Assignment 2: Synthesis

1. Before you do any work in the laboratory you must be familiar with the General safety regulations of Kemicentrum, which can be found at www.kc.lu.se.

2. Make a risk and safety analysis of the synthesis.

3. **If anything happens inform your supervisor immediately. Don’t panic!**

   For the specific laboratories you will be working in, the following things are important to have in mind.

   Clean all tools and desks after you finished your work. In case of a fire switch off the burner and close all doors. It is important that you do not use the fire extinguishers in the lab, because they are not useful for metals. For the same reason you cannot use water. To extinguish small fires sand is usually the best choice. There are buckets with sand in the lab. You can use a fire blanket (Swedish: Brandfilt) as well. Check their locations in the labs before you start to work.

   To avoid **injury** it is necessary that you protect yourself before you start. There are special gloves available for heat protection, working with liquid nitrogen and cutting glass. Do not hesitate to ask for this equipment. It is mandatory to wear safety goggles even though you have normal glasses – especially when you cut glass or use the vacuum line. There are special glasses for the burner available. Please check the location of the closest emergency showers and the first aid kits before you start. Use the fume hoods every time it is necessary.

   You will produce **waste**. Acids are deposited in a container labeled with “acid waste”. Gloves, paper and any other kind of normal waste can be disposed in the garbage cans. Please bin glass and silica pieces in the glass waste. There is a special container for used niobium ampoules. Other solid chemicals need to be disposed in containers with the label “solid waste”. But dissolve and neutralize everything possible to avoid accidents. Your projects are connected to our research and therefore your samples are no waste: Label your samples properly.

   **Have fun in the lab.**

4. Select a synthesis to perform and prepare for the session by (i) reading the introduction to the synthesis, (ii) check the relevant sections in the text book or other relevant literature.

5. Do not forget to bring your safety glasses and protective coats. If you do not have any, they will be provided at the lab.
The goal of this lab is to give you an introduction in basic inorganic solid state synthesis and characterization methods on a concrete example. You are expected to write a short report in the form of a research article and to report your project in a 5-10 minutes oral presentation.

**Introduction**

Solders are important materials for electric devices and plumbing. But on the interfaces between the solder and the substrate the formation of brittle, binary or ternary intermetallic phases is possible. In order to avoid usage of the well known but toxic lead containing solders, the focus of the research in this field has shifted to lead-free solders. To design those solders it is necessary to investigate the ternary phase diagrams and the crystal structures at low temperatures (synthesis or working temperatures, room temperature to 400 °C).

Intermetallic compounds are no alloys. An alloy is a solid solution of two or more metals where the lattice parameters follow Vegard’s Law. An intermetallic compound is a line phase in the phase diagram which means that it has a defined composition and lattice parameters. In between these two extremes are so called intermetallic phases that have discrete phase broadening in which composition and lattice parameters can differ.

Cu₂Sb is one of the binary intermetallic compounds that are formed in ternary systems Cu-In-Sb or Cu-Sn-Sb which are relevant for new lead free solders. The structure was described by Elander et al. in 1935 and reinvestigated by Nuss et.al. later [1, 2]. Even though the compound is available from the elements one can improve the crystal growth by the so called metal flux technique [3]. A variation of this well-known synthesis method is the “centrifuge” method [4]. The samples are reacted in evacuated silica ampoules that contain quartz wool filters. After an annealing period the hot sample will be centrifuged. The metal flux and the synthesis product will remain separated from each other without any need of further separation.

You are going to synthesize the intermetallic compound Cu₂Sb from elemental copper and antimony with an antimony flux and a tin flux and compare the two methods (or the standard way compared to the centrifuge method).

Powder X-Ray Diffraction on a Stoe Stadi MP equipped with Cu-\(K\alpha_1\) radiation will be used to characterize the reaction products. Furthermore you will study the crystal structure by selecting the best crystal out of three or four single crystals and measuring it on an Oxford Diffraction XCalibur 3 diffractometer equipped with Mo-\(K\alpha\) radiation. As last step you are going to
investigate your sample with the DTA-TG sensor on a Netzsch STA 449 Jupiter F3 system in order to receive information on the thermodynamic behavior of your reaction product.


Which other phases are known in the copper antimony phase diagram [6]?

What are alternative synthesis routes? What would be a suitable reaction, respectively annealing temperature?

All mentioned literature references are available electronically via LibHub (http://libhub.sempertool.dk/libhub) or in the Kemicentrum library and it is expected that you prepare yourself before the lab.

**Working Schedule**

Make a risk analysis before you start. Don’t forget to bring lab coats and safety glasses.

