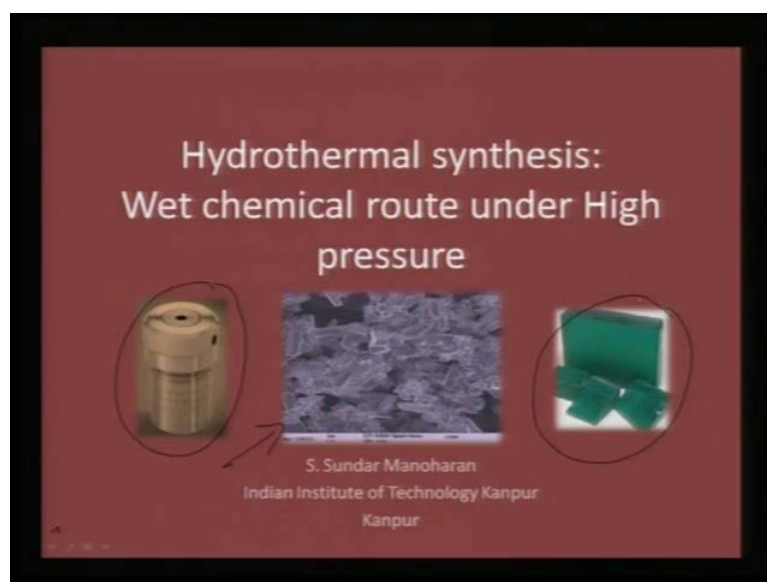


Materials Chemistry
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Module - 1
Lecture - 8
Preparative Routes High Pressure Hydrothermal Technique

In this lecture, I will be concentrating on very important aspect of material synthesis, that is through hydrothermal route.

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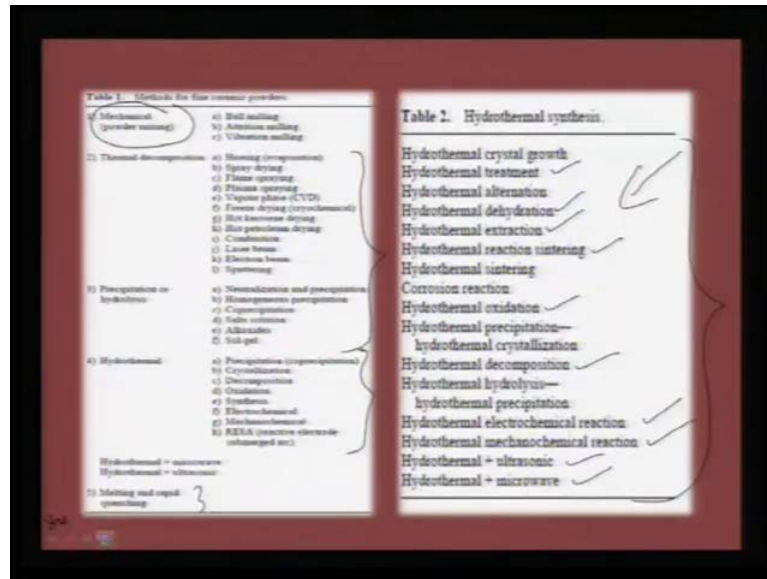


And hydrothermal synthesis is a very important technique, because it combines the principle of both chemistry as well as physical approach, where we are trying to use chemical routes, but incorporating high pressures. So, this is one technique which is fifty, fifty of both physical as well as chemical approach, therefore I have dedicated one full lecture on this to understand, the principle behind it how we can fine tune, and the scope of this method which is not only being used for lab scale synthesis, but also has gone into tons of material synthesis in the past few decades.

As I have pointed out, hydrothermal is a high pressure synthesis, therefore the moment you think about high pressure, you think of a bomb or a enclosure. In other words you do the reaction in a confined system, closed system. Therefore high pressures will be generated from within. And this is another cartoon which we will see down through the

slides, the specificity of hydrothermal route by which one can aim for a particular morphology of a crystal and then you can get it. And also, if you want to grow crystals this is one of the fissile route by which you can grown single crystals, as you would see this is one of the gem stone, which is prepared with a near perfection. And hydrothermal can therefore, be used for scalability also it is not just limited to lab scale approach.

