

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 inhomogeneities 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 alcoxides 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-alcoxides are attractive precursor to prepare metal-oxides.

Ferroelectricity was first observed with BaTiO₃ ($T_C = 130\text{ }^\circ\text{C}$). 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 transform to lower symmetry systems below room temperature. In the tetragonal BaTiO₃, the potential of Ti^{4+} along the c-axis can be reversed by an electric field towards the polarizing direction 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).

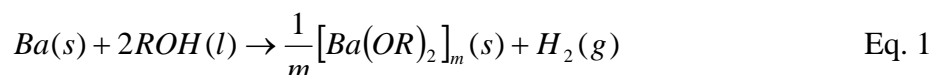
Only nano-particles are formed during the crystallization from the alcoxide gel. Hence, the phase transition through the Curie temperature (130 °C) upon cooling will not be energetically favourable. The formed product will therefore be meta-stable cubic. Heat treatment at 800-900 °C is required to observe 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.

Alcoxide:

It is desirable to operate with as low organic content as possible to avoid carbon-containing impurities. Small aloxides like metoxide and ethoxide are usually unstable or form insoluble complexes. A common applied alcoxide is isopropoxide. Titanium isopropoxide is commercial available. Here, we have to synthesize Barium isopropoxide, which is an oligomer expressed as $1/m[Ba(O^iPr)_2]_m$. 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 alcoxide can synthesize directly by mixing the metal and the alcohol.



The rate of reaction increases with the acidity of the alcohol, less steric obstruction, the basicity 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 (N₂, 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 CaH_2 or a corresponding metal alcoxide (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 N_2 . Note that the vacuum valve and the N_2 valve at the same exit should not be open at the same time.

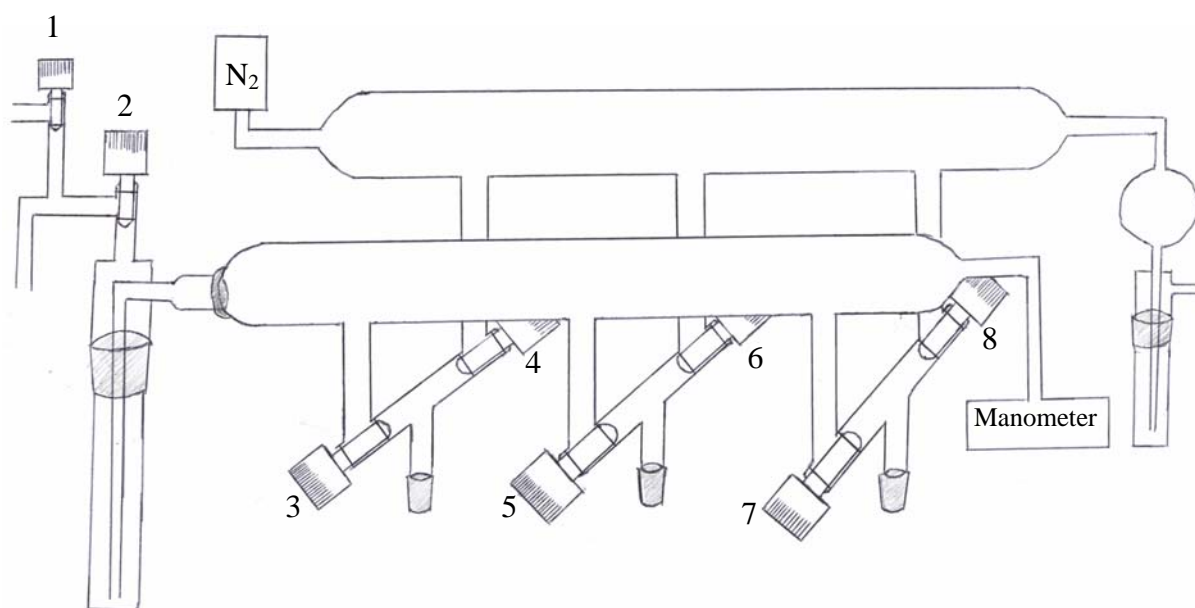


Figure 1. Illustration of the vacuum line.

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 supply 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 (O_2 , H_2O) 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 is 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-OⁱPr 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)(OⁱPr)₅(PrⁱOH)₃]₂:

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

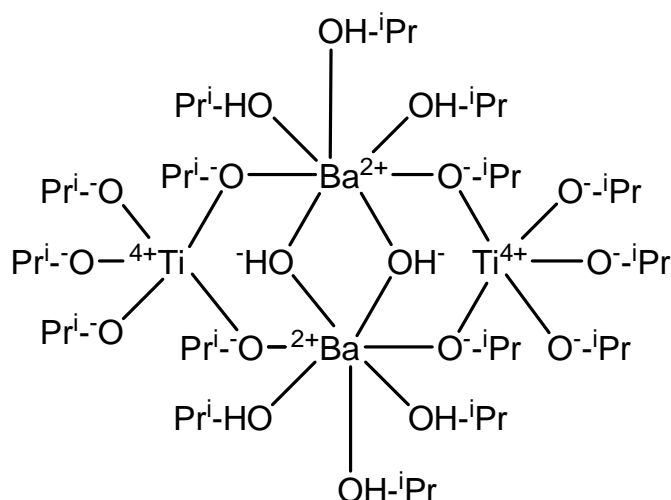


Figure 2. Structural formula of [BaTi(OH)(OⁱPr)₅(PrⁱOH)₃]₂.

Write the reaction equation of formation of [BaTi(OH)(OⁱPr)₅(PrⁱOH)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 $\text{Ti}(\text{O}^i\text{Pr})_4$ and isopropanol.
- Insert the other end of the Teflon tube through the septum of the flask containing $\text{Ti}(\text{O}^i\text{Pr})_4$ 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 $\text{Ti}(\text{O}^i\text{Pr})_4$ 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).

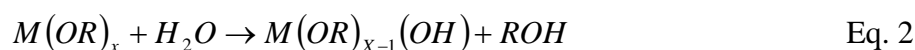
Start the synthesis by heating the flask to reflux for 3 hours. Remember to apply cooling. Note that Barium isopropoxide oligomer slowly dissolves. Since we have added less Titanium (Ba:Ti = 1:0.98) to react with Barium isopropoxide oligomer, the solution will remain unclear. The dissolved species should be $[\text{BaTi}(\text{OH})(\text{O}^i\text{Pr})_5(\text{Pr}^i\text{OH})_3]_2$, isopropanol and hexane. These species can be isolated by filtration and the solution should contain perfect Barium to Titanium ratio. The $[\text{BaTi}(\text{OH})(\text{O}^i\text{Pr})_5(\text{Pr}^i\text{OH})_3]_2$ 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.

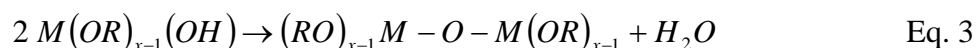
- Open valve 8 and the valve on the 250 ml schlenk flask. The gas will escape from the side tube of the schlenk flask.
- Connect “gas in” (open) to the side tube of the 250 ml schlenk flask. The gas is now entering the system from “gas in” (open) and the vacuum line and exit through the gas washing flask 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 alcoxide results formation of a gel. During the hydrolysis, an extended network of Oxygen bridges is formed. Hydrolysis of alcoxide occurs in reaction with water.



Simultaneously, a condensation process happens:



The degree of hydrolysis is defined as followed:

$$h = \frac{[H_2O]}{[M(OR)_x]} \quad \text{Eq. 4}$$

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 N_2 .

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, N_2 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 quartz 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.

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.

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.

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 $\text{Ba}(\text{OH})_2$ as a reactant to synthesize BaTiO_3 results always the metastable cubic phase. The reason is the particle size is too small. The reported solution is to use BaCl_2 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 alcoxide instead of citric acid?
- For what purposes will metal alcoxide 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 BaTiO₃?