Synthesis of BaTiO$_3$ by hydrothermal methods and via a heterometallic alkoxide.

Introduction:

During the last decades the use of functional oxides for new applications has lead to increased demand regarding purity and homogeneity. Traditional methods used for synthesis of heterometallic oxides usually employ high temperature and will often result in inhomogeneity at a microscopic level. Other sol-gel methods, like the citrate route, do circumvent these problems, but may lead to contamination with carbon, often in the form of carbonates. This is especially important for elements, which easily form carbonate.

When utilizing the materials in microelectronic devices it is often necessary to synthesize the materials as thin films (e.g. 100-500 nm thickness for ferroelectrical capacitors). Methods used for producing films in this thickness range are e.g. suttering, PLD (pulsed laser deposition) and CSD (chemical solution deposition). In the CSD method a solution (or sol) of metalorganic compounds with the same stoichiometry as the desired product is used. CSD is much used as the method does not require much equipment and there is no need for time consuming optimization of parameters in order to obtain the correct stoichiometry. For practical application, the crystallization temperature is important in order to avoid damage to other components during the heat treatment. The crystallization temperature is reduced when reducing the diffusion distance needed for the atoms to organize into a crystalline arrangement. Therefore, homogeneity on a nanometer scale is an advantage. This is not accomplished by traditional sol-gel methods where several precursors are used.

Multimetallic alkoxides are molecular species which contain to or more metal atoms. These molecules then already have a homogeneous distribution of the metal atoms on a nanometer scale, which is maintained during a decomposition process. Crystallization often takes place at temperatures from 450°C to 550°C. Thus, metal alkoxides are attractive precursors for metal oxide synthesis.

Ferroelectricity was observed for the first time in BaTiO$_3$ (T$_C$=130 $^{\circ}$C). This material takes the perovskite structure and below T$_C$ it is tetragonal with a dipolar moment along the c-axis. Above the Curie temperature the material is cubic with zero net dipolar moment.The material transforms to structures with lower symmetry below room temperature. In tetragonal BaTiO$_3$ the potential of Ti^{4+} along the c-axic form a double-well. An electrical field opposite the polarization direction may pull Ti4+ over the potential barrier, thereby reversing the polarization. BaTiO$_3$ is a technologically

important dielectric material and is used e.g. in capacitors (ϵ_r = 2000-10000) and PTC-resistors (positive temperature coefficient). All ferroelectrica are also piezoelectric, but other piezoelectric materials are more important than $BaTiO_3$.

Particles formed by crystallization of alkoxide-gels are very small. This makes the phase transition at 130°C by cooling energetically unfavourable. The powder resulting from the synthesis is therefore in a metastable cubic modification and must be heated to 800-900°C in order to obtain traces of the tetragonal phase forming by cooling. In order to achieve 100% conversion, heating to above 1000°C is necessary.

As it is the tetragonal phase which is ferroelectric and therefore the technologically important material, the possibility of synthesizing tetragonal $BaTiO_3$ directly at low temperature has been pursued. The challenge is to obtain sufficient crystal growth at low temperature in order to avoid the tetragonal-cubic phase at 130°C. This may be possible by using hydrothermal synthesis, where it is possible to crystallize metal oxides from 150°C.

In this exercise we will use X-ray powder diffraction to investigate structure (symmetry) and phase purity.

Synthesis:

Alkoxide:

We want the organic content to be as low as possible in order to avoid carbon contamination. Small alkoxide groups like methoxy and ethoxy result in either unstable alkoxides or alkoxides with low solubility. Iso-propoxy is a much used alkoxy group, and we are going to use this for our reactions. A heterometallic alkoxide may be prepared by reacting the homometallic alkoxides under reflux. Titanium iso-propoxide is readily available and therefore we will synthesize only barium isopropoxide. This is an oligomeric compound, $1/m[Ba(OPr^i)_2]_m$, which is dissolved during the reaction with Ti-isopropoxide. This is also a good indication that a larger heterometallic species is formed, as these generally have higher solubility.