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Now, where does hydrothermal synthesis stands if you look at the conventional methods for fine ceramic powders, the top down approach is the mechanical milling, where you start from powders of irregular size and shape and then ball mill it and try to get it in nano size. And then comes, the chemistry routes a long list of chemistry routes where precipitation or thermal decomposition of different natures can help in making materials. And as you would see here, hydrothermal itself now transcends to be a area of research because of the fissile nature by which, we can modulate the synthesis.

And on the right side this cartoon shows a list of hydrothermal synthesis that has emerged over the years. As you would see this is a endless result you can start with just a crystal growth and we often think hydrothermal is to initiate a crystal growth or crystallization process. But, it is much more than that you can actually do hydrothermal treatment, do dehydration, extraction that is leaching from minerals then you can also attempt for hydrothermal sintering, we can do hydrothermal oxidation and decomposition reactions can be done.

And then hydrothermal electrochemical, mechano chemical reactions can also be engineered, and over the years the usefulness of a hydrothermal process as also transcended a fusion of two different approaches. For example, hydrothermal ultrasonic, hydrothermal microwave reactions also aimed, so that whatever target compounds that we have, it is very easy to prepare, if we can integrate two different approaches. And then of course, you also have this melting and rapid quenching which is nothing but crystal growth technique, which we will also see in one of our lectures.

So, as you would see here this is an endless route and there are a lot of combinations that are possible, and as we record this lecture today a decade from now hydrothermal can transcend to other various avenues also. So, we will just look at a few examples, first of all the principles of hydrothermal, growth or hydrothermal process and then take specific examples to understand, what are its limitations and what is the land scale of this hydrothermal process.

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Hydrothermal Synthesis

- The reactants are dissolved (or placed) in water or another solvent (Solvo thermal) in a closed vessel
- Bomb is heated above BP
- Conventional or MW oven
- Commercially:
– Tons of zeolites daily

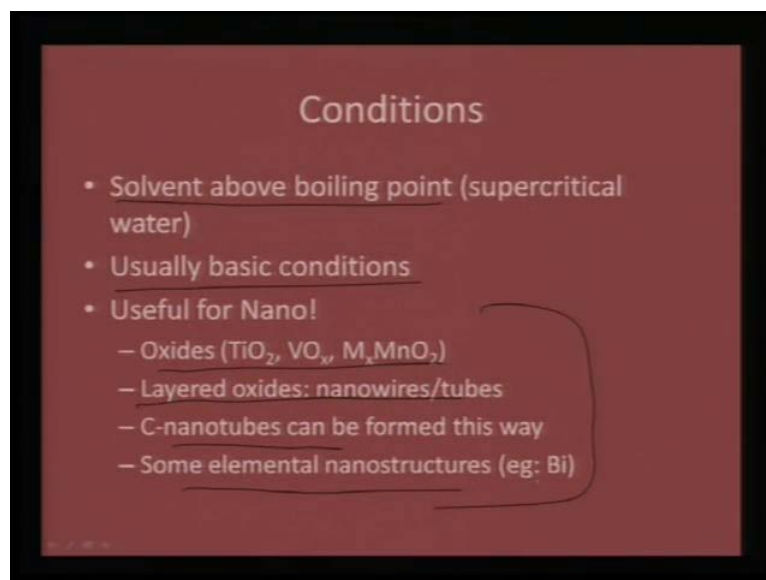
Nazari, G.A., Pistoria, G. *Lithium Batteries*; Klumer Academic Pubs., Boston, 2004

To start with let us say, hydrothermal synthesis is all about the reactants are dissolved or placed in water or another solvent. If you put it in some solvent, organic or inorganic solvents then you call that as solvo thermal, you call it hydrothermal if you just use water or you can use water with some additives, that is also called a solvo thermal in one sense. Now, you put the whole thing in a bomb and this is actually a metal, outer surface is a metal, but then what you see inside can be a bomb with Teflon containers.

