FW : 225,808 g/mol
- ✓ BaCO$_3$ FW : 197,35 g/mol
- ✓ CuO FW : 79,54 g/mol
- ✓ CuCO$_3$·Cu(OH)$_2$·0,5 H$_2$O FW : 230,11 g/mol
- ✓ Citric acid monohydrate

The starting materials may adsorb water and/or CO$_2$ from the atmosphere. This may lead to wrong assumption of the formula weight per cation compared to that given by the producer. All reagents are controlled regarding water and carbonate content, and the empirical formula weights given here are corrected (if needed) for the composition of the reagents.

**Flux growth:**

**Procedure:**

Weigh Y$_2$O$_3$, CuO og BaCO$_3$ so that the total composition of the sample is: 6.25 mol % Y, 29.77 mol % Ba og 63.98 mol-% Cu. (BaCO$_3$ decomposes to BaO by heating.) Start by weighing carefully ca. 1 g Y$_2$O$_3$. Your calculations must be approved before mixing the three ingredients in a mortar and press them into pellets.

See Figure 6 for use of the pellet press. Do not use excessive force when pressing- it should be possible to remove the pellet from the equipment without destroying it. The press equipment is cleaned using 96% ethanol. The piston should be moved up and down in the cylinder in order to remove traces of solids from the walls.

**NB! DO NOT USE WATER OR ACID TO CLEAN THE PRESS EQUIPMENT. KEEP THE EQUIPMENT CLEAR OF PLACES WHERE HCl IS USED**
Load the pellets in an alumina crucible so that the samples have the least possible contact with the walls of the crucible. Put some pellets close in the bottom of the crucible, then build a tower of pellets on top, so that the upper pellets are not in contact with the walls of the crucible. The crucible is placed on a MgO plate, which is situated in a quartz glass boat and placed in the furnace. Put an extra quartz boat into the furnace at the same time. Program the furnace with the temperature profile you have been provided with by the laboratory responsible (see the manual for the temperature regulator). Different heating profiles may be tried during the course, and the results should be compared at the end of the laboratory course in order to determine the best synthesis conditions with respect to cooling rate and end temperature.

**Fig. 7:** Temperature profile for flux growth of YBa$_2$Cu$_3$O$_7$.

When the temperature has reached $Y^\circ$C the flux is poured quickly into the extra quartz boat, see Figure 8. In order to get rid of the flux residues, the crucible is place upside-down on the MgO plate and the furnace is closed.

**DURING THESE OPERATIONS YOU MUST USE THE WELDING MASK AND HEAT RESISTANT GLOVES. POURING OF THE FLUX MUST ONLY BE DONE WITH THE LABORATORY RESPONSIBLE PRESENT.**

Because the pouring of the flux must be done quickly, you should practice using the tongs and protection gear at room temperature before pouring the flux from the actual sample in the furnace.
The next day the crucible is removed from the furnace. The crucible is put right-side-up and placed on a heat resistant plate to cool. The crystals are loosened from the walls of the crucible. Look at them in the microscope, estimate the size, and pick some for later heat treatment in the furnace with oxygen stream together with the samples prepared by the citrate method.

It is a good idea to start preparing the citrate method samples while the flux-sample is in the furnace.

Fig. 8: Pouring of the flux.

**The citrate method:**

**Procedure:**

Weigh approximately 25g citric acid in a 150 ml beaker. Put in the bar magnet for a magnetic stirrer. Weigh carefully ca. 0.5 g Y₂O₃ and put it into the beaker. Citric acid and yttrium oxide is stirred at room temperature with a watch glass as lid in order to avoid dust. In the mean time stoichiometric amounts of BaCO₃ and CuCO₃ • Cu(OH)₂ • 0.5 H₂O (ca. 1.8 and 1.5g, respectively) is weighed.

The citric acid (with Y₂O₃) is melted quickly under stirring on a hot plate which in advance has been turned on at maximum temperature. It may be useful to introduce a very small amount (a few drops) of distilled water in order to avoid local decomposition of the citric acid. Because Y₂O₃, due to kinetics, is difficult to dissolve in dilute solutions of citric acid it is important not to add too much water at this point. When the acid is completely melted the beaker is put on a hot plate which has been set at 180C in order to complete dissolution of
Y$_2$O$_3$. It is necessary to this low temperature in order to avoid too early decomposition of the citric acid. (Decomposition is detected as a yellow colouring of the melt. When Y$_2$O$_3$ is completely dissolved, BaCO$_3$ is added gradually. It is important to add only a small amount at a time in order to limit the evolution of CO$_2$ gas. It is necessary to avoid spill over due to froth formation in the beaker. Use distilled water to rinse the last of the powder from the container used for weighing into the beaker, so that everything is introduced into the mixture. (Contrary to Y$_2$O$_3$, BaCO$_3$ and CuCO$_3$ • Cu(OH)$_2$ • 0.5 H$_2$O are easily dissolved in dilute citric acid.)

The basic copper carbonate is added little by little. Again froth is formed due to carbon dioxide formation. Use distilled water to add the last of the powder into the beaker. The solution is then diluted with distilled water to a total volume of ca. 50 ml. Depending on the degree of dilution the liquid will vary strongly in viscosity (from black currant syrup to honey like). In some cases a "mother of pearl"-like appearance is obtained. This is probably caused by polymerization and does usually not influence the process. The xerogel will be amorphous anyway.

When all starting compounds are dissolved, the solution is transferred to a porcelain bowl. This is covered by aluminium foil and put into a laboratory furnace at 180°C to decompose overnight. The next day the sample is removed from the furnace. It should now be a brown porous crust. The crust is easily crushed using a pistil and the bowl is put into a muffle furnace at 450°C for two hours or until the mixture no longer glows when the door to the furnace is opened. In this step most of the organic part is burned off.

After cooling the sample is pressed into one or several pellets as described in the flux-synthesis part. The pellet(s) are put into an alumina boat. The porcelain bowl is first washed with water and then put into a 1:1 solution of HCl for 15 minutes in order to dissolve the residues. Finally it is washed with water.

**Annealing and sintering:**

The alumina boat containing the pellets is placed in a furnace, heated to 900°C and left at that temperature over night. Turn off the furnace and let the boat stand in the furnace until it is no longer red-hot before taking out the alumina boat. Cool the samples in air. Crush each pellet in a mortar (cover with a plastic bag to minimize loss of the product). After the preliminary crushing the samples should be transferred into the ball mill containers. The balls are introduced and acetone is added up to ca 1 cm below the rim of the container. Ball mill the samples for 5 minutes.
When using the ball mill both containers must be placed in the mill and the weight must be approximately equal. This means that two samples must be run simultaneously. It is possible to run one of the containers only with balls and acetone, but this should be avoided as it is wearing out on the balls and container.

When the ball milling is completed the containers are removed from the mill, the lids are removed and the containers are placed in a fume hood until the acetone has evaporated. When the acetone has evaporated the samples are pressed into pellets and placed in a furnace with oxygen flow for the final heat treatment. Remember to include the crystals from the flux growth in this treatment.

Procedure for using the furnace:

1. Put in the sample.
2. Close the ends of the alumina tubes with the end-plugs.
3. Turn on the cooling water.
4. Program the temperature regulator with the following temperature profile:
   (Refer to the manual for the unit)

   ![Temperature Profile Diagram]

5. Set the oxygen flow to 2 l/h. refer to the calibration curve for the flow meter. Directions for using the reduction valve is posted at the oxygen cylinder.
6. Start the temperature program.

After this heat treatment the samples are finished and ready for testing with respect to phase purity, crystal structure, oxygen content, superconducting properties etc. results from characterization of previous samples will be distributed.

The alumina boat is put into 1:1 HCl : water for cleaning. It is then rinsed with water and dried in a laboratory furnace at 180C.
Questions for the report:

Characterization:

On one of the lab benches there are a Dewar with liquid nitrogen and a magnet. Test the superconductivity of your samples by putting the magnet on top of the cold sample and see if any levitation is observed.

As mentioned earlier, you should compare the size of your flux grown crystals with other made at slightly different synthesis conditions, and attempt to find the most suitable conditions for flux growth of large crystals. Remember to give the approximate size of the crystals in the report.

Comment on the differences between citrate and the flux growth method.

Comment:

When preparing single crystals of YBa$_2$Cu$_3$O$_7$ by flux growth it is observed that the unit cell parameters are not identical to those for samples prepared using different methods. This is especially true for samples prepared in alumina crucibles and is caused by attack of the flux on the crucible. This results in Al$^{3+}$ being released into the melt, and these ions are incorporated in YBa$_2$Cu$_3$O$_7$. Research has shown aluminium contents up to YBa$_2$Cu$_{2.874(8)}$Al$_{0.10(1)}$O$_{6.31}$. (The low oxygen content is obtained because the sample was analyzed before the final heat treatment in oxygen.)

This illustrates one of the problems with flux growth. At the high temperatures the flux is chemically aggressive and it is difficult to find suitable materials for the crucible. Furthermore, there is a larger tendency to incorporate contaminants into the single crystals.
Synthesis of BaTiO₃ by sol-gel and hydrothermal methods

Introduction:

In the past decades, the extended applications of functional oxides in advanced technologies have increased the demand of the purity and homogeneity of the compound. Hetero-metallic oxides have traditionally been synthesized through ceramic method that often requires high temperatures, resulting in-homogeneities on atomic scale. The most common sol-gel method, using citric acid, may avoid this problem, but can give impurities like metal carbonate phases. In nano-technological applications, synthesis of materials as thin films is a field of interest (100-500 nm for ferro electric capacitor). Typical methods to synthesize thin film in this range are PLD (pulsed laser deposition) and CSD (chemical solution deposition). In CSD, a solution (sol) of metal-organic compounds at the desired stoichiometric ratio is applied. CSD is quite common due to easy preparation of the solution and only simple equipments are needed. In practical applications, low crystallizing temperature is preferable to avoid further undesirable reaction with the environment. The crystallization temperature may be lowered when the diffusion path between the atoms is reduced. Hence, homogeneous mixture of the atoms at nano-scale is preferred. Multi-metallic alkoxides are molecular species which contain two or more metal atoms. The metal atoms are already homogeneously mixed at nano-scale in the molecular species and the homogeneity will be maintained upon decomposition of the organic part. Typical crystallization occurs between 450 °C and 550 °C. Thus, metal-alkoxides are attractive precursor to prepare metal-oxides.