Alkoxides of electropositive metals may be synthesized by direct reaction between metal and the alcohol (Lewis base), e.g.:

$$Ba(s) + 2ROH \rightarrow \frac{1}{m}[Ba(OR)_2]_m + H_2 \uparrow \qquad \text{Eq. 1}$$
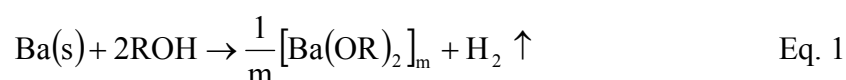
The reaction rate increases with the acidity of the alcohol, decreasing steric hindrance, basicity of the metal and the solubility of the product. All alkali metals react very fast with light alcohols to give pure well defined products. The alkaline earth metals give

more complex products and the least electropositive metals need a catalyst in order to speed up the reaction rate (e.g. Mg). Barium is, however, very electropositive and needs no catalyst. When a very soluble product is formed cooling is necessary. Barium isopropoxide is, however, insoluble and forms a barrier between metal and alcohol which slows down the reaction. A suitable reaction rate between barium and isopropanol at room temperature is obtained by using fairly small particles, 0.2 – 0.5mm. Note that barium is generally very reactive toward hydroxyl containing compounds, such as water. **All handling of barium must therefore be done in inert atmosphere.**

Synthesis of alkoxides of metals which do not react directly with alcohols may be performed by alcolysis of metal amides. The starting compound is here a metal halide:

$$MCl_2 + 2\,LiN(C_2H_5)_2 \rightarrow M[N(C_2H_5)_2]_2 + 2\,LiCl\downarrow \qquad\qquad \text{Eq. 2}$$
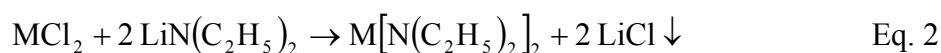
LiCl is removed by filtering and the alcolysis is readily done by adding alcohol to the amide:

$$M[N(C_2H_5)_2]_2 + 2\,ROH \rightarrow M(OR)_2 + 2\,HN(C_2H_5)_2 \uparrow \qquad\qquad \text{Eq. 3}$$
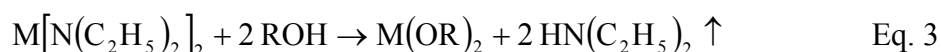
Another method is to react metal halides with alkoxides of alkali metals, e.g.:

$$MCl_3 + 3\,NaOR \rightarrow M(OR)_3 + 3\,NaCl\downarrow \qquad\qquad \text{Eq. 4}$$
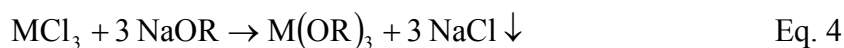
Reactions often give less than 100% yield and purification e.g. by sublimation or recrystallization must be used to enrich the alkoxide.

Things to consider during the exercise:

You must now synthesize and handle compounds which are very air sensitive. Directions of how to use the vacuum line will be given. However, not all steps may be covered; it may not be specifically noted that a flask needs to be evacuated on the vacuum line before connecting it to the rest of the system. **It is therefore important to constantly consider whether air may enter the system in any way and get into contact with other compounds on the vacuum line.** You must therefore deveop routines and sequences for opening and closing of valves for various operations e.g. putting an empty flask on the vacuum line. Remember that air diffuses from one place to another. **It is therefore important to close the access to other flasks containing air sensitive compounds before evacuating a flask containing air. It is also important to avoid access to flasks containing solvents when you evacuate the**

line. Otherwise the content may boil and enter the line. All ground glass joints (NO: slip) must be secure by clamps or elastic bands.