Therefore, this is not the container by itself this is a bomb to just control and release, and through this RFS you can also try to leak out a gas. So, that if it is not a controlled closed vessel reaction, it can turn out to be a bomb, therefore you can actually release it with a small diaphragm which can actually leak out excess pressure. So, this is the simplest way we can define a hydrothermal reaction, and this bomb is heated above the boiling point of the liquid, either solvent or water.

So, that you reach it is super criticality and we can also try to do this heating, in a conventional furnace or we can do have a special arrangement by which we can heat it inside or we can engineer it in a more sophisticated way now a day's using microwave oven. And commercially tons of zeolites being made by hydrothermal process, mainly because making zeolites or cage structures is a very challenging work or very challenging attempt. And therefore, expertise is needed to get the size and shape control of the product. So, zeolites I will show one example of how this has made into application, but we can actually talk in terms of tons of zeolites can be made using such auto clips.

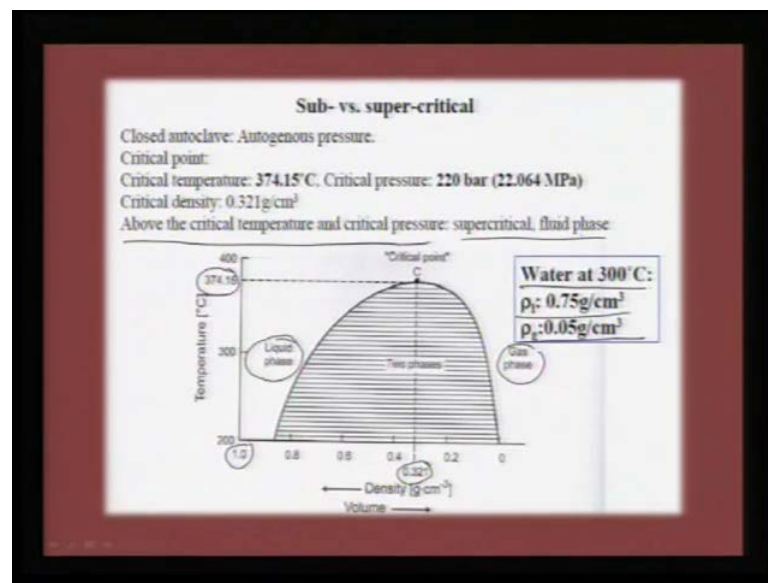
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Now, what are the conditions solvent whether it is water or any other solvent, it is taken to it is boiling point and usually some basic solvents are also added, like sodium hydroxide, potassium hydroxide. So, most of the reactions are done in basic conditions and this particular method is also used for, making nano oxides for example, simple

oxides or substituted ones, layered oxides can be transformed into nano wires or tubes. And then carbon nano tubes has been formed this way, and some elemental nanostructures also has been attempted. So, this is not just confined to bulk material, but also nano materials.

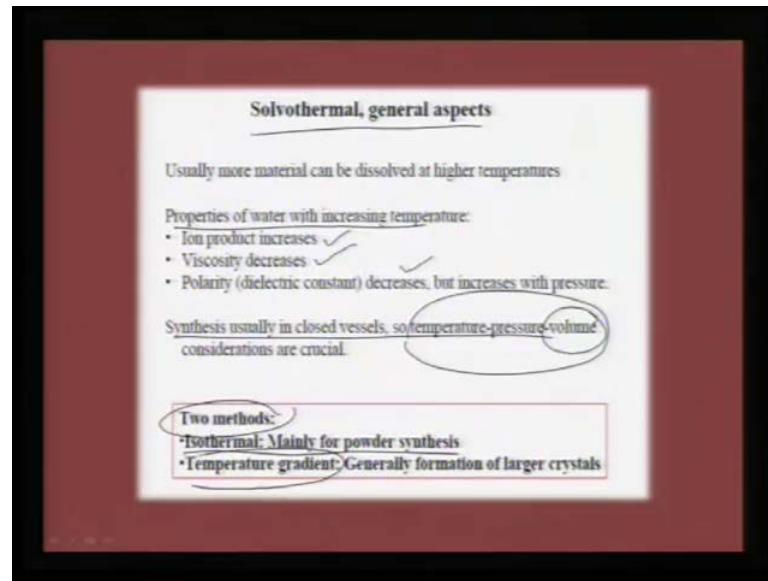
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Now, when we look at the phase diagram and then look at how we get into this critical point. As we heat the auto clay now water actually will show different density and as a function of temperature, as you would see at low temperatures or at room temperature the density of water is one. But, as we heat the water you have a competition between the liquid phase and the gas phase, and at precisely 374.15 which is the critical temperature of water, you can achieve this critical point with the density of 0.321. So, density or the viscosity of your water will change with temperature.