Ferroelectricity was first observed with BaTiO₃ ($T_C = 130$ °C). The material has a perovskite type structure. Below $T_C$, the structure is tetragonal with a dipole moment along the c-axis. Above the Curie temperature, the structure transforms to a cubic symmetry with zero dipole moment. The material may transforms to lower symmetry systems below room temperature. In the tetragonal BaTiO₃, the potential of Ti⁴⁺ along the c-axis can be reversed by an electric field towards the polarizing direct ion and defeat the barrier, results a reversible polarization. BaTiO₃ is an important dielectric material and is used to produce capacitors and PTC resistance (positive temperature coefficient).

Only nano-particles are formed during the crystallization from the alkoxide gel. Hence, the phase transition through the Curie temperature (130 °C) upon cooling will not be energetically favourable. The formed product will therefore be meta-stable cubic. Heat treatment at 800-900 °C is required to observe trace of the tetragonal phase. To obtain 100 % conversion, the sample needs to be treated above 1000 °C. Since the technologic important phase is the tetragonal modification (having ferro-electric properties), direct synthesis of BaTiO₃ at low temperature has received a lot of attention. The challenge is to form sufficient large crystals at low temperature that the phase transition at 130 °C occurs. Later on, BaTiO₃ has been successfully synthesized by hydrothermal method at low temperature.
Alkoxide:

It is desirable to operate with as low organic content as possible to avoid carbon-containing impurities. Small alloxides like metoxide and ethoxide are usually unstable or form insoluble complexes. A common applied alkoxide is isopropoxide. Titanium isopropoxide is commercial available. Here, we have to synthesize Barium isopropoxide, which is an oligomer expressed as $1/m[Ba(O\text{Pr})_2]_m$. This oligomer will react with Titanium isopropoxide and forms soluble and large heterometallic specie. Generally, larger complexes have higher solubility. Thus, dissolution of the oligomer indicates that a reaction occurs. Electropositive metal alkoxide can synthesize directly by mixing the metal and the alcohol.

$$Ba(s) + 2ROH(l) \rightarrow \frac{1}{m}[Ba(OR)_2]_m(s) + H_2(g) \quad \text{Eq. 1}$$

The rate of reaction increases with the acidity of the alcohol, less steric obstruction, the basisity of the metal and solubility of the formed product. The alkali metals react rapidly with lighter alcohols and give pure products. The earth alkali metals form complicate complexes and the less electropositive elements (like Mg) need a catalyst to obtain a reasonable rate of reaction. If the product is soluble, extensive cooling is needed. Barium is very electropositive and the reaction occurs even without a catalyst. However, Barium isopropoxide is insoluble which will slow down the rate of reaction. Rational rate may be obtained by mixing isopropanol and small Barium particles (0.2-0.5 mm) at ambient temperature. Note that Barium is extremely reactive towards hydroxyl containing compounds, especially water. Thus, Barium and the synthesized derivates must always be treated in inert atmosphere ($N_2$, Ar).

Caution:

This exercise includes treatment of air sensitive compounds. Hence, synthesis steps involving air sensitive compounds must perform under absence of air ($O_2$, $H_2O$). Vacuum line is often used to do air sensitive reactions. An introduction of the vacuum line will be given during the exercise. Everything inside the line should be regarded as air sensitive. Our vacuum line can switch between vacuum and inert atmosphere ($N_2$). The most important thing is to avoid air leakage into the vacuum line. You should always make sure that air has no possibility to diffuse into the line (upon connecting flasks or other equipments and adding chemicals in presence of air sensitive compounds). Remember that the boiling point of a solvent depends on the pressure around the solvent. If the pressure around the solvent is reduced (upon evacuation), the boiling point is also reduced. Thus, close the valve of the flask containing solvent before you start to evacuate the vacuum line, otherwise the solvent will evaporate. You can also freeze the solvent with liquid Nitrogen and evacuate the solvent flask if necessary. In addition, the connectors should be secured since they may fall apart at higher pressures (of the inert gas).
**Solvent treatment:**

Synthesis involving moisture sensitive compounds the applied solvents need to be dried before use. Most of the non-polar organic solvent, like pentane, heksane, benzene, THF and diethyl ether can be dried by reflux for an hour with 5×5 mm Sodium (since they are not reacting directly with Sodium). To remove the last water content (for extremely sensitive compounds), 10 g benzophenone per litre solvent can be added and set to reflux until the solution turns to be purple (due to presence of a radical). The solvent can then be distilled and stores in presence of Sodium.

Alcohols undergo a reaction with Sodium and need to be dried with CaH₂ or a corresponding metal alkoxide (for example Mg). Reflux the solution for 12 hours, then distil the solvent and store the solvent in presence of molecule sieves.

The dried solvent should be stored in inert atmosphere. Upon solvent transfer, a continuous stream of an inert gas should be applied (to avoid diffusion of air). Evacuate the syringe with an inert gas and take the needed amount.

The solvents will be dried and are ready to use in the laboratory day.

**The vacuum line:**

The vacuum line is illustrated in Figure 1. The upper part is connected to Nitrogen flow and the lower part is connected to a vacuum pump. The sample can be connected to the exits. Valve 1 is a port separating the environment and the vacuum pump. Valve 2 is the main valve of vacuum line which connect the line and the pump. Hence, valve 3, 5 and 7 can make vacuum of the connected sample while valve 4, 6 and 8 can expose the sample to N₂. Note that the vacuum valve and the N₂ valve at the same exit should not be open at the same time.

![Figure 1. Illustration of the vacuum line.](image-url)
The cooling trap between the pump and the line will protect the pump for exposure of organic compounds and water. This trap should be filled with liquid Nitrogen as long as the line is in use, especially when volatile organic compounds are connected to the line. The vacuum line is equipped with two additional tubes from the left and the right exit, respectively. These tubes supplies Nitrogen gas and will be useful to transfer chemicals and accessories at inert condition. The left tube is connected to a syringe tip, herein called “gas in” (tip), and the right tube has just an opened end, denoted as “gas in” (open). In addition, there are two tubes (not a part of the vacuum line) present. Both tubes are connected to a gas washing flask and will be used to transfer the excess pressure out of a system. One of them has a syringe tip in the other end, herein named “gas out” (tip) and the other tube has the end open, herein called “gas out” (open).

**Prepare the vacuum line:**

Connect a condenser to the middle exit. Attach a T-shaped connection to the bottom of the condenser. Close the whole system (line, connections and condenser) by a stopper and a septum. Make sure that every connection is covered with grease and secured. Have all the valves closed and turn on the vacuum pump. Open valve 2 when the pump starts to get warm. Evacuate the vacuum line. The pressure in the line is displayed on the manometer. Check for leakage by closing valve 2. If the pressure starts to increase, then there is a leakage. Repair the leakage before continue. When the pressure is stable, fill the cooling trap with liquid Nitrogen and keep evacuating. Open the Nitrogen flask carefully. Valve 4, 6 and 8 should be closed. The gas should flow nice and gently through the gas washing flask. Keep flowing for a while to evacuate the air in this part of the line.

To shut down the pump, remove liquid Nitrogen from the trap. If a pale blue liquid is condensed, evacuate the liquid. The pale blue liquid is condensed Oxygen and may explode as the trap is getting warm. If the trap seems to be clear, close valve 2 and open valve 1 slowly to compensate the pressure in the line. Finally, turn off the pump.

**Synthesis of Barium isopropoxide oligomer:**

Metallic Barium is air sensitive and stores in the glovebox. The glovebox will be introduced by the supervisor. You should keep the inner door of the glovebox closed once you have transferred the elements into the glovebox to avoid leak if the main door is opened accidentally. Having air (O₂, H₂O) inside of the glovebox may destroy the compounds already stored in the glovebox. Here, Barium isopropoxide oligomer is synthesized according to Eq. 1. The synthesis performs at room temperature after mixing Barium and isopropanol together. Note that both
Barium and Barium isopropoxide are air sensitive. The whole process includes scaling, chemical transferring and stirring must perform at inert atmosphere. The reaction is exothermic and Hydrogen is formed as a product. Such condition may result an explosion if no further safety effort is applied. The heat of formation can be transferred to the environment by dilute the reaction mixture with a solvent (hexane in this case). Finally, the formed Hydrogen needs to be removed from the reaction chamber. Thus, a continuous inert gas flow through the reaction chamber should be applied.

Bring a dry and clean 250 mL schlenk flask, a tweezer, a stirring magnet and a septum into the glovebox. Transfer the stirring magnet and 0.5 g (note the exact weight) to the schlenk flask. Close the schlenk flask with a septum covered with grease and make sure that the valve of the flask is closed. Bring the schlenk flask out of the glovebox and add 20 ml dry hexane. Note that Barium is air sensitive. The solvent must be transferred at inert condition. A possible procedure is described below:

- Open valve 4 and valve 8, let Nitrogen flow through the pipes for a while.
- Try to insert “gas in” (tip) and “gas out” (tip) simultaneously through the septum and into the flask with dried hexane.
- Evacuate a syringe with N₂ in the hexane flask. Fill the syringe with N₂ from the schlenk flask and remove the gas outside of the flask. Repeat the procedure.
- Transfer 20 ml dry hexane (with an evacuated syringe) to the 250 ml schlenk flask with Barium. Inject the solution through the septum.

Connect the schlenk flask with Barium to the vacuum line. Remember that Barium is air sensitive. Exposing the element to air may destroy the synthesis. The connection must be performed at inert condition. The procedure is described below:

- Open valve 4, 6 and 8.
- Insert “gas in” (tip) and “gas out” (tip) simultaneously through the septum and into the 250 ml schlenk flask containing Barium and hexane. You should observe that gas in flowing through the gas washing flask.
- Open the valve of the 250 ml schlenk flask. The gas should now enter from “gas in” (tip) and exit through the side opening of the schlenk flask.
- Connect “gas in” (open) to the side opening of the 250 ml schlenk flask. At this moment, N₂ is entering from “gas in” (tip) and “gas in” (open) and exit through “gas out” (tip).
- Remove the septum from the 250 ml schlenk flask and close valve 4. The gas is now entered from “gas in” (open) through the side tube and flowing out of the opening. Diffusion of air towards the flowing direction can be ignored. However, the connection should be carried out as fast as possible.
- Remove the stopper from the T-shaped connection. N₂ gas should flow out from the condenser connected to the vacuum line.
- Connect the 250 ml schlenk flask to the system (T-shaped connection) as fast as possible. Secure the connection.
- Close the valve of the 250 ml schlenk flask, remove “gas in” (open) and close valve 8. N₂ in the vacuum line will fill the flask and leave the system through the gas washing flask.