Readying the vacuum line:

In order to protect the vacuum pump there must always be liquid nitrogen in the cold trap before the pump. Start the pump with valves 1 and 2 closed (refer to drawing). If there is a gas ballast valve this should be left open until the pump is warm. This increases the life time of the pump. Open valves 2, 4, 8 and 10 in order to evacuate the system. After a couple of minutes valve 2 may be closed, then nitrogen is released into the system from the cylinder (until bubbles are observed in the mercury container)??. Then evacuation is repeated.
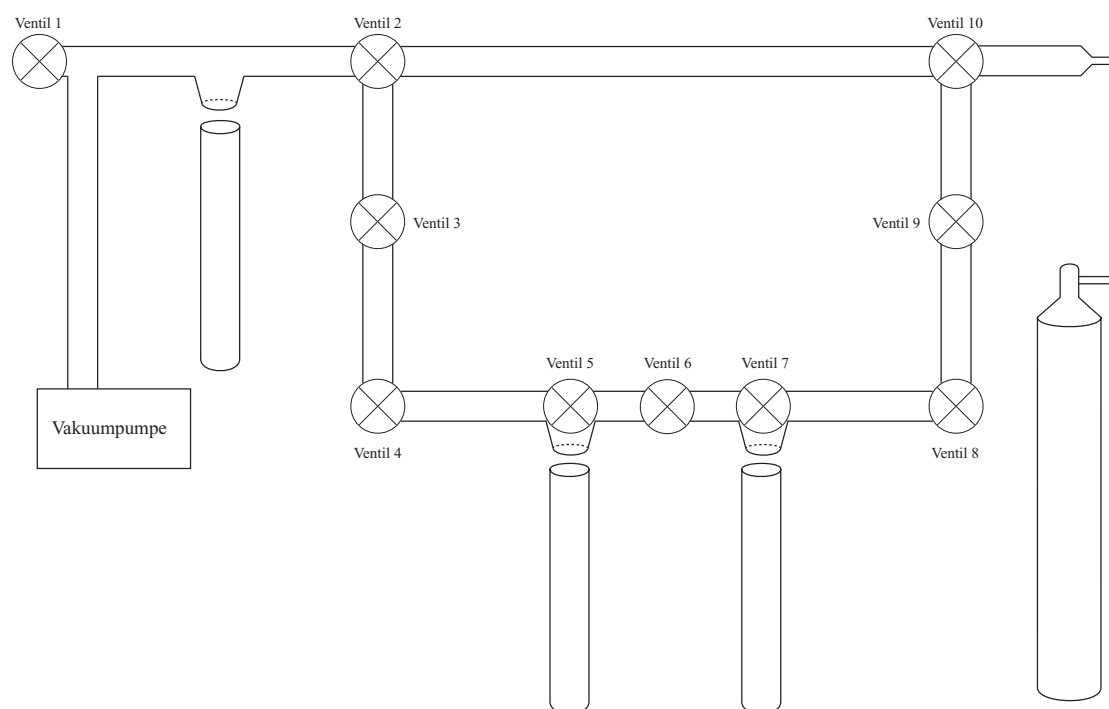

Figure 1: Illustration of the vacuum line for synthesis under inert conditions.

Solvent drying:

When synthesizing compounds which are sensitive to Lewis bases it is important to dry all solvents used. Liquids as hexane, benzene, THF, di-ethyl ether etc.do not react with sodium metal. These may therefore be pre-dried by refluxing with 5x5mm pieces of sodium for 1 hour. In order to remove the last traces of water and dissolved gasses, 10g benzophenone per liter is added and the mixture is refluxed for until a blue/violet

solution is obtained. The colour indicates the presence of a radical and the solution is therefore free of reactive species. The solvent may then be distilled.

Alcohols, on the other hand, react with sodium and must be dried by refluxing with e.g. CaH_2 or a corresponding metal alkoxide. After 12 hours the solvent may be distilled.

Solvents which do not react with sodium metal are stored over 5x5mm sodium bits or wire. All solvents are stored under nitrogen in a schlenk-flask. Nitrogen flow is used when taking solvent by a pipette in order to avoid uptake of moisture from the air.

For this exercise you will be receive dry solvents.