So, the water at 300 degree C will have a density of 0.75 gram per CC for the liquid phase, and for the gas phase it will be 0.05 gram per centimeter cube. So, above the critical temperature and critical pressure, you have this super critical and fluid phase. So, this is the critical point that we try to achieve in the bomb or in the autoclave.

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When we think of solvo thermal reactions there are certain general aspects that we can have in mind, usually more material can be dissolved at high temperatures. Therefore, we slowly increase the temperature in the bomb, and the properties of the water also changes along with the material that we are dissolving for example, with increasing temperature, the ionic product increases viscosity will decrease, and the polarity will decrease. But, with pressure polarity of water that is the dielectric constant will also change.

As a result, the reaction of water itself behavior of water itself will be different, in it is critical temperature. So, is synthesis usually in closed vessels, so all three parameters become very crucial, so they are inter dependent we cannot just simply worry about the temperature and pressure. Because, volume is a intrinsic tough which is involved there therefore, volume place a very critical role in modifying the dynamics of hydrothermal process.

There are two methods by which we can do this, one is isothermal mainly for powder synthesis where you just take the reaction temperature to 70 degrees or 100 degrees and put this in a furnace for 3 days, 6 days and 7 days and so on. So, re crystallization for example, re crystallization oriented powder synthesis, usually involves a long period of time and those are isothermal experiments. And then you also have temperature gradient experiments, usually if you want to grow a crystal, you try to seed a crystal and then

slightly try to provide a temperature gradient. So, as you are going to pull it for over a period of time, this crystals will start growing on the seed crystals and you get huge crystals, we will see some examples later.

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So, in solvothermal synthesis a typical single crystal that is formed is shown here, synthesis from liquids above boiling point at 1 bar is usually realized.

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Hydrothermal/solvothermal

Hydrothermal synthesis: H_2O , temperatures above $100^\circ C$.

Other solvents:

NH_3 , HF , HBr , Cl_2 , HCl , CO_2 , SO_2 , H_2S , CS_2 , C_2H_5OH , CH_3NH_2 , CH_3OH , $HCOOH$, ++

NH_3 is a common solvent (ammonothermal) and carbon dioxide is becoming important.

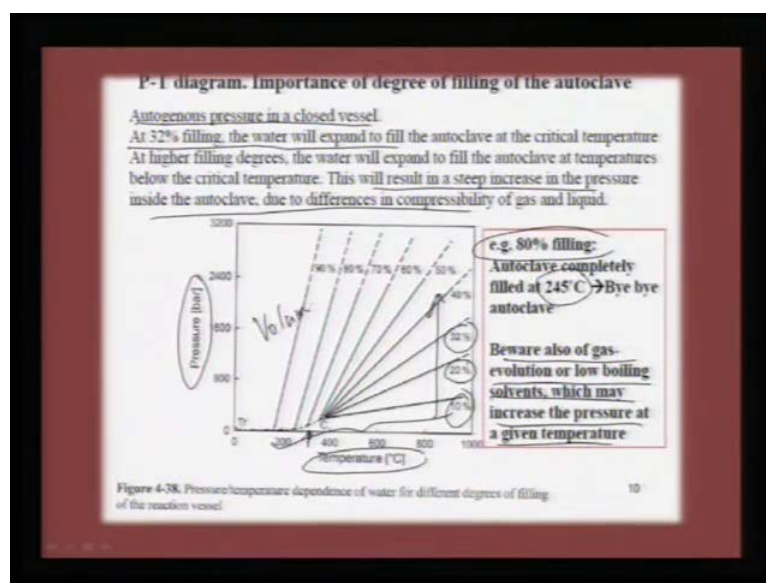
1. Hydrothermal crystallization of large crystals and gem stones
2. Hydrothermal synthesis of e.g. powder samples of oxides (e.g. zeolites)
3. Hydrothermal leaching (e.g. for treatment of ores). $\rightarrow Al_2O_3$