Calculate the amount of isopropanol needed. The density of isopropanol is 0.785 g/ml. Add an excess amount of isopropanol to the Barium/hexane mixture with a syringe to ensure that the Barium is consumed. The procedure is described above. Inject through the septum of the T-shaped device.

Start the synthesis by placing a magnetic stirrer under the schlenk flask and start stirring. Barium will dissolve afterwards and H₂ is formed. The product Ba-O'Pr oligomer is unsoluble. The reaction has occurred if the solution becomes unclear. Keep stirring until Barium has reacted (usually takes a night).

**Synthesis of [BaTi(OH)(O⁻Pr)₅(Pr⁺OH)₃]₂:**

The heterometallic alkoxide can usually be synthesized by mixing the respective monometallic alkoxide together. Our product, [BaTi(OH)(O⁻Pr)₅(Pr⁺OH)₃]₂, with a structural formula is given in Figure 2, can be synthesized by mixing the respective metal alkoxide together. Note that the product is a large complex with 1:1 ratio of Barium and Titanium.

![Figure 2](image_url)  
*Figure 2. Structural formula of [BaTi(OH)(O⁻Pr)₅(Pr⁺OH)₃]₂.*

Write the reaction equation of formation of [BaTi(OH)(O⁻Pr)₅(Pr⁺OH)₃]₂. An additional reactant is required to balance the equation. What reactant is needed? Calculate the amount of Titanium needed to obtain a stoichiometric ratio of Ba:Ti = 1:0.98. The questions should be answered and included in the report.

A small flask containing degassed Ti(IV) isopropoxide is already prepared by the supervisor. Add 5 ml dry isopropanol to the small flask and transfer the content to the reaction mixture at inert condition. A possible procedure is given below:
- Make sure that valve 4, 6 and 8 is open. Attach “gas out” (open) to the side tube of the schlenk flask and open the valve.
- Insert a Teflon tube through the septum at the T-shaped connection. You should expect some of the gas is flowing out of the Teflon tube.
- Insert “gas in” (tip) and “gas out” (tip) simultaneously through the septum of the flask containing Ti(O\text{Pr})_4 and isopropanol.
- Insert the other end of the Teflon tube through the septum of the flask containing Ti(O\text{Pr})_4 and isopropanol and remove “gas out” (tip) from the septum.
- Close valve 6. The gas is now flowing from “gas in” (tip), through the small flask, Teflon tube, 250 ml schlenk flask and “gas out” (open).
- Lower the Teflon tube to the bottom of the flask containing Ti(O\text{Pr})_4 and isopropanol. The solution will be pressed through the Teflon tube to the 250 ml schlenk flask.
- When the transfer is finished, open valve 6 again, remove the Teflon tube, close the valve of 250 ml schlenk flask and remove “gas out” (open).

Start the synthesis by heating the flask to reflux for 3 hours. Remember to apply cooling. Note that Barium isopropoxide oligomer slowly dissolves. Since we have added less Titanium (Ba:Ti = 1:0.98) to react with Barium isopropoxide oligomer, the solution will remain unclear. The dissolved species should be \([\text{BaTi(OH)}(\text{OPr})_3(\text{Pr}^{\text{t}}\text{OH})_3]_2\), isopropanol and hexane. These species can be isolated by filtration and the solution should contain perfect Barium to Titanium ratio. The \([\text{BaTi(OH)}(\text{OPr})_3(\text{Pr}^{\text{t}}\text{OH})_3]_2\) complex is still air sensitive. The filtration must be performed at inert condition. A possible procedure is suggested:

- Put a long syringe needle through a septum from the bottom.
- Cover the top of the needle with filter paper. Secure the filter paper with Teflon tape.
- Put a Teflon tube through the tip side of the needle.
- Open valve 8 and the valve on the 250 ml schlenk flask. The gas will escape from the side tube of the schlenk flask.
- Connect “gas in” (open) to the side tube of the 250 ml schlenk flask. The gas is now entering the system from “gas in” (open) and the vacuum line and exit through the gas washing flask connected to the vacuum line.
- Close valve 6 and remove the 250 ml schlenk flask immediately from the vacuum line. Close the schlenk flask with the modified septum (with syringe needle). It should still be inert atmosphere in the 250 ml schlenk flask. The gas is entering the flask from “gas in” (open) and exit through the Teflon tube attached to the syringe needle.
- Put the other side of the Teflon tube into a new 100 ml schlenk flask through a septum. Keep the valve on this flask closed.
- Insert “gas out” (tip) immediately through the septum of the 100 ml schlenk flask. The gas is now flowing from “gas in” (open), through the filter paper, syringe needle, Teflon tube to the 100 ml schlenk flask and out via “gas out” (tip). Keep the continuous gas flow for 15
minutes. This procedure is a degassing procedure to create an inert atmosphere in the new 100 ml schlenk flask.
- After 15 minutes, press the needle down to the solution in the 250 ml schlenk flask. The pressure will press the liquid through the filter paper and over to the 100 ml schlenk flask.
- After the filtration, close the 100 ml schlenk flask on a safety way without letting air inside.

**Hydrolysis:**

Hydrolysis of the alkoxide results formation of a gel. During the hydrolysis, an extended network of Oxygen bridges is formed. Hydrolysis of alkoxide occurs in reaction with water.

\[
M(OR)_x + H_2O \rightarrow M(OR)_{x-1}(OH) + ROH
\]

Eq. 2

Simultaneously, a condensation process happens:

\[
2 M(OR)_{x-1}(OH) \rightarrow (RO)_{x-1}M - O - M(OR)_{x-1} + H_2O
\]

Eq. 3

The degree of hydrolysis is defined as followed:

\[
h = \frac{[H_2O]}{[M(OR)_x]}
\]

Eq. 4

The transformation from sol (solid on liquid) to gel is complicated. However, by adjusting parameter like temperature, concentration, rate of reaction and additional reactant (like coordinating solvents), the physical properties of the gel can be controlled. The reaction can be catalysed at acidic or basic environment. Acid catalysed hydrolysis often results formation of linear polymer with few branches. Such structure is suitable for fibre production. Using a base as catalyst often gives a random polymerization in different direction, resulting clusters. The absence of a network structure in base catalysed hydrolysis may complicate the gel formation.

By removing the solvent from the gel, the remaining xerogel consists of nano particles with high reactivity. The xerogel can be sintered to high density material at relative low temperature. Using other methods, the synthesis requires higher temperature (to make the same product with same density). It has been evident that the melting point of a material (as xerogel) is reduced compare to the bulk material, basically due to the high surface area of the nano particles.

Note that if \( h \) exceeds 2 (refer to Eq. 4), the gel may precipitate from the solution.

We are going to use a dropping funnel to add water drop wise to the solution containing BaTi-complex. Remove the glass pieces from the vacuum line (middle exit), connect the T-shaped
device and the funnel to the vacuum line. Close the remaining exit of the T-shaped connection with a septum and the dropping funnel with a stopper. Evacuate this area and refill with N₂. Connect the schlenk flask containing BaTi-complex to the vacuum line at inert condition. We are also going to catalyze the reaction with 100% acetic acid. Calculate the amount of water and acetic acid needed to obtain $h = 0.5$ and $[H^+] / [BaTi] = 0.05$. Transfer the calculated amount of water and acetic acid to a clean 100 ml schlenk flask. Degas the flask for 15 minutes (use the syringe needles) and then add 25 ml dry isopropanol (use a syringe). Transfer the content to the dropping funnel at inert condition. Remember to close the valve of the funnel. The solvent can transfer like that:

- Connect “gas out” (open) to the side tube of the flask with BaTi-complex and open the valve.
- Insert a Teflon tube through the septum. Since valve 6 should be open, N₂ will flow out.
- Remove “gas out” (tip) and insert immediately the other end of the Teflon tube into the flask containing water/acetic acid/isopropanol.
- Close valve 6. The gas is now coming from “gas in” (tip) and passing a 100 ml schlenk flask with water/acetic acid/isopropanol, a Teflon tube, the dropping funnel, a 100 ml schlenk flask with BaTi-complex and “gas out” (open).
- Press the Teflon tube down to the solution. The liquid will be pressed through the Teflon tube by the pressure to the dropping funnel.
- When the water/acetic acid/isopropanol solution has been transferred to the funnel, open valve 6 and remove the Teflon tube from the T-shaped connection.
- Start the stirring and add the content in the dropping funnel drop wise for gel formation. 1 drop per second is preferable.

After the hydrolysis, transfer the content to a beaker and remove the solvent by heating at 40-50 °C. The compound is now hydrolyzed and can be exposed to air. The resulted xerogel should be divided and crystallize at 500 °C and 800 °C, respectively for one hour. Determine the modification of the product by powder X-ray diffraction.

**Hydrothermal synthesis**

**Introduction:**

Hydrothermal synthesis means that the reactants are mixing with water in an autoclave which is sealed and heated to a temperature above 100 °C (the boiling point of the applied solvent at 1 bar). The pressure inside the autoclave may vary from 1-200 bar, depends on the reactants and the applied temperature. In hydrothermal conditions, the solubility of the compounds will normally increase. The nature of water undergoes changes in this condition, for example decrease in the viscosity, results higher mobility of the ions.
Hydrothermal synthesis performs at relative low temperatures. At such conditions, certain compounds which usually not crystallize at higher temperatures may be formed (for example compounds containing OH$^-$ groups or water confined in the crystal structure). High temperature syntheses usually result thermodynamically stable phases at standard conditions. Actually, it is more than temperature that decides whether the formed product is thermodynamically stable or not. Adjusting other parameters like pressure, concentration and temperature can result a specific product distribution and its particle size. In fact, there is no general model to describe the crystallization. Thus, the obtained results (formed phases, particle size) are based on empirical experiments and are depend on your operating system. Organic solvents may be applied as well, denoted as solvothermal synthesis. Many inorganic hybrid metal-organic compounds are synthesized under solvothermal conditions. Lots of compounds in the nature are formed through hydrothermal conditions, for example quarts and zeolites.