Week 1: Synthesis, Annealing
Week 3: Powder Diffraction, Thermal Analysis
Week 5: Single Crystal X-Ray Diffraction
Week 7: Oral presentation of your work

Because not all students can use the machines at the same time it is necessary that you book measurement time with your supervisor. This can vary from the scheduled course time.

**Literature**

2.3 & 2.4. Ion-exchanged swelling clay mineral

The goal of this lab is to give you an introduction in basic inorganic solid state synthesis and characterization methods on a concrete example. You are expected to write a short report in the format of a research article and to report your project in a 5-10 minutes oral presentation. Start by reading the section on the atomic structure of silicates (1.6.9) and the section on clay minerals (7.9) in the text book [1]. Descriptions of the X-ray and thermal techniques can also be found in the text book.

**Introduction**

Clays consist by definition of mineral particles less than 4 micrometers in diameter. The small size of the particles gives the clays their well known properties, for example the formation of a plastic solid when mixed with the appropriate amount of water. The most common clay minerals are sheet silicates that are built of silicate layers with a negative charge alternating with layers of positive ions like Na⁺ and Ca²⁺. The negative layer charge can go down to zero in some minerals and then no positive ions are present. In other clay minerals, the positive ions present are hydrated, so that the mineral also contains water inside the solid particles. If the negative layers have an intermediate amount of charge per unit area, swelling clay (smectite) is obtained. The most common smectite mineral is montmorillonite and this is the mineral used in this exercise and which is described in the following text. Montmorillonite intercalates (incorporates) a different number of water layers depending on the relative humidity in the surrounding air. Due to the open layer structure and small size of the particles, clay minerals can also act as ion-exchangers. If the solid particles are placed in a salt solution containing the ion A⁺, the original cations inside the mineral will diffuse out into the solution and the pure A-form of the mineral will form, at least if the procedure is repeated a couple of times with fresh A-solution.

In Ca-montmorillonite between \( n = 0 \) and \( n = 3 \) water layers can be intercalated (in special cases even \( n = 4 \) is observed). Each water layer is approximately 3 Å thick and the repeat distance \( c \) in the stacking direction is 10 Å in the structure without water molecules. Thus, for a dehydrated montmorillonite \( (n = 0) \) \( c = 10 \) Å. For a mineral with one layer of water \( (n = 1) \) \( c = 10 + 3 = 13 \) Å and consequently: \( n = 2, c = 16 \) Å; \( n = 3, c = 19 \) Å; and \( n = 4, c = 22 \) Å. In contact with the atmosphere, the Ca-mineral will have \( n = 0 - 2 \), depending on the moisture content of the air, while in pure liquid water, the Ca-montmorillonite will usually not expand further than to \( n = 3 \). The Na-montmorillonite exhibits a very different behaviour. In the presence of water vapour, the hydrates with \( n = 0 - 2 \) will form depending on the relative humidity, while in pure liquid water infinite swelling occurs and the silicate layers separate into a gel. As little as 3 wt% of Na-montmorillonite in water is needed to form a gel. A comparison of the freezing behaviour of Na- and Ca-montmorillonite can be found in Ref.[2].

The swelling and gel-forming properties of the smectites are utilized in a wide variety of technical applications. They can be found in cosmetic foundations, clearing additives for wine,
hygiene products for cats, non-drip paints, and cleaning agents for toilets, just to mention a few examples. A large-scale application is engineered barriers for the storage of nuclear and chemical waste materials and the confinement of polluted soils and garbage dumps. The clay that you will investigate is a bentonite from Wyoming. A mineralogical characterization of this clay can be found in the report [3]. The Wyoming bentonite consists of more than 80 wt% montmorillonite. Bentonites are formed in Nature by the reaction of volcanic ash (glass) and water containing salt. Bentonite is found in many places on Earth, the localities nearest to Lund are in Södra Sandby and Röstånga.

**Experimental**
- Purify the Wyoming bentonite using sedimentation and ion-exchange it with Na\(^+\) and Ca\(^{2+}\), respectively using 1 M NaCl and CaCl\(_2\) solution.
- Notice any differences in behaviour between the two ion-exchanged montmorillonites.
- Collect and evaluate the powder X-ray diffraction patterns of the wet Na and Ca-montmorillonites. Are there any minor minerals present in your samples? Alternative procedure: Instead use the dry powder that has been equilibrated with the ambient atmosphere in the laboratory. What relative humidity is expected in indoor air?
- Record the TGA/DTA-curves for the air-dried samples. Identify the reactions responsible for the features observed in the measurements.

**Working Schedule**
Make a risk analysis before you start. Don’t forget to bring lab coats and safety glasses.
- Week 1: Synthesis
- Week 3: Powder X-ray diffraction
- Week 5: Thermal analysis
- Week 7: Oral presentation of your Work

Because not all students can use the machines at the same time it is necessary that you book measurement time with your supervisor. This can vary from the scheduled course time.

**Literature**
The goal of this assignment is to give you an introduction to intermetallic chemistry and synthesis methods in metallic melts. You are expected to write a short report in the format of a research article and to report your project in a 5-10 minutes oral presentation. Descriptions of the X-ray techniques can be found in the text book [1]. The phase diagram below illustrates the synthesis conditions needed.

**Introduction**

Intermetallic compounds are formed in reactions between metals and they constitute a large class of materials that are distinctly different from the parent metals from which they are made. When the difference in electronegativity of the constituent metals is large, the intermetallics that form are polar, meaning that they have somewhat salt-like qualities. Typical examples are the Zintl compounds that form between alkali metals/alkaline earth metals and main group metals. The reaction can be seen as an electron transfer from the electropositive alkali/alkaline earth metal to the main group metal and the structure of the compound can be
rationalized in terms of isoelectronic analogies. A simple example is the reaction between Na and Pb. The electropositive Na donates one electron to Pb to form the expected Na\(^+\) ion, while Pb\(^-\), isoelectronic with P and As forms the tetrahedral ion Pb\(^4-\) resembling the gas phase species of the neighboring elements. For combinations of elements with smaller differences in electronegativity, valence rules are more relaxed, and quite frequently systems with substantial solid solution ranges are encountered. In the system studied in this assignment, Mn-Sb, the electronegativity difference is considerably smaller, and we expect the compounds to be metallic, and compositions may vary a lot. Both the two phases found in this system, Mn\(_2\)Sb and MnSb have significant composition intervals, and we expect cell parameters for the structures to vary accordingly. You will focus on the equimolar phase and prepare samples with compositions that probe the entire range for 400\(^\circ\)C. You will then determine cell parameters using powder diffraction and the composition using EDS.

**Experimental**
- Purify metallic Mn. When stored in air, Mn quickly gets covered by a relatively thick oxide layer. To purify the Mn, enclose it in a quartz ampoule and heat to 1000\(^\circ\)C. This will cause the surface MnO to react with the quartz and form a highly stable manganese silicate, leaving the metallic manganese in pure form.
- Prepare five samples with different compositions, seal them in quartz and prereact them in an induction furnace. Anneal the samples at 400\(^\circ\)C.
- Collect and evaluate the powder X-ray diffraction patterns of the samples to determine the cell parameters. Are the samples homogeneous?
- Check the composition using EDX.

**Working Schedule**
Make a risk analysis before you start. Don’t forget to bring lab coats and safety glasses.
5-9/9: Synthesis
19-23/9: Powder X-ray diffraction

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**Literature**
2.6. The Sb rich part of the system Mn-Sb at 600°C

The goal of this assignment is to give you an introduction to intermetallic chemistry and synthesis methods in metallic melts. You are expected to write a short report in the format of a research article and to report your project in a 5-10 minutes oral presentation. Descriptions of the X-ray techniques can be found in the textbook [1]. The phase diagram below illustrates the synthesis conditions needed.

Introduction

Intermetallic compounds are formed in reactions between metals and they constitute a large class of materials that are distinctly different from the parent metals from which they are made. When the difference in electronegativity of the constituent metals is large, the intermetallics that form are polar, meaning that they have somewhat salt-like qualities. Typical examples are the Zintl compounds that form between alkali metals/alkaline earth metals and main group metals. The reaction can be seen as an electron transfer from the electropositive alkali/alkaline earth metal to the main group metal and the structure of the compound can be rationalized in terms of isoelectronic analogies. A simple example is the reaction between Na
and Pb. The electropositive Na donates one electron to Pb to form the expected Na\(^+\) ion, while Pb\(^-\), isoelectronic with P and As forms the tetrahedral ion Pb\(_4\)^{4+} resembling the gas phase species of the neighboring elements. For combinations of elements with smaller differences in electronegativity, valence rules are more relaxed, and quite frequently systems with substantial solid solution ranges are encountered. In the system studied in this assignment, Mn-Sb, the electronegativity difference in considerably smaller, and we expect the compounds to be metallic, and compositions may vary a lot. Both the two phases found in this system, Mn\(_2\)Sb and MnSb have significant composition intervals, and we expect cell parameters for the structures to vary accordingly. You will focus on the equimolar phase and prepare samples with compositions that probe the entire range for 600°C. You will then determine cell parameters using powder diffraction and the composition using EDS.

**Experimental**
- Purify metallic Mn. When stored in air, Mn quickly gets covered by a relatively thick oxide layer. To purify the Mn, enclose it in a quartz ampoule and heat to 1000°C. This will cause the surface MnO to react with the quartz and form a highly stable manganese silicate, leaving the metallic manganese in pure form.
- Prepare five samples with different compositions, seal them in quartz and prereact them in an induction furnace. Anneal the samples at 600°C.
- Collect and evaluate the powder X-ray diffraction patterns of the samples to determine the cell parameters. Are the samples homogeneous?
- Check the composition using EDX.

**Working Schedule**
Make a risk analysis before you start. Don’t forget to bring lab coats and safety glasses.
5-9/9: Synthesis
19-23/9: Powder X-ray diffraction

**Because not all students can use the machines at the same time it is necessary that you book measurement time with your supervisor. This can vary from the scheduled course time.**

**Literature**
2.7. Synthesis of the superconductor YBa$_2$Cu$_3$O$_7$

Supervisor: Sven Lidin
Written report: Before the written exam.

The goal of this assignment is to prepare a superconducting ceramic using a sol-gel method for homogeneity. You are expected to write a short report in the format of a research article and to report your project in a 5-10 minutes oral presentation. Descriptions of the X-ray techniques can be found in the textbook [1].

Introduction
The discovery of high temperature copper oxide superconductivity produced an enormous activity in the field of solid state science that still has not abated. Superconductivity was first discovered in mercury by Kammerling Onnes on the 8th of April 1911, and he received the 1913 Nobel prize in chemistry for the discovery. The effect was later explained by Bardeen, Cooper and Schriffer (the BCS theory) and their explanation was awarded the same prize in 1972. (This was Bardeens second price. He also shared the price in 1956 for the transistor. Not a stupid man, Bardeen.) The BCS theory explains superconductivity as a pairing of electrons mediated by lattice vibrations, phonons. The relative energies involved precludes superconductivity above 30K. This higher limit of superconductivity was approached with the very best materials, such as Nb$_3$Sn. In 1986, this was disproven by the work on Bednorz and Müller who discovered superconductivity at considerably higher temperatures in an oxide material. Similar materials have now been shown to superconduct well over 100 K, and specifically over the temperature of liquid nitrogen.

To prepare well defined ceramics is a tricky business since the product often has a high melting point and forms as a layer between the grains of the original material, effectively stopping the reaction. The classical way to overcome this is to grind and regrind the powder mixture used for the synthesis. A more efficient way of preparing homogeneous starting mixtures is to coprecipitate the components of the synthesis as nanocrystallites. By using highly concentrated solutions of gel-forming organic components, the crystal growth of the inorganic material is hindered, and a mixture of nanoscopic crystalline inorganic material in an organic gel is produced. By firing this gel at elevated temperatures, the inorganic powders are reacted with each other, and a well defined product is achieved.

Experimental
- Prepare a solution (100mL) that is 14M in urea and 0.5M in oxalic acid.
- Mix 2.7g Y(NO$_3$)$_3$·5H$_2$O, 5.10g Cu(NO$_3$)$_2$·2.5$\text{H}_2$O and 3.80g Ba(NO$_3$)$_2$ in a beaker add to the urea-oxalic acid solution and stir to dissolve the powders.
- Place the solution in a water bath and heat to 100°C for 1h. Gases evolve during this process.
- Check the pH of the solution. If this is close to 7, allow to cool. Otherwise keep heating at 100°C.
- Add 100mL deionized water to dissolve unreacted urea and then filter the pale blue precipitate in a Büchner funnel. If the filtering process is slow, undissolved urea may need to be removed by adding more water.
- Dry the precipitate in a cabinet at 140°C for several hours.
- Heat the dry powder to 900°C in air for 16h.
- Form pellets in a press and heat to 900°C for 4 hours under nitrogen, and then for 24 hours at 500°C under oxygen. Allow to cool under oxygen.
- Collect and evaluate the powder X-ray diffraction patterns of the samples to determine the cell parameters. Are the samples homogeneous?
- Check if the material is superconducting by examining if it displays the Meissner effect.

Working Schedule
Make a risk analysis before you start. Don’t forget to bring lab coats and safety glasses.
5-9/9: Synthesis
19-23/9: Powder X-ray diffraction, Meissner effect measurement.

Because not all students can use the machines at the same time it is necessary that you book measurement time with your supervisor. This can vary from the scheduled course time.

Literature