Hydrothermal or solvo thermal reactions, as you as we see water is usually used or we can also use ammonia, some mineral acids can be used even carbon dioxide and SO_2

can be used. And these days because of green chemistry supercritical carbon dioxide is now, taking more attention than even hydrothermal process because carbon dioxide in its critical state can become a very good solvent also. So, this is actually becoming a prime focus in green chemistry, and of also you can see alcohols which can perform the job if we are aiming for sulfides then H_2S gas can be used.

So, a variety of solvents can be used, ammonia is a common solvent and carbon dioxide is becoming important. So, in hydrothermal crystallization we are actually aiming for large crystals and gem stones, this is how they are made and in hydrothermal synthesis by enlarging we are talking about preparing powder samples of oxides, when we talk about leaching take ore and then try to leach it, with the treatment with some alkali. For example, alumina you try to take it over and then try to leach it with sodium hydroxide, then you will be able to get Al_2O_3 on calcinations. So, this is one way you can try to do a leaching, so several things can happen in the bomb.

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And we can see some of the issues in the slides, one of the prime criteria for hydrothermal synthesis is the pressure temperature diagram, which is very important. And we need to know what is the loading factor that will give you the optimum pressure that you are looking for, the autogenous pressure in a closed vessel can achieve different proportions depending on the filling. For example, if you are talking about 32 percent filling of water in a autoclave, then it will expand as you increase the temperature it will

fill the autoclave at the critical temperature, at a higher filling degrees the water will expand to fill the autoclave, at temperatures below the critical temperature.

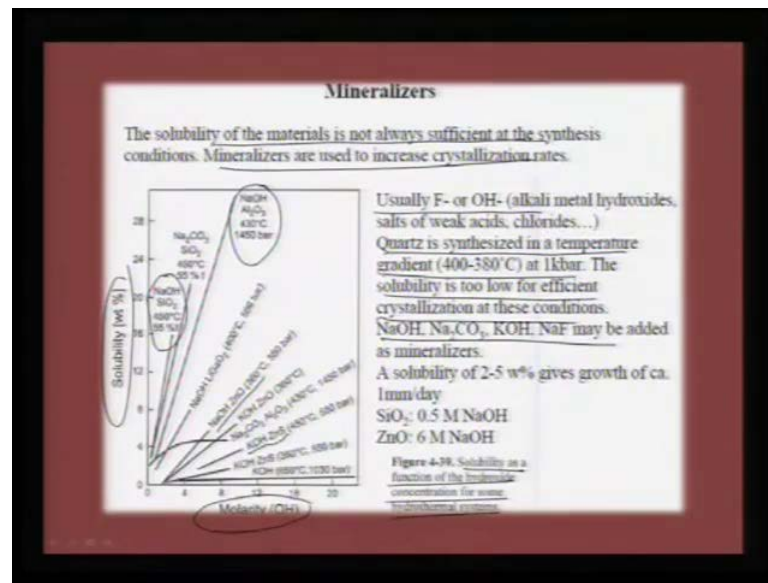
So, this will actually result in a steep increase in pressure inside the autoclave due to differences in compressibility of gas and liquid. For example, you take the case of 80 percent filling of autoclave, then at 245 degree C we are somewhere here, we can actually blow of the autoclave. So, optimum filling is somewhere around 20, 30 where you see, the pressure is not steeply increasing it is moderately increasing therefore, you have a fine control over the pressure build up inside the vessel.