Synthesis of inorganic compounds can be obtained by mixing stoichiometric quantities together. Both insoluble solids (at standard conditions) and soluble salts can be used as reactant. Note that stable ions (both cation and anion like Na$^+$, K$^+$, protonated amines, F$^-$, Cl$^-$, Br$^-$, OH$^-$, nitrates) may be incorporated in the final structure if they are used as reactant. The mixture must be sealed in an autoclave before heating. Up to 250 °C, a Teflon-lined steel autoclave can be applied. Another common design is gold-lined autoclaves which can resist up to 500 °C assume that no reaction between the gold and the mixture occurs.

**Figure 1:** Autoclave with a Teflon lining which may be used up to 250 °C$^2$.

The degree of filling affects the pressure inside of the autoclave. Figure X shows a graphic presentation of how the degree of filling affects the pressure at a given temperature. The situation is crucial at high degree of filling, due to the expansion of the solvent at higher temperatures.
Figur 2: The pressure in a closed container as a function of temperature and degree of filling².

Water expands a lot upon heating. Moreover, the vapour pressure of water increase exponentially with respect to temperature, as illustrated in figure X. Hence, the autoclave may explode if the degree of filling is too high.

Figur 3: Water vapour pressure as a function of temperature.

The laboratory work:

Performing hydrothermal syntheses are simple compare to other methods. The whole synthesis consists of one single step. Hopefully, the desired product forms after the synthesis. Previous research found that by using Ba(OH)₂ as a reactant to synthesize BaTiO₃ results always the metastable cubic phase. The reason is the particle size is too small. The reported solution is to use BaCl₂ as reactant since Cl⁻ accelerates the crystal grows. Sufficient large crystals are crucial to have the phase transformation at 130 °C.
Dissolve 0.01 mol NaOH in 10 mL distilled water in a Teflon vessel. Add 0.025 mol BaCl$_2$ and TiO$_2$ to the solution. Then seal the autoclave and leave it in an oven at 240 °C for a week. Isolate the product by filtration and remove the excess base by washing with distilled water. Dry the solid at 80 °C and control the modification by powder XRD.

**Questions:**

- We used reduced stoichiometric amount of Ti-isopropoxide to make a perfect stoichiometry of our product. Can you imagine how we can obtain a perfect stoichiometry by using non-stoichiometric amount of the reactants?
- Discuss the advantage and disadvantage to do synthesis via alkoxide instead of citric acid?
- For what purposes will metal alkoxide be preferred as a precursor?
- Mention some acids or bases you can use to catalyze the hydrolysis reaction and what are the criteria?
- Explain the reason that you obtain different modification of BaTiO$_3$?
7: GeO$_2$ crystals prepared by a chemical transport reaction

In this exercise single crystals will be prepared using a chemical transport reaction. GeO$_2$ is chosen as an example because transport of this compound is well documented from earlier studies. Thermodynamic data for the system are known and the transport rates at various conditions have been measured and compared with theoretical calculations. In this exercise these experiments will be repeated at a basic level in order to demonstrate kinetic effects at various conditions.

The material

GeO$_2$ have two polymorphs. At low temperature a tetragonal rutile type structure (Fig. 1a) is the thermodynamically stable modification, while a hexagonal cristobalite type structure (Fig. 1b) is stable at temperatures above 1033ºC. GeO$_2$ melts at 1116ºC. There are significant differences in the physical properties of the two modifications, e.g. large differences in the density and hardness. The rutile modification has a density of 6.24 g/cm$^3$ and a hardness measures as VHN of ca. 1500 i.e. harder than corundum (2100). In contrast, the cristobalite polymorph shows values of 4.23 g/cm$^3$ and VHN 300-400. (Properties at 25ºC)

Fig. 1: Modifications of GeO$_2$. a) Rutile-type structure. b) Cristobalite-type structure; • Ge, O  O
The Method

A chemical transport reaction may in principle be written as:

\[ i \ A_{(s)} + k \ B_{(g)} \Leftrightarrow j \ C_{(g)} \]

Here A is the compound which is transported; B is the transport species which is added. C is the gaseous intermediate species which is critical for transporting compound A, and which includes the transport species, B. The reaction is most often more complicated than described by this equation. Other gaseous intermediate species than C often exist and these must also be transported in the system in order to transport the A compound.

By tuning the temperatures \( T_1 \) and \( T_2 \) in two zones in the reaction tube, A reacts to C in one zone while the reaction is reversed in the other zone, releasing A. Usually the purpose of this type of reaction is either to purify a material or to grow high quality single crystals, for instance for single crystal structural studies.

The usual convention is to write the equation so the the solid which is transported is on the left side of the equation. Furthermore, it is conventional to define \( T_1 < T_2 \). (!!Note!! In the book used for the course: “Synthesis of Inorganic Materials” by Ulrich Schubert and Nicola Hüsing, the definition is that transport occurs from \( T_1 \) to \( T_2 \)) For an endothermic reaction, \( \Delta H > 0 \), A will be transported from the highest to the lowest temperature zone, while for an exothermic reaction, \( \Delta H < 0 \), will have a transport from the cold to the hot zone.

Usually the transport is done in a cylindrical ampoule, Fig. 2.

---

**Fig. 2:** Chemical transport in a cylindrical ampoule. \( T_1 < T_2, \Delta H > 0 \).
The rate of gas diffusion is often the rate limiting step of a transport reaction. When this is the case the amount of transported species A (in our case GeO$_2$) can be calculated as:

$$n_A = \frac{i}{j} \cdot \frac{Dqt}{sRT} \cdot \Delta P_c$$

(2)

$n_A =$ total amount mol A transported  
i = coefficient in the reaction equation  
j = coefficient in the reaction equation  
$D =$ diffusion coefficient ($cm^2s^{-1}$) for gas mixture B+C  
$q =$ inner cross section (area) of the tube  
t = time duration (in seconds)  
$s =$ length of the tube (reaction chamber)  
$R =$ gas constant  
$T =$ temperature in the tube  
$\Delta P_c =$ difference between the equilibrium pressure of C at the end of the tube

By approximations the previous equation may be simplified to:

$$n_A = \frac{i}{j} \cdot \frac{\Delta P}{\Sigma P} \cdot \frac{T^{0.8}qt'}{s} \cdot 1.8 \cdot 10^{-4}$$

(2)

$\Sigma P =$ total pressure in the system (atm)  
$T =$ average temperature in the tube  
t' = experimental duration (in hours)

The other parameters are as defined above.

This approximation is valid for closed systems with a fixed amount of molecules according to the reaction equation. It is not valid if one of the gaseous species is hydrogen.

It is not always the diffusion in the gas phase which is the rate limiting step for the transport. The rate of reaction between gas and solid may decrease the transport rate, while thermal convection may lead to an increase. Convection occurs because the densities of gases at low and high temperature are different. The cold gas will sink while the hot gas will rise, resulting in circulation in the ampoule.

Which parameter limits the transport rate will, amongst other, depend on the total pressure, see Fig. 3. Here the transport efficiency, Q, is defined as:

$$Q = \frac{n_A(measured)}{n_A( theoretical)}$$

where $n_A$ (theoretical) is calculated from the equation above, assuming diffusion limited transport.
The relation between Q and total pressure may be illustrated as follows:

![Figure 3: Transport efficiency, Q, as a function of total pressure. In area I, the rate determinate step is the heterogeneous reaction between the gas and A. In area II, the rate determinate step is diffusion in the tube. Area III is an effect of thermal convection and diffusion.](image)

Transport of GeO₂ is carried out by the reaction:

\[
\text{GeO}_2(s) + 2 \text{Cl}_2(g) \leftrightarrow \text{GeCl}_4(g) + \text{O}_2(g)
\]

As seen, GeO₂ is transported as GeCl₄ and O₂. GeCl₄ is similar to C in the general reaction equation. The number of gaseous species are not changed in the reaction and H₂(g) is not present. Therefore the transport may be calculated using equation (2) above.

In the original work, thermodynamic evaluations were used in order to choose the reaction conditions. The hexagonal high temperature phase may, due to kinetic effects, be present also below 1033°C. The reaction was therefore evaluated using both the tetragonal and the hexagonal polymorph as the starting material. In both cases the reaction is endothermic, and transport occurs from T₂ to T₁ (High to low temperature). Calculations showed that the fastest transport should occur when starting with the metastable cristobalite modification, and deposit the modification having the rutile structure.
Furthermore, the possibility of the presence of other gaseous species, such as GeCl$_2$, GeOCl$_2$ and Ge$_2$OCl$_6$ was investigated. From the equilibrium constants it was found that only GeCl$_4$, O$_2$ and Cl$_2$ have any appreciable contributions to the total pressure and the transport in the system in the temperature range 600 – 1150K. The equilibrium partial pressures of these species are shown in Figure 4.

Following the theoretical calculations the transport reaction was performed using a number of different experimental conditions. In all experiments, $T_1$ was chosen so that the rutile (tetragonal) modification of GeO$_2$ was deposited. The experiments showed the transport (as expected) was fastest when the hexagonal phase, rather than the tetragonal, was used as the starting material. The tetragonal phase reacted very slowly with Cl$_2$, which indicates that the reaction is kinetically restricted by surface reaction. Furthermore, the temperature for the phase transition was lower in Cl$_2$ than in air. Thus, it is possible to start with, and obtain, the hexagonal cristobalite polymorph even at temperatures, $T_2$, below 1033ºC. If $T_2$ is chosen in the stability region for the rutile structure, the phase transition is so slow that it will not interfere with the reaction with Cl$_2$. In addition, newly formed tetragonal GeO$_2$ will be as a fine powder, resulting in increased reactivity. All this points toward using the cristobalite modification as the starting material independent of the chosen temperature. In all cases the transport efficiency, $Q$, of the order of $10^{-2}$, which indicates that the heterogeneous reaction was rate limiting, see Fig. 3.