Synthesis of $1/m[Ba(O^iPr)_2]_m$

Before starting the laboratory responsible will show you how to operate the glove box. **<u>Please remember always to close the air lock from the inside when you work</u>**. This is easy to forget if e.g. more equipment has to be brought into the glove box.

Take a clean, dry round-bottomed flask, a funnel with ground glass joint and a glass stopper with some vacuum grease and a spatula into the glove box. Ba(s) is found inside the glove box. Weigh 0.5g Ba, put on the stopper, secure with a string and take the equipment out of the glove box. Evacuate a T-piece and place the flask in this.

An important thing to remember when working with liquid/soilid reactions which are fast and/or releases heat is to always dissolve or disperse the solid in an inert solvent. If you add a reactive liquid directly to a solid it will produce a large amount of heat just where the liquid is in contact with the solid without any possibility of transporting the heat away. Decomposition of the product may occur. Therefore, 20 ml dry hexane and a bar magnet is added to the flask containing the barium metal. Calculate the amount of isopropanol needed and add a surplus to the flask under stirring. After a short while, evolution of hydrogen will start and then $1/m[Ba(OPr^i)_2]_m$ will precipitate. Continue stirring until all barium has reacted.

Synthesis of $[BaTi(OH)(O^iPr)_5(Pr^iOH)_3]_2$:

Synthesis of heterometallic alkoxides are often performed by simply reacting the monometallic alkoxides[1]. As this is a Lewis acid-base reaction, reactivity decreases with decreasing difference in Lewis acid/base strength of the reactants.

Task:
Write the reaction equation for formation of $[BaTi(OH)(O^iPr)_5(^iPrOH)_3]_2$. What must be present in addition to $1/m[Ba(OPr^i)_2]_m$ og $Ti(O^iPr)_4$?

We chose to weigh the amount of Ti-(O^{i}Pr)$_4$ in stead of using a pipette as this will be more precise. This must be done in the glove box. Calculate how much Ti-(O^{i}Pr)$_4$ is needed in order to obtain a ration between Ba and Ti of **1:0.98**. This is done in order to ensure a perfect stoichiometry in the final product. ***Can you think of why we may obtain stoichiometry by using non-stoichiometry here?***

In the glove box you will need:

- A couple of Pasteur pipettes with rubber ball.
- A flask containing **dry** 2-propanol, secured by strings.
- A weighing container
- The flask containing 1/m[Ba(OPr^i)$_2$]$_m$ secured with strings.

Weigh the calculated amount of Ti-(O^{i}Pr)$_4$ into the weighing container and add this to the flask. Flush with 2-propanol. Be careful not to spill anything and rinse well. Replace the stopper, take the equipment out of the glove box and mount the flask on the cooler, which previously has been mounted on the vacuum line via a T-piece, and evacuated. Reflux for three hours. Note the dissolution of barium isopropoxide after a short while.
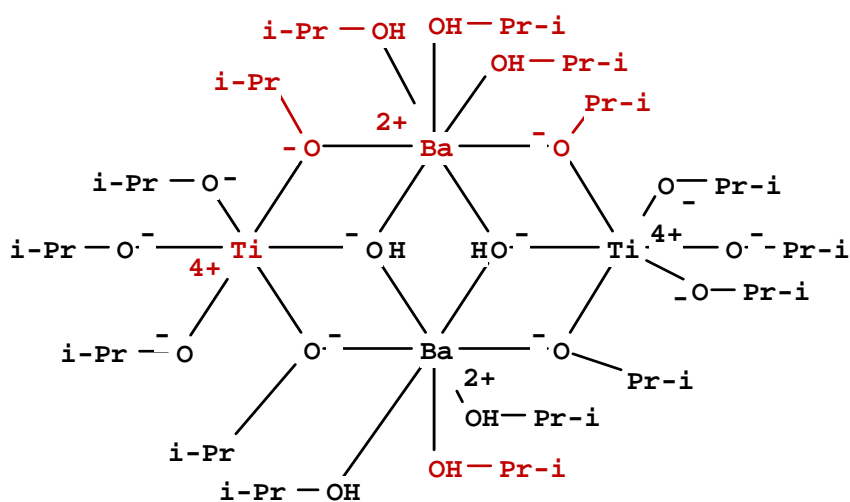

Figure 2: [BaTi(OH)(O^{i}Pr)$_5$(^{i}PrOH)$_3$]$_2$

As we have used a small surplus of Ti-(O^{i}Pr)$_4$ you will notice that the solution does not become entirely clear. As the molecule produced does have an exact 1:1 stoichiometry between Ba and Ti we may now ensure perfect stoichiometry by filtering off the surplus of 1/m[Ba(OPr^i)$_2$]$_m$.

When doing this you must take the flask off the line and into the glove box. Remember the strings! For filtering a 0.2μm syringe filter is used. You may leave the flask for precipitation for a few minutes in order to avoid clogging the filter. Place the piece of PVC hose on the syringe and suck up the content from the top, avoiding too much precipitate. Then switch to using the filter, and press the liquid through. This may be a bit hard. **Be careful that the filter is not pressed off or destroyed**. If the filter clogs up, it may help to pull the syringe back a bit.

When you have done this you have obtained a solution of $[BaTi(OH)(O^iPr)_5(^iPrOH)_3]_2$-molecules in Pr^iOH and hexane.

Hydrolysis:

In order to transform the solution to a gel-like state the alkoxide must be hydrolysed. During hydrolysis a three dimensional framework of oxygen bridges is formed.
Alkoxides hydrolysis in contact with water:

$$M(OR)_x + H_2O \rightarrow M(OR)_{x-1}(OH) + ROH \qquad \text{Eq. 5}$$
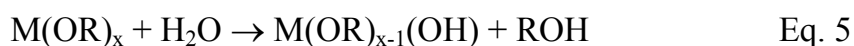
At the same time a condensation process occur:

$$2\, M(OR)_{x-1}(OH) \rightarrow (RO)_{x-1}M\text{-}O\text{-}M(OR)_{x-1} + H_2O \qquad \text{Eq. 6}$$

The degree of hydrolysis is defined as:

$$h = [H_2O]/[M(OR)_x] \qquad \text{Eq. 7}$$

and depends on the purpose of the produced material. The transition from a sol to a gel is a very complex process and may involve many more steps than described here. By controlling

og er avhengig av hvilket formål vi skal benytte produktet vårt til. Selve overgangen fra sol til gel er en meget komplisert prosess og kan innebære mange flere ledd enn beskrevet her. Ved å styre parametere som temperatur, konsentrasjon, reaksjonshastighet, tilsettingsstoffer (for eksempel koordinerende løsningsmidler) etc. kan man styre hvilke fysiske egenskaper den endelige gelen vil få. Man kan katalysere prosessen i surt eller basisk miljø. Syrekatalysert hydrolyse gir en lineær polymer med få greiner. En slik polymerstruktur kan egne seg for eksempel til produksjon av fiber.
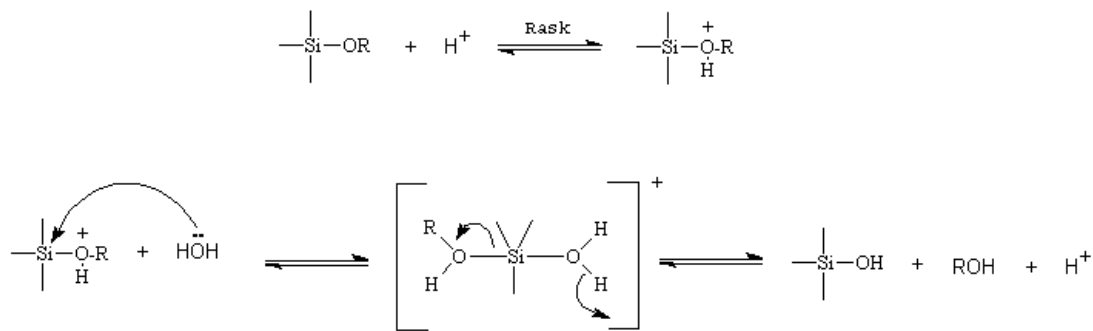
Figur 3: Syrekatalysert hydrolyse

Ved bruk av base som katalysator vil polymeriseringen foregå tilfeldig i 3 dimensjoner og man får dannet partikkelklustere. Ved basekatalyse vil man ikke få en nettverksstruktur og det dannes ikke gel på samme måte som ved bruk av syre.
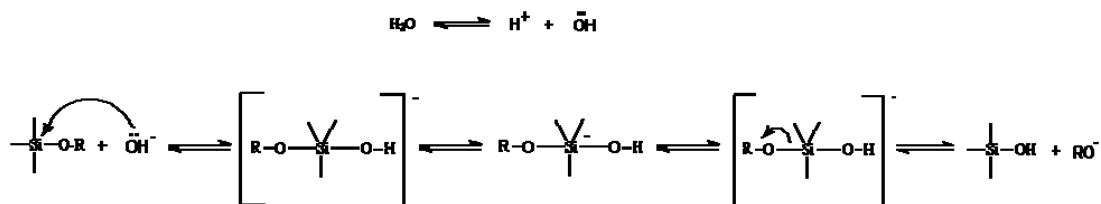
Figur 4: Basekatalysert hydrolyse

Når man tar bort løsningsmiddelet vil den resulterende xerogelen bestå av nanopartikler, og vil følgende ha meget stor reaktivitet. Tabletter laget av gel fra vårt produkt vil derfor for eksempel kunne sintres til høyere tetthet ved lavere temperaturer enn ved andre metoder. Det er også eksempler på at materialet faktisk kan smelte en del lavere enn det virkelige smeltepunktet da nanopartikler vil gi andre fysikalske egenskaper p.g.a. det høye overflatearealet. Man vil også ved rette betingelser kunne lage oksidglass. Dersom h overstiger 1.5-2 vil nettverket bli så tett at "gelen" feller ut fra løsningsmiddelet.

For hydrolyse av blandingen bruker vi en dryppfunnel. Monter og evakuer denne på linja via en t-overgang. Husk på tomvolumet i kranen.
Vi skal syrekatalysere hydrolysen med eddiksyre. Regn ut hvor mye vann og eddiksyre du trenger for at h=0.5 og $[H^+]/[BaTi]=0.05$. Hvis eddiksyra inneholder vann må du ta dette med i beregningen. Husk å skru igjen kranen på funnelen før du tilsetter vann, eddiksyre og ca. 25 ml **tørr** 2-propanol. Husk å blande vannet og eddiksyren godt med alkoholen. Monter kolben med alkoksidet på funnelen og tilsett innholdet dråpevis under sterk omrøring. 1 dråpe i sekundet er passe hastighet. Normalt tar geldannelsen en stund, slik at etter tilsettingen helles innholdet i et begerglass for geldannelse over natten. Vi fjerner løsningsmiddelet samtidig ved å

sette begerglasset på en kokeplate på lav varme (40-50 ^{o}C). Den resulterende xerogelen deles i to og krystalliseres ved henholdsvis 500 og 800 ^{o}C i en time. Sjekk hvilken modifikasjon av BaTiO$_3$ prøvene dine har ved hjelp av røntgen.

Hydrotermal syntese:

Introduksjon:

Ved hydrotermal syntese krystalliserer vi produktet vårt i vandig miljø ved temperaturer over 100 ^{o}C og normalt ved trykk fra 1-200 atm. Vi utnytter at løseligheten av stoffer i vann øker drastisk med temperatur og trykk. Flere fysikalske egenskaper hos vann er veldig avhengig av temperatur og trykk. Bl.a. så avtar viskositeten med økende temperatur. Dette gjør at mobiliteten til løste ioner og molekyler er større enn under normale forhold.

Den lave temperaturen gjør at vi kan lage stoffer som ellers er vanskelige å krystallisere ved høyere temperaturer. Man kan for eksempel lage stoffer som inneholder vann/hydroksyl i strukturen. Ved bruk av metoder som trenger høy temperatur får man imidlertid nesten alltid termodynamisk stabile produkter. Vi skal imidlertid finne ut i løpet av denne oppgaven at det er mer enn temperatur som avgjør om man for det termodynamisk stabile produktet eller ikke. Ved å styre parametere som trykk, temperatur og konsentrasjoner kan vi styre hvilket produkt som blir dannet og ofte også hvilken partikkelstørrelse dette skal ha. Dette baserer seg vanligvis på empiri. Normalt skal man få god homogenitet, men det forkommer at man får segregering av elementer i kornene. Særlig hvis man har mange forskjellige kationer.

Andre løsningsmidler enn vann kan også brukes og man kan slik utvide begrepet hydrotermal syntese til solvotermal syntese. Mange av krystallene vi finner ute i naturen er for øvrig av hydrotermal opprinnelse. For eksempel kvarts, ametyst og zeolitt.

For syntese av uorganiske forbindelser lages en blanding av de ønskede kationer. Både faste stoffer og vannløselige salter som nitrater kan brukes. Ved bruk av anioner som ikke kan dekomponeres slik som halogenider kan disse i noen tilfeller inkorporeres i strukturen. Hydrolysert alkoksider er ofte også brukbare utgangsstoffer. Utgangsstoffene blandes eller suspenderes i en vannløsning som gjerne er tilsatt et krystalliseringshjelpemiddel (ofte en base e.g. KOH eller fluorid), og tilsettes en autoklav. Opp til 250 ^{o}C kan man bruke en stålautoklav med tefloninnlegg (Figur 5). Disse kan motstå trykk opp mot 150 bar hvis de er riktig designet. Høyere temperaturer krever andre typer autoklaver. En gullforet autoklav kan brukes opp til 450-500 ^{o}C.
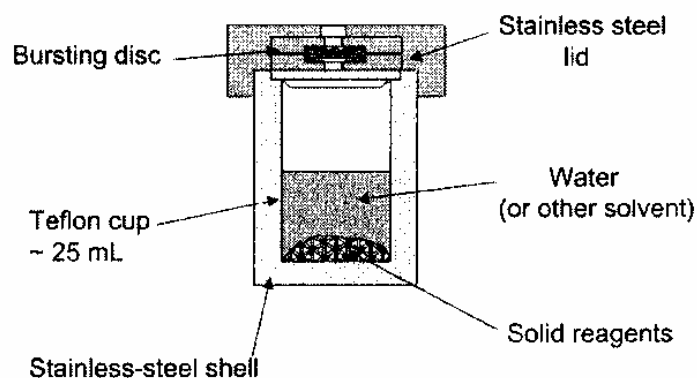
Figur 5: Autoklav med tefloninnlegg som kan brukes opp til 250 °C[2].

Det er viktig å styre fyllingsgraden av autoklaven. En figur som viser trykk som funksjon av temperatur og fyllingsgrad er vist i Figur 6. Normalt fyller man autoklaven så den er ca 75 % full. Vann utvider seg en del når det varmes opp, slik at hvis autoklaven fylles helt kan denne sprenge. Vann er som kjent tilnærmet innkompressibelt i væskeform. Dette kan sees som meget raske trykkøkninger i Figur 6. Figur 7 viser vanndamptrykket som funksjon av temperatur når autoklaven ikke er helt full.
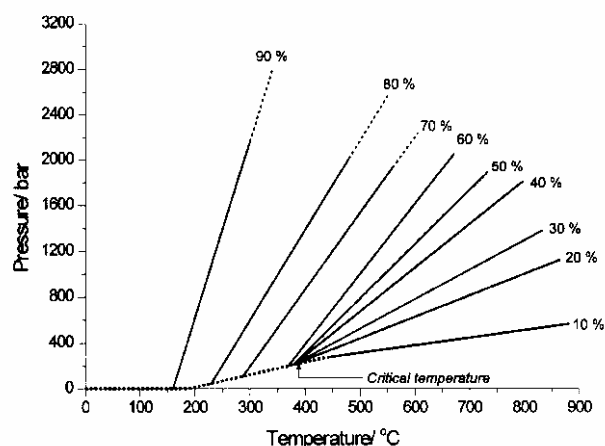
Figur 6: Trykk i lukket beholder som funksjon av temperatur og fyllingsgraden av vann[2].
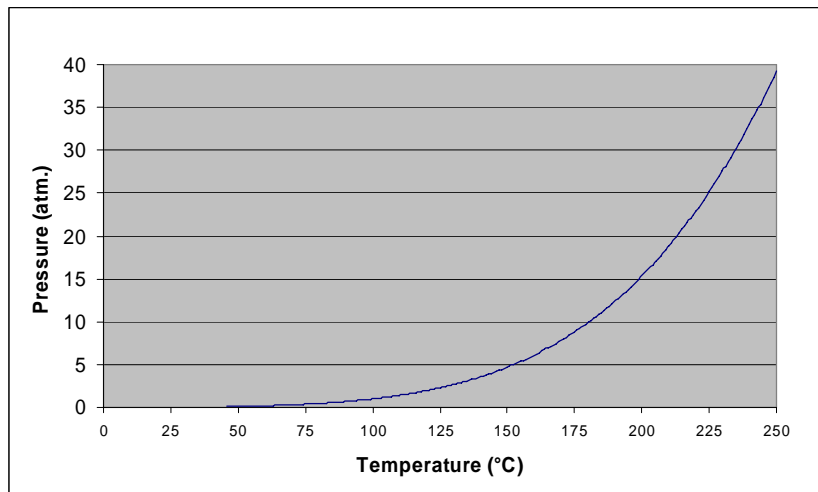
Figur 7: Vanndamptrykk som funksjon av temperatur

Selve oppgaven:

Prosedyrer for hydrotermal syntese er som oftest enkle i forhold til andre metoder. En stor fordel er at hele syntesen foregår i ett trinn.

Ved å bruke $Ba(OH)_2$ som utgangsstoff fant Dutta og Greg[3] ut at produktet alltid hadde metastabil kubisk modifikasjon på grunn av liten kornstørrelse. Løsningen var å bruke $BaCl_2$ siden klorid akselererte veksten. Kornene må ha en størrelse på ~1µm for at den ferroelektriske overgangen ved 130 ^{o}C skal være energetisk gunstig.

Vei ut 0.01 mol NaOH og løs dette i 10 ml ionebyttet vann i teflonkoppen. Tilsett deretter 0.025mol $BaCl_2$ og TiO_2 (Anatas). Lukk autoklaven og sett denne ved 240 ^{o}C i en uke. Det ferdige produktet filtreres fra løsningen og vaskes med mye ionebyttet vann for å fjerne lut og klorid. Tørk deretter stoffet på et urglass i et varmeskap. Sjekk deretter hvilken modifikasjon av $BaTiO_3$ du har fått ved hjelp av røntgen. Hvis det er mulighet er det interessant å sammenligne alle prøvene du nå har laget i SEM.

Spørsmål til oppgaven:

- Hvilke fordeler har syntese via alkoksid sammenlignet med for eksempel sitratmetoden?
- Hvilke fordeler og ulemper har henholdsvis alkoksidsyntese og hydrotermal syntese i forhold til hverandre?
- Til hvilke formål er metall-alkoksider spesielt godt egnet som forløpere?
- Til hvilke formål er hydrotermal syntese en god metode?
- Nevn noen typer syrer eller baser man vil kunne bruke til katalyse av hydrolyse
- Forklar bakgrunnen for de forskjellige modifikasjonene av $BaTiO_3$ du fikk og hvorfor hydrotermal syntese er å foretrekke for $BaTiO_3$ i bulkform.