So, this pressure versus temperature plot gives you an idea, suppose I am going to take only 10 percent of the filling, then I can play around with this whole regime of temperature because the pressure that is achieved is highly controllable. So, depending on the volume of the pressure vessel that you are taking, and depending on the nature of oxide that we are trying to prepare, we can play around with any one of this parameter. So, this is a guideline to ascertain whether you are in a safe zone.

So, if we happily tried to fill the pressure vessel which is 80 or 70 percent, then even at 200 degree C you will be generating very, very high pressures where, the pressure vessel cannot stand such a pressure. So, we should be beware of gas evolving or low boiling solvents which can increase the pressure at a given temperature. So, we should also understand that the starting materials by itself should not release extra gases, apart from the pressure that we are generating.

So, during the reaction if some decomposition process is happening and that is going to release some more of gas, then that will add up to the inherent pressure that is getting built up. Therefore, we should be cautious or a back calculation is needed, as to how much of starting materials on heating at what temperature will give, what amount of pressure. So, all this has to be calculated, so pressure and temperature along with the volume is a very governing criteria. So, this is a useful information that one should know.

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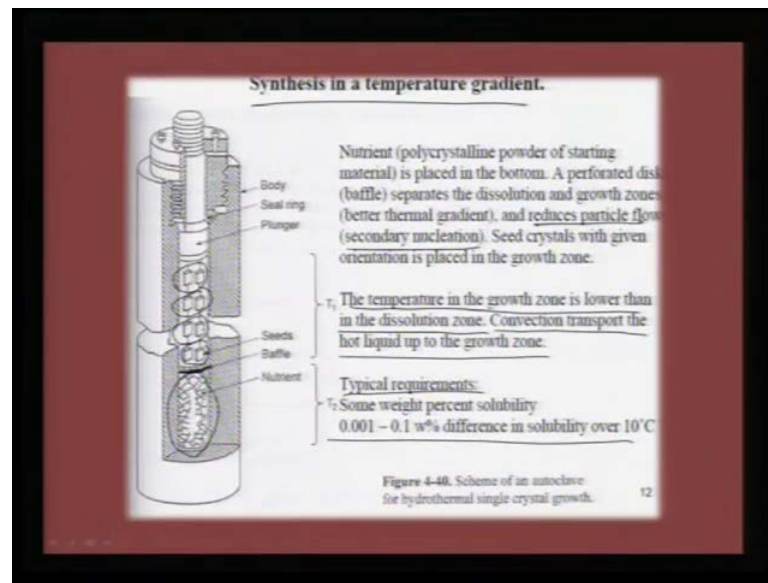


But, in some cases hydrothermal process is very reluctantly progressing mainly because it needs some amount of catalyzing agent, which we call it as mineralizers. Such mineralizers are, usually needed for the crystallization to occur, the solubility of the materials is not always sufficient. So, mineralizers are generally used for crystallization process, the best examples of such mineralizers are either some alkali fluorides, alkali hydroxides, alkali metal hydroxides which can do the job.

For example, quartz is synthesized in a temperature gradient at 1 kilo bar, the solubility is too low for efficient crystallization as a result, several mineralizers are added to improve on the solubility of SiO₂. So, if you want to make some silicates or zeolites just taking pure silica in water is not sufficient therefore, you can put any of these mineralizers, as you can here solubility is going to increase very rapidly, if you are going to work out with the sodium hydroxide. And again the molarity of the hydroxides are also matter in increasing the solubility of SiO₂.

So, you can see variety of combinations there for example, zinc sulfide you want to grow then potassium hydroxide is a very good candidate, zinc oxide if you want to go sodium hydroxide is a very good mineralizer, and alumina also requires such mineralizers for formation. So, solubility as a function of hydroxide concentration is a very useful parameter to know, because this can enhance the process to a greater extent.