In order to compensate for this, small amounts of various chlorides and oxides were added. It was shown that especially NaCl, KCl and MnO resulted in an increased transport rate in the system. The additives were melted at the reaction conditions, but the vapour pressures are low, so that one need not take new gaseous species into account. By adding NaCl, KCl or MnO the crystal growth at $T_1$ was changed so that long needle-like crystals were obtained in stead of broad columns. This may be due to formation of a liquid layer of the added salt covering the nuclei, which somehow increase the deposition rate. The effect was especially significant for MnO with $Q$ approaching 1. This may be caused by MnO being more efficient as promoter than NaCl or KCl, or it could be due
to an increased amount of MnO compared to NaCl and KCl. (It is not possible to add much NaCl or KCl due to reactions with the quartz glass ampoule.)

Different reaction conditions result in various colours of the obtained crystals. A satisfactory explanation of this has not been found.

The exercise

In this exercise we will perform three parallel transport experiments, one without added transport promoting additives, one with KCl and one with MnO.

Starting materials and compounds:
- ✓ GeO₂ (hexagonal modification)
- ✓ Cl₂
- ✓ KCl mixed with GeO₂
- ✓ MnO mixed with GeO₂

Procedure:
Weigh the GeO₂ mixtures so that you get 0.2 mg KCl in one ampoule and 0.19 mg MnO in another. This gives the same amount (mol) promoter in the two ampoules, making a direct comparison of the efficiencies of the two promoters possible. Add pure GeO₂ to a total of 1 g in each ampoule. A third ampoule is filled with 1 g GeO₂ without promoter.

Let the laboratory responsible narrow down a section of each ampoule, giving a ampoule length of 10 to 12 cm. Put the ampoules successive into the equipment for drying and filling with Cl₂, see Fig. 5.

NB! Remember that the vacuum lines are placed in a fume hood because the window will provide some protection from explosions or implosions. In addition you are working with Cl₂(g), which is poisonous. Always pull down the window completely when you are not operating the valves etc. on the vacuum line.
Fig. 5: The vacuum line for drying quartz glass ampoules and subsequent filling of \( \text{Cl}_2(g) \). NB: Today a Pirani head is used in stead of the mercury column to check the vacuum. In addition the reduction valve with a possibility of flushing with nitrogen has been exchanged by a needle valve.

First heat the ampoule to 1000ºC under vacuum in order to remove water from the quartz glass:

1. Place the thermocouple in the movable furnace and set the temperature regulator at 1000ºC.
2. Connect the sample quartz tube to vacuum line
3. Leave stopcock 1 open while all other stopcocks are closed.
4. Turn on the Pirani head and the pump. Close stopcock 1 and open stopcock 2. Then open stopcock 3. Be careful so to avoid turbulence in the Pirani head, which may ruin the filament.
5. Open stopcocks 4 and 5 and read off the pressure. Make sure that the vacuum is preserved when closing valve 2. Wait for 1 minute and monitor the pressure. If the low pressure is preserved you may carefully re-open stopcock 2.
6. Pour liquid nitrogen into the cold trap.
7. Move the furnace so that the ampoule and sample is heated. The temperature should be 950 – 1050ºC. Leave the ampoule to dehydrate for ca. ten minutes. Then move the furnace away from the ampoule. (NOTE: After dehydrating the last ampoule remember to turn off and disconnect the furnace.)

Prepare the chlorine part of the vacuum line by filling the last washing flask with 30 g \( \text{Na}_2\text{SO}_3 \cdot 7 \text{H}_2\text{O} \), 42 g \( \text{NaHCO}_3 \) and ca. 180 ml water. In this flask the destruction of surplus \( \text{Cl}_2 \) takes place:
$$\text{Cl}_2(g) + \text{SO}_3^{2-}(_{\text{aq}}) + 2 \text{OH}^-(_{\text{aq}}) \rightleftharpoons 2 \text{Cl}^-(_{\text{aq}}) + \text{SO}_4^{2-}(_{\text{aq}}) + \text{H}_2\text{O}$$

NaHCO₃ functions as a buffer in the solution dispersion.

Now the ampoule must be cooled to room temperature and be filled with chlorine.
For the Cl₂ cylinder a needle valve is used. This is because the chlorine is condensed and the vapour pressure is sufficiently low so that a reduction valve is not needed. Chlorine reacts with moisture in the air and forms concentrated HCl, which is very corrosive. It is therefore important that the needle valve is removed, flushed with compressed air and stored in a desiccator when not in use. If the Cl₂ regulator is not already in use, please call the laboratory responsible to help both with installing and removing the needle valve!

Let chlorine flow slowly through the system for ca. five minutes, so that most of the nitrogen in the system is removed and you obtain a chlorine pressure of ca. 1 atm.
When the quartz glass ampoule is cooled to room temperature it must be filled with chlorine. Proceed according to the following guidelines. Refer again to Figure 5.

1. Close stopcock 4
2. Open stopcock 6, so that the ampoule is filled with chlorine. Then close stopcocks 5 and 6.
3. Close the needle valve (B) to stop the flow of chlorine.
4. Take the ampoule including stopcock 5 from the vacuum and gas line and let the laboratory responsible melt the ampoule closed.
5. Remove the gas-washing bottle containing NaSO₃ and NaHCO₃ from the line in order to avoid back suction into the system as Cl₂ reacts with the solution.
6. Connect the hose of the water aspirator (vannstrålepumpe) to the exit by stopcocks 4 and 6. Carefully evacuate all the Cl₂-gas from the system. This must be done in order to avoid that traces of corrosive chlorine gas attack the Pirani head.

When the next ampoule is to be evacuated, it must be connected to stopcock 5 and replaced on the line. There should already be a vacuum in the system before stopcock 4. Open carefully stopcocks 4 and 5 and control that the line is evacuated. Remember to check whether the system is still leak proof by closing and opening stopcock 2. Then repeat the procedure for dehydrating and filling of Cl₂.
Remember that you have chlorine in the system after stopcock 6, so that it should be enough to close stopcock 4 and open valve B and stopcock 6 to fill the ampoule with chlorine. Before starting the Cl₂-flow you must reconnect the gas washing bottle with NaSO₃ and NaHCO₃.
After filling the last ampoule, the vacuum part of the line must be filled with air. Proceed according to the following (refer again to Fig. 5):

1. Close stopcock 2 and open stopcock 1
2. Turn off the pump
3. Slowly remove the Dewar with liquid nitrogen from the cold trap. When condensates present melts, stopcock 2 may be carefully opened to allow air to fill the system.

In general, if stopcock 2 is opened too soon, $O_2$ may condensate in the cold trap. If easily oxidizable condensates are present, unwanted reactions may occur. If one waits too long before opening stopcock 2, the condensates present may evaporate, thereby increasing the pressure in the system. There is then a risk of the glass equipment blowing up.

In order to control that the melting of the ampoule is good enough, the ampoules are put in a furnace at 950ºC. If they withstand this treatment they are ready for the transport furnace.

The furnace used has the possibility of temperature regulation in two zones. A sketch of the furnace is shown in Figure 6.

Place the ampoules in the furnace with a thermocouple in each end. It may be a good idea to initially transport the powder, which is left on the inner walls of the ampoule during the previous procedures, back to the “starting point”. Set the furnace so that $T_1 = 820ºC$ and $T_2 = 880ºC$. These conditions should give $\Delta P = 0.242$ atm. and $\Sigma P = 3.75$ atm. Place the ampoule so that the main part of the GeO$_2$ is situated at the lowest temperature, $T_1$.

Next day the gradient is reversed so that GeO$_2$ is transported to the empty end of the ampoule.

![Fig. 6: Transport furnace for growth of single crystals.](image-url)
Use equation (2) to calculate how long time the ampoules must be in the furnace in order to transport all the weighed GeO$_2$ from T$_2$ to T$_1$. Leave the samples in the transport furnace for some hours less than calculated.

When the transport is finished, the ampoules are removed from the furnace. Open the ampoules carefully and weigh the transported GeO$_2$ crystals.

Questions for the report

1) Calculate the transport efficiency, Q, for the different reaction conditions.
2) What limits the reaction rate in your experiment?
3) What are the advantages/disadvantages of the various ways of producing single crystals?

Characterization:
Study the crystals under a microscope. Describe them and comment on variation in size, colour and shape (if any).
Vedlegg 1: Temperatur-regulering
Basert på ”Forelesninger for kjemikere om instrumentering” av E. Hertel-Aas.

Reguleringsmetoder

1. Av-på regulering:
Maksimalt pådrag (=effekt) når temperaturen er under ønsket verdi. Eventuelt med dødbånd, dvs. at det maksimale pådraget beholdes til litt over ønsket temperatur og startes når temperaturen er litt under ønsket verdi.

![Fig. 1](image1.png)

Fig. 1: Illustrasjon av hvordan pådraget er i forhold til avviket fra ønsket temperatur for de to mulighetene av av-på regulering: med og uten dødbånd.

2. Proposjonalregulering (P-regulering):
Pådrag = k • avvik, der avvik er T\text{ ønsket} - T\text{ målt}.
Pådraget er mellom 0 og 100%. Det avvik som gir et pådrag på 100% kalles regulatorens proporsjonalitetsbånd. Ulempe: Man oppnår aldri ønsket verdi.

![Fig. 2](image2.png)

Fig. 2: Pådraget i forhold til avviket fra ønsket temperatur for P-regulering.
3. **Proposjonal-integrasjonsregulering (PI-regulering):**

\[ \text{Pådrag} = k_1 \cdot \text{avvik} + k_2 \int \text{avvik} \, dt \]

Når et integrasjonsledd legges til proposjonalitetsleddet vil ønsket verdi oppnås; så lenge måleverdien er lavere enn ønsket verdi øker integral-delen i pådraget. Ulempe: Innsvingningstiden blir lang – om man i det hele tatt blir kvitt den.

![Fig. 3: PI-regulering; arealene på undersiden av den øverste skraverte linjen virker positivt inn på pådraget, mens arealene på oversiden har en negativ effekt.](image)

4. **Proposjonal-integrasjon-derivationsregulering (PID-regulering):**

\[ \text{Pådrag} = k_1 \cdot \text{avvik} + k_2 \int \text{avvik} \, dt - k_3 \cdot \frac{d(\text{avvik})}{dt} \]

Derivationsleddet ”demper” raske svingninger og fall.

![Fig. 4: Temperaturutviklingen ved PID-regulering.](image)

Det finnes fungerende – om enn tidkrevende – prosedyrer for å finne frem til de rette konstantene ved PID-regulering. Endel regulatorer gjør dette automatisk ved funksjonen ”autotuning”.
Vedlegg 2: Sonesmelting

9.3 SOLIDIFICATION OF ALLOYS

When an alloy solidifies, the solid that forms generally has a different composition than the liquid from which it is freezing. Therefore, the distribution of a solute in the solid will generally be different than it was in the liquid prior to freezing. This redistribution of the solute produced by solidification is frequently termed segregation. In this section we are interested in quantitatively describing segregation. The discussion will be limited to binary alloys in order to simplify the presentation.

A. EQUILIBRIUM FREEZING

Figure 9.12 presents the solid–liquid region of a eutectic-type phase diagram. At any temperature such as $T_1$, this diagram tells us the fractional compositions of the solid and of the liquid that will be in equilibrium with each other. The equilibrium distribution coefficient, $k_0$, is defined as the ratio of the equilibrium solid and liquid compositions:

$$k_0 = \frac{X_{\text{solidus at } T}}{X_{\text{liquidus at } T}} = \frac{X_s}{X_l}$$ (9.10)

Consequently, $k_0$ is the ratio of the solidus to liquidus composition at any temperature of interest. You may show yourself that $k_0$ is a constant independent of composition if the solidus and liquidus are straight lines.

If one cools a volume of liquid of uniform composition $X_0$ to temperature $T_1$, then solid composition $k_0X_0$ will begin to form if no nucleation barrier interferes. If the temperature is lowered to $T_2$, and if equilibrium
freezing occurs, then from the well-known lever law we have

\[
\text{Wt fraction liquid} = \frac{\text{Length } A-B}{\text{Length } A-C} \quad (9.11)
\]

This result is obtained from mass balances on the liquid and solid for (1) the solute component, and (2) both components together. One obtains two equations that combine to give Eq. 9.11, the lever law. In deriving this result one assumes that all of the liquid is at composition \( C \) and all of the solid is at composition \( A \). Consequently, the lever law requires all of the liquid and all of the solid to have uniform composition. This latter requirement is infrequently obtained in solidification, so that the lever law has only very limited usefulness in describing the solidification of real systems. For instance, the lever law indicates that the last liquid freezes at temperature \( T_s \) and at this point all of the solid has composition \( X_s \). This condition is infrequently obtained because the first solid formed with a composition \( k_sX_s \) and it is difficult for this solid to increase its composition to \( X_s \) by the time the last liquid freezes.

B. NONEQUILIBRIUM FREEZING

In this discussion we make two major assumptions that will later be examined in detail:

I. Uniform liquid composition
II. A flat solid-liquid interface

9.3 Solidification of Alloys 247

Consider now a horizontal cylinder of liquid alloy having uniform composition \( X_s \). This initial uniform composition is plotted below the alloy in Fig. 9.13(a). We now cool the left end of the rod allowing a small amount of solid to form. The solid-liquid interface is then located at position 1. The area under the curve of Fig. 9.13(a) between any two points \( Z \) and \( Z_2 \) is proportional to the mass of solute in the rod between points \( Z \) and \( Z_2 \).

After the initial small volume of liquid freezes, the composition in this volume has dropped from \( X_s \) to \( k_sX_s \). Therefore, a mass of solute proportional to the cross-hatched area to the left of position 1 on Fig. 9.13(a) has been removed from the solid and rejected into the liquid. This must cause the liquid composition to rise above \( X_s \) a small amount as shown. We know from the previous section that at the solid-liquid interface the temperature will be within 0.01-0.05°C of the equilibrium temperature. Hence, we consider that a local equilibrium exists at the solid-liquid interface. This means that Eq. 9.10 applies at the interface so that we may write \( X_t = k_sX_t \). The composition of the solid and liquid are "tied together" at the interface by this equilibrium relation. Consequently, as the liquid composition rises due to the solute rejection at the interface, the solid composition must also rise. After the interface has advanced to position 2, the solid composition will have gradually risen as shown in Fig. 9.13(a) due to the increasing liquid composition, and the interface temperature will have dropped from 1 to 2 as shown in Fig. 9.13(b). Notice that this is not equilibrium freezing because the solid has a nonuniform composition. A uniform solid composition could only be obtained by solid-state diffusion, which is frequently so slow that it has an insignificant effect on the solid composition profile. After the entire rod has solidified.

\[ \text{Composition} \]

\[ \text{Position, } Z \rightarrow \]

\[ \text{Liquid} \]

\[ \text{Solid} \]

\[ X_s \]

\[ X_t \]

\[ \text{corresponding phase diagram for alloy of } (a) \]
Figure 1.1: Composition profile along the x-axis of Figure 1. Fig. 1.1.
If we replace volume concentration $C$ by weight fraction concentration $X$, and $Z/L$ by the weight fraction of the alloy solidified then it may be shown that Eq. 9.17 is obtained in terms of these variables without needing assumption V. Restrictions III and IV are frequently satisfied in practice. Equation 9.17 presents us with a first-order approximation to nonequilibrium freezing, which for some cases is quite adequate.

C. ZONE MELTING

It was pointed out above that normal freezing produces a purification in the first portion of the rod to solidify, as shown in Fig. 9.14. In 1952 W. G. Pfannt published a famous paper showing that a much more effective way of purification could be obtained by the technique of zone melting. In this technique a small zone of length $L$ is melted in the rod and it is passed down the rod as illustrated in Fig. 9.16. After the zone has passed down the rod the first time ($n = 1$) a purification is obtained as shown. By carrying out a mass balance similar to above for the solute in the zone, you may show yourself that after one pass of the zone the concentration in the rod would be

$$C_n = C_0(1 - (1 - k_0)e^{-kn})$$  \hspace{1cm} (9.18)

The purification after one pass is less than that obtained in normal freezing. However, with zone melting one may repeatedly pass the zone down the rod and an increased purification is obtained after each pass, until after many passes an ultimate distribution is reached. The equations for concentration versus length after more than one pass of the zone are more complex than Eq. 9.18 and will not be discussed here.

Zone melting is an extremely effective method of removing impurity elements having $k_0$ values of less than 0.5. For example, with an impurity of $k_0 = 0.1$ the average concentration of the impurity in the first half of the rod is reduced by a factor of around 1000 after only five passes (Ref. B, p. 287). It is important to remember, however, that this result as well as Eq. 9.18 are subject to the same five restrictions that apply to the normal freeze equation as listed above. Again, the last three assumptions generally have very little influence in practice. However, the first two restrictions, I and II, are quite important and are discussed separately in the next two sections.

D. MIXING IN THE LIQUID

In the derivations of both the normal freeze equation (9.17) and the zone melting equation (9.18) the assumption of uniform liquid composition was employed (assumption I, p. 246). This turns out to be a very severe restriction, as we shall now see.

Convection currents in the liquid fraction of a solidifying alloy will tend to produce a uniform liquid composition. Natural convection is difficult to eliminate from liquid metal alloys because of their low viscosity and high density, so that one might expect a uniform liquid composition to generally be obtained. However, there is a fundamental characteristic of fluid flow that prevents this. When a fluid flows past a solid surface the velocity of the fluid right at the surface is always found to be zero. This is called the no-slip condition. It is not at all obvious that it should obtain. If one passes a fluid down a pipe at a low velocity as in Fig. 9.17(a) the fluid flows parallel to the pipe wall at all points and is termed laminar flow. The flow velocity is a maximum at the center and drops parabolically to zero as the wall is approached. At very high velocities the flow becomes turbulent, involving many eddies and swirls in the center of the pipe where the mean velocity is almost constant across the diameter. However, the velocity must always drop to zero at the wall. Hence, a thin boundary layer of laminar flowing fluid is always present at the wall. Such a boundary layer is always present in the liquid at the solid-liquid interface, and it inhibits a uniform liquid composition.

As explained above, solute is continually being rejected from the solid into the liquid at the solid-liquid interface during solidification. In order to obtain a uniform liquid composition, this solute must be transported very quickly throughout the liquid. Two transport mechanisms are available to
1. Derivation of the Equation for $k_z$. To proceed it is first necessary to derive the differential equation that governs the liquid concentration, $C$, in the boundary layer (Fig. 9.20). We take the interface as our reference point. The liquid flows toward an observer on the interface so that the flux of solute due to fluid flow at any point in the liquid is $-RC$, where $C$ is the local liquid volume concentration, and $R$ is the rate at which the liquid moves toward the observer (interface rate). The minus sign is required because this flow flux is directed in the minus $Z$ direction and we are taking $R$ itself as a positive number. The total flux due to diffusion and fluid flow is

$$J = -RC - D \frac{dC}{dZ} \tag{9.20}$$

We now apply the continuity equation (Eq. 6.7) just as we did on p. 140 to obtain Fick's second law; here we obtain

$$D \frac{d^2C}{dZ^2} + R \frac{dC}{dZ} - \frac{dC}{dt} \tag{9.21}$$

After the initial transient has passed, the amount of solute in the boundary layer remains relatively constant and so we assume $\frac{dC}{dt} = 0$ after the transient. This is an assumption because the value of $(C_0)$ continues to rise after the transient. However, the solute profile in the boundary layer becomes nearly constant after the transient, and experiments have shown this assumption to be quite good. Therefore the differential equation describing the solute level, $C$, in the boundary layer after the transient becomes

$$D \frac{d^2C}{dZ^2} + R \frac{dC}{dZ} = 0 \tag{9.22}$$

![Figure 9.20](image)

Figure 9.20 The fluxes of solute in the liquid relative to the solid-liquid interface.

We must now solve this equation for the conditions that prevail at the two boundaries of the boundary layer region. The left-hand boundary is the solid-liquid interface and we obtain this boundary condition from a flux balance of solute across the interface,

$$\text{Flux directed into interface} = \text{Flux directed out from interface} \tag{9.23}$$

Again, we take the interface as our reference point, and from Fig. 9.21 we see that the only mechanism by which solute enters the interface is fluid flow from the liquid, so we have

$$\text{Flux directed into interface} = R(C_0) \tag{9.24}$$

Notice, however, that a flux is directed away from the interface by three mechanisms, flow into the solid, diffusion into the liquid, and also diffusion into the solid. As before, we neglect diffusion into the solid and we obtain

$$\text{Flux directed out from interface} = R(C_0) - D \frac{dC}{dZ} \tag{9.25}$$

We need the minus sign on the diffusion term because $(dC/dZ)$ is negative. Combining Eqs. 9.23, 9.24, and 9.25 with the relation $(C_0) = k_a(C_0)$, we obtain

Boundary condition 1: \( D \frac{dC}{dZ} + R(C_0)(1 - k_a) = 0 \) at \( Z = 0 \)

\( (9.26) \)

(You will note that we have implicitly assumed equal solid and liquid densities.) As shown on Fig. 9.21, the boundary layer thickness is defined as, and we assume that beyond a distance $\delta$, the liquid concentration is...
(9.5) \[ c = \frac{1}{1 - \frac{d}{d_0}} \]

boundary region is contained, we obtain:

\[ \text{for the case of } d = d_0 \text{, we assume the usual solution in the } \]

area of the solution region we can expand a mass function similar to that

use of the characteristic equation for the solution. We shall obtain the

The above equation is then the solution of the problem.

(9.6) [25] A plot of the diffusion-phenomenon function for the

If the solution region is contained, we obtain:

\[ \text{any of the above equations, having the same solution for } \]

The above equation is then the solution of the problem.

(9.7) A plot of the diffusion-phenomenon function for the

If the solution region is contained, we obtain:

\[ \text{any of the above equations, having the same solution for } \]

The above equation is then the solution of the problem.
You've probably seen calculators that have solar cells - calculators that never need batteries, and in some cases don't even have an off button. As long as you have enough light, they seem to work forever. You may have seen larger solar panels - on emergency road signs or call boxes, on buoys, even in parking lots to power lights. Although these larger panels aren't as common as solar powered calculators, they're out there, and not that hard to spot if you know where to look. You have also seen solar cell arrays on satellites, where they are used to power the electrical systems.

You have probably also been hearing about the "solar revolution" for the last 20 years - the idea that one day we will all use free electricity from the sun. This is a seductive promise - on a bright, sunny day the sun shines approximately 1,000 watts of energy per square meter of the planet's surface, and if we could collect all of that energy we could easily power our homes and offices for free.

In this edition of How Stuff Works we will examine solar cells to learn how they convert the sun's energy directly into electricity. In the process you will learn why we are getting closer to using the sun's energy on a daily basis, but we still have more research to do before the process becomes cost effective.

Using Silicon to convert photons to electrons

The solar cells that you see on calculators and satellites are photovoltaic cells or modules (modules are simply a group of cells electrically connected and packaged in one frame). Photovoltaics, as the word implies (photo = light, voltaic = electricity), convert sunlight directly into electricity. Once used almost exclusively in space, photovoltaics are used more and more in less exotic ways. They could even power your house. How do these devices work?

Photovoltaic (PV) cells are made of special materials called semiconductors such as silicon, which is currently the most commonly used. Basically, when light strikes the cell, a certain portion of it is absorbed within the semiconductor material. This means that the energy of the absorbed light is transferred to the semiconductor. The energy knocks electrons loose, allowing them to flow freely. PV cells also all have one or more electric fields which act to force electrons freed by light absorption to flow in a certain direction. This flow of electrons is a current, and by placing metal contacts on the top and bottom of the PV cell, we can draw that current off to use externally. For example, the current can power a calculator. This current, together with the cell's voltage (which is a result of its built-in electric field or fields), defines the power that the solar cell can produce.

That's the basic process, but there's really much more to it. Let's take a deeper look into one example of a PV cell: the single crystal silicon cell.

Silicon has some special chemical properties, especially in its crystalline form. An atom of silicon has 14 electrons, arranged in 3 different shells. The first 2 shells, those closest to the center, are completely full. The outer shell, however, is only half full, having only 4 electrons. A silicon atom will always look for ways to fill up its last shell (which would like to have 8 electrons). To do this, it will share electrons with 4 of
its neighbor silicon atoms. It's like every atom holds hands with its neighbors, except that in this case, each atom has 4 hands joined to 4 neighbors. That's what forms the crystalline structure, and that structure turns out to be important to this type of PV cell. We've now described pure, crystalline silicon. Pure silicon is a poor conductor of electricity because none of its electrons are free to move about as electrons are in good conductors like copper. Instead, the electrons are all locked in the crystalline structure. The silicon in a solar cell is modified slightly so that it will work as a solar cell.

Our cell has silicon with impurities - other atoms mixed in with the silicon atoms, changing the way things work a bit. We usually think of impurities as something undesirable, but in our case, our cell wouldn't work without them. These impurities are actually put there on purpose. Consider silicon with an atom of phosphorous here and there, maybe one for every million silicon atoms. Phosphorous has 5 electrons in its outer shell, not 4. It still bonds with its silicon neighbor atoms, but in a sense, the phosphorous has one electron that doesn't have anyone to hold hands with. It doesn't form part of a bond, but there is a positive proton in the phosphorous nucleus holding it in place.

When energy is added to pure silicon, for example in the form of heat, it can cause a few electrons to break free of their bonds and leave their atoms. A hole is left behind in each case where an electron could bond. These electrons then wander randomly around the crystalline lattice looking for another hole to fall into. These electrons are called free carriers, and can carry electrical current. There are so few of them in pure silicon, however, that they aren't very useful. Our impure silicon with phosphorous atoms mixed in is a different story. It turns out that it takes a lot less energy to knock loose one of our "extra" phosphorous electrons because they aren't tied up in a bond - their neighbors aren't holding them back. As a result, most of these electrons do break free, and we have a lot more free carriers than we would have in pure silicon. The process of adding impurities on purpose is called doping, and when doped with phosphorous, the resulting silicon is called n-type (n for negative) because of the prevalence of free electrons. N-type doped silicon is a much better conductor than pure silicon is.

Actually, only part of our cell is n-type. The other part is doped with boron, which has only 3 electrons in its outer shell instead of 4, to become p-type silicon. Instead of having free electrons, p-type silicon (p for positive) has free holes. Holes really are just the absence of electrons, so they carry the opposite (positive) charge. They move around just like electrons do.

So where has all this gotten us? The interesting part starts when you put n-type silicon together with p-type silicon. Remember that every PV cell has at least one electric field. Without an electric field, the cell wouldn't work, and this field forms when the n-type and p-type silicon are in contact. Suddenly, the free electrons in the n side, who have been looking all over for holes to fall into, see all the free holes on the p side, and there's a mad rush to fill them in. Before now, our silicon was all electrically neutral. Our extra electrons were balanced out by the extra protons in the phosphorous. Our missing electrons (holes) were balanced out by the missing protons in the boron. When the holes and electrons mix at the junction between n-type and p-type silicon, however, that neutrality is disrupted. Do all the free electrons
fill all the free holes? No. If they did, then the whole arrangement wouldn't be very useful. Right at the junction, however, they do mix and form a barrier, making it harder and harder for electrons on the n side to cross to the p side. Eventually equilibrium is reached, and we have an electric field separating the two sides. This field acts as a diode, allowing (and even pushing) electrons to flow from the p side to the n side, but not the other way around. It's like a hill - electrons can easily go down the hill (to the n side), but can't climb it (to the p side).

Figure 1. The effect of the electric field in a PV cell

Now, when light, in the form of photons, hits our cell, its energy frees electron-hole pairs. Each photon with enough energy will normally free exactly one electron, and result in a free hole as well. If this happens close enough to the electric field, or if they happen to wander into its range of influence, the field will send the electron to the n side, and the hole to the p side. This causes further disruption of electrical neutrality, and if we provide an external current path, electrons will flow through the path to their original side (the p side) to unite with holes the electric field sent there, doing work for us along the way. The electron flow provides the current, and the cell’s electric field causes a voltage. With both current and voltage, we have power, which is the product of the two.

Figure 2. Operation of a PV cell

How much sunlight energy does our PV cell absorb? Unfortunately, the most that our simple cell could absorb is around 25%, and more likely is 15% or less. Why so little? Visible light is only part of the electromagnetic spectrum. Electromagnetic radiation is not monochromatic - it is made up of a range of different wavelengths, and therefore energy levels. (See the article titled "How Special Relativity Works", by John Zavisa,
for a good discussion of the electromagnetic spectrum.) Light can be separated into different wavelengths, and we can see them in the form of a rainbow. Since the light that hits our cell has photons of a wide range of energies, it turns out that some of them won't have enough energy to form an electron-hole pair. They'll simply pass through the cell as if it were transparent. Still other photons have too much energy. Only a certain amount of energy, measured in electron volts and defined by our cell material (about 1.1 eV for crystalline silicon), is required to knock an electron loose. We call this the **band gap energy** of a material. If a photon has more energy that the required amount, then the extra energy is lost (unless a photon has twice the required energy, and can create more than one electron-hole pair, but this effect is not significant). These 2 effects alone account for the loss of around 70% of the radiation energy incident on our cell.

Why can't we choose a material with a really low band gap, so we can use more of the photons? Unfortunately, our band gap also determines the strength (voltage) of our electric field, and if it's too low, than what we make up in extra current (by absorbing more photons), we lose by having a small voltage. Remember that power is voltage times current. The optimal band gap, balancing these two effects, actually is around 1.4 eV for a cell made from a single material.

We have other losses as well. Our electrons have to flow from one side of the cell to the other through an external circuit. We can cover the bottom with a metal, allowing for good conduction, but if we completely cover the top, then photons can't get through the opaque conductor and we lose all our current (in some cells transparent conductors are used on the top surface, but not in all). If we put our contacts only at the sides of our cell, then the electrons have to travel an extremely long distance (for an electron!) to reach the contacts. Remember, silicon is a semiconductor - it's not nearly as good as a metal for transporting current. Its internal resistance (called **series resistance**) is fairly high, and high resistance means high losses. To minimize these losses, our cell is covered by a metallic contact grid that shortens the distance that electrons have to travel while covering only a small part of the cell surface. Even so, some photons are blocked by the grid, which can't be too small or its own resistance will be too high.

There are a few more steps left before we can really use our cell. Silicon happens to be a very shiny material, which means that it is very reflective. Photons that are reflected can't be used by the cell. For that reason, an antireflective coating is applied to the top of the cell to reduce reflection losses to below 5%. The final step is the glass cover plate which protects the cell from the elements. PV modules are made by connecting several cells (usually 36) in series and parallel to achieve useful levels of voltage and current, and putting them in a sturdy frame complete with a cover glass and positive and negative terminals on the back.
Single crystal silicon isn't the only material used in PV cells. Polycrystalline silicon is also used in an attempt to cut manufacturing costs, although resulting cells aren't as efficient as single crystal silicon. Amorphous silicon, which has no crystalline structure, is also used, again in an attempt to reduce production costs. Other materials used include gallium arsenide, copper indium diselenide and cadmium telluride. Since different materials have different band gaps, they seem to be "tuned" to different wavelengths, or photons of different energies. One way efficiency has been improved is to use two or more layers of different materials with different band gaps. The higher band gap material is on the surface, absorbing high energy photons while allowing lower energy photons to be absorbed by the lower band gap material beneath. This technique can result in much higher efficiencies. Such cells, called multi-junction cells, can have more than one electric field.

Powering a house
Now that we have our PV module, what do we do with it? What would you have to do to power your house with solar energy? Although it's not as simple as just slapping some modules on your roof, it's not extremely difficult to do either. First of all, not every roof has the correct orientation or angle of inclination to take advantage of the sun's energy. Non-tracking PV systems in the northern hemisphere should point towards true south (this is the orientation). They should be inclined at an angle equal to the area's latitude to absorb the maximum amount of energy year round. A different orientation and/or inclination could be used if you want to maximize energy production for the morning or afternoon, and/or the summer or winter. Of course, the modules should never be shaded by nearby trees or buildings, no matter the time of day or the time of year. In a PV module, even if just one of its 36 cells is shaded, power production will be reduced by more than half.

If you have a house with an unshaded, south facing roof, you need to decide what size system you need. This is complicated by the facts that your electricity production depends on the weather, which is never completely predictable, and that your electricity demand will also vary. These hurdles are fairly easy to clear. Meteorological data exists which gives average monthly sunlight levels for different geographical areas. This takes into account rainfall and cloudy days, as well as altitude, humidity, and other more subtle factors. You should design for the worst month, so that you'll have enough electricity all year round. With that data, and knowing your average household demand (your utility conveniently lets you know...
how much energy you use every month!), simple methods exist allowing you to
determine just how many PV modules you'll need. You'll also need to decide on a
system voltage, which you can control by deciding how many modules to wire in
series.

You may have already guessed a couple of problems that we'll have to solve. First,
what do we do when the sun isn't shining? Certainly, no one would accept only
having electricity during the day, and then only on clear days, if they have a choice.
We need energy storage - batteries. Unfortunately, batteries add a lot of cost and
maintenance to the PV system. Currently, however, it's a necessity if you want to be
completely independent. One way around the problem is to connect your house to
the utility grid, buying power from the utility when you need it, and selling to them
when you produce more than you need. This way, the utility acts as a practically
infinite storage system. The utility has to agree, of course, and in most cases will buy
power from you at a much lower price than their own selling price. You will also need
special equipment to make sure that the power you sell to your utility is synchronous
with theirs, in other words that it shares the same sinusoidal waveform and
frequency. Safety is an issue as well. The utility has to make sure if there's a power
outage in your neighborhood, that your PV system won't try to feed electricity into
lines that a lineman may think is dead. This is called islanding.

If you decide to use batteries, keep in mind that they will have to be maintained, and
replaced after a certain number of years. The PV modules should last 20 years or
more, but batteries just don't have that kind of useful life. Batteries in PV systems can
also be very dangerous because of the energy they store and the acidic electrolytes
they contain, so you'll need a well-ventilated, non-metallic enclosure for them.

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What kind of batteries are used in PV systems? Although
several different kinds are commonly used, the one
characteristic that they should all have in common is that
they are **deep cycle batteries**. Unlike your car battery,
which is a **shallow cycle battery**, deep cycle batteries can
discharge more of their stored energy while still
maintaining long life. Car batteries discharge a large
current for a very short time - to start your car, and are then
immediately recharged as you drive. PV batteries generally
have to discharge a smaller current for a longer period
(such as all night), while being charged during the day.

The most commonly used deep cycle batteries are lead-acid
batteries (both sealed and vented), and nickel cadmium
batteries. Nickel cadmium batteries are more expensive, but
last longer and can be discharged more completely without
harm. Even deep cycle lead-acid batteries can't be
discharged 100% without seriously shortening battery life,
and generally PV systems are designed to discharge lead-acid batteries no more than 40 or 50%. Also, the use of batteries requires the installation of another component called a **charge controller**. Batteries last a lot longer if care is taken so that they aren't overcharged, or drained too much. That's what a charge controller does. Once the batteries are fully charged, the charge controller doesn't let current from the PV modules continue to flow into them. Similarly, once the batteries have been drained to a certain predetermined level, controlled by measuring battery voltage, many charge controllers will not allow more current to be drained from the batteries until they have been recharged. The use of a charge controller is essential for long battery life.

The other problem is that the electricity generated by your PV modules, and extracted from your batteries if you choose to use them, is direct current, while the electricity supplied by your utility (and the kind which every appliance in your house uses) is alternating current. You will need an **inverter**, a device which converts DC to AC. Most large inverters will also allow you to automatically control how your system works. Some PV modules, called AC modules, actually have an inverter already built into each module, eliminating the need for a large, central inverter, and simplifying wiring issues.

Throw in the mounting hardware, wiring, junction boxes, grounding equipment, overcurrent protection, DC and AC disconnects and other accessories and you have yourself a system. Electrical codes must be followed (there's a section in the National Electrical Code just for PV), and it's highly recommendable that the installation be done by a licensed electrician who has experience with PV systems. Once installed, a PV system requires very little maintenance (especially if no batteries are used), and will provide electricity cleanly and quietly for 20 years or more.
If photovoltaics are such a wonderful source of free energy, then why doesn't the whole world run on solar power? Some people have a flawed concept of solar energy. While it's true that sunlight is free, the electricity generated by PV systems is not. As you can see from our discussion of a household PV system, quite a bit of hardware is needed. Currently, an installed PV system will cost somewhere around $9 per peak Watt. To give you an idea of how much a house system would cost, let's consider the Solar House - a model residential home in Raleigh, North Carolina, with a PV system set up by the North Carolina Solar Center to demonstrate the technology. It's a fairly small home, and it is estimated that its 3.6 kW PV system covers about half of the total electricity needs (this system doesn't use batteries - it's connected to the grid). Even so, at $9 per Watt, this installed system would cost you around $32,000.

That's why PV is usually used in remote areas, far from a conventional source of electricity. Right now, it simply can't compete with the utilities. Costs are coming down as research is being done, however. Researchers are confident that PV will one day be cost effective in urban areas as well as remote ones. Part of the problem is that manufacturing needs to be done on a large scale to reduce costs as much as possible. That kind of demand for PV, however, won't exist until prices fall to competitive levels. It's a catch-22 situation. Even so, demand and module efficiencies are constantly rising, prices are falling, and the world is becoming increasingly aware of environmental concerns associated with conventional power sources, making photovoltaics a technology with a bright future.

References


Links

- NC Solar Center Homepage
- Collection of fact sheets from the NC Solar Center
- DOE's National Center for Photovoltaics program
- Sunelco solar systems
- National Renewable Energy Laboratory
- Sandia National Laboratories
Vedlegg 4: PIRANI-HODE FOR TRYKKMÅLING

Det fins flere alternativer for å sjekke trykkforholdene i en vakuumlinje. Mens det i øvelse 6 benyttes en kvikksølvkolonne, blir det i oppgave 7 benyttet et Pirani-hode. Det fysiske prinsippet som anvendes i disse trykk-målerene kan kort oppsummeres ved: ulike gassers evne til å lede varme er gitt som en funksjon av trykk. Et typisk instrument består av en tynn vaier (filament, vanligvis wolfram), som varmes opp ved å sende en elektrisk ladning gjennom (se Fig. 1). Filamentet utsettes så for trykket som skal måles. Ved **høy trykk** vil et stort antall molekyler kollidere med filamentet og dermed overføre varme til veggene inni Pirani-hodet. Temperaturen på filamentet vil da avta. Ved **konstant trykk** vil temperaturen innstille seg ved et konstant nivå, med det ved **lav trykk** vil være færre molekyler tilstede og dermed også færre kollisjoner med filamentet. Mindre varme fjernes da fra filamentet, hvilket fører til økning i temperaturen og følgelig også endringer i den elektriske motstanden i filamentet. Filamentet er en del av en "Wheatstone-bridge" og denne "broen" kommer ut av balanse når spenningen i filamentet endres. Denne endringen anvendes som et mål på gasstrykket.

![Fig. 1: Prinsippskisse av et typisk Pirani-hode.](image-url)
Det finnes flere typer utforminger av Pirani-hodene. En mulighet er "constant-voltage" Pirani der spenningen i filamentet holdes konstant, mens temperaturen endres. En annen form er "constant-temperature" Pirani der spenningen endres kontinuerlig for å opprettholde konstant temperatur på filamentet.

De fleste Pirani-hodene er kalibrert for tørr nitrogen og korreksjoner er derfor påkrevd ved nøyaktige målinger når andre gasser dominerer (se Fig. 2). Generelt sett har lette molekyler relativt høy termisk ledningsevne ved lave trykk. siden vi i denne oppgaven kun skal kontrollere at et konstant vakuum er oppnådd er strengt tatt ikke kalibreringer og korreksjoner nødvendige.

Fig. 2: Korreksjonskurve for kalibrering av Pirani-hode.
Vedlegg 5: Litteraturliste

Dette er noe litteratur som er benyttet ved utarbeidelse av de enkelte øvelsene. Innholdet kan være generell omtale av og teori for metodene, utstyrbeskrivelse, rapportering av syntesegang for et spesifikt produkt eller beskrivelse av egenskapene for et stoff.

InSb

TiN
1. Fremstilling av titantetraklorid, oppgave fra de tidligere kursene K 106 og KJ 212

YBa$_2$Cu$_3$O$_7$

BaTiO$_3$

GeO$_2$, transportreaksjon