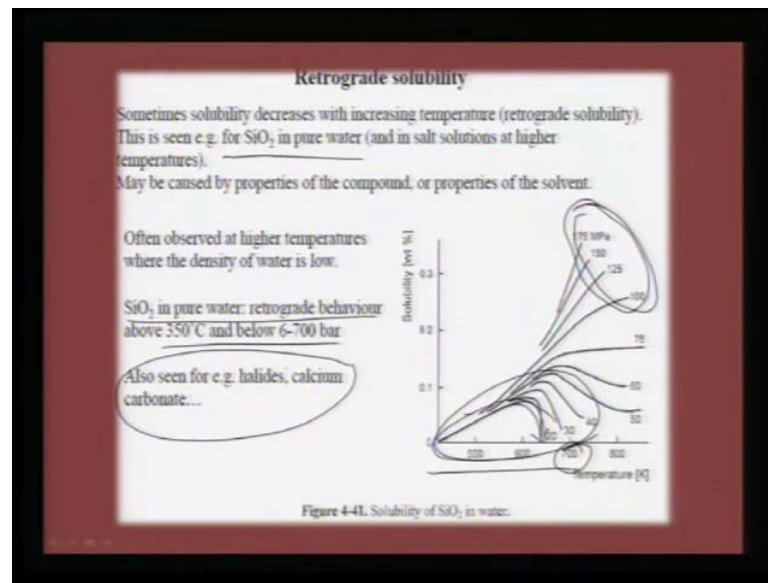
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When we think about growing large crystals, then in a typical autoclave you need to have a temperature gradient. And this is how it is we will come to this scheme later, but generally you need to have a temperature gradient, where you take the nutrients which is nothing but your starting material. And then these are the seed crystals where which is hanging there and there is an orifice which will prevent, actually the particle flow which is the secondary nucleation from occurring.

Therefore, the seed crystals are in a temperature gradient zone, where slowly these mineralizers these nutrients will actually propagate through this baffle, and then larger crystals start growing. So, this is another way of making the larger crystals and typical requirements are you need to have, some weight percent solubility ranging from 0.001 to 0.1 weight percent. And the temperature in the growth zone has to be lower than the dissolution zone. Otherwise you cannot create a progressive temperature gradient, and the convection transport the hot liquid up to the growth zone, which is the way this seed crystals start acting as nucleation sites for larger crystals to grow.

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There are some problems also where, a retro grade solubility is also encountered specially if you take the case of silica in pure water, and in some solved solutions at higher temperatures you would see, the solubility actually would come down. So, this also has to be noted, you take the case of silica in pure water above 350 degree C, as you would see here. As you keep on increasing the solubility at very low pressures, you would see increase in solubility and then coming down.

So, this range is a retro grade solubility therefore, when you are trying to go to very high temperatures, then you need to have a compromise with the pressure in build up inside the bomb otherwise, you would not be getting the end product. So, we need to have some idea about these phase diagrams where, you would know, what is the temperature at which I should play, and what is the optimum pressure that is required for the quartz's for example, to grow quartz's. So, this is a very useful parameter that one should have in mind and we can also have similar calibrations made for halides and carbonates as mineralizers.

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Other solvents for solvothermal synthesis

Table 4-3. Examples for hydrothermal processes in non-aqueous environments.

Solvent	Examples of synthesized compounds
NH ₃	nitrides, imides, amides, CsOH, Cs ₂ Se ₂
HF	MO ₂ F ₄ (M = Mo, W)
HCl, HBr	AuTe ₂ Cl, AuSeCl, AuSeBr, Mo ₂ S ₂ Cl ₄
Br ₂	SbSBr, SbSeBr, BiSBr, BiSeBr, MoOBr ₂
S ₂ Cl ₂	MoS ₂ Cl ₂ , Mo ₂ S ₂ Cl ₄
S ₂ Br ₂	Mo ₂ S ₂ Br ₄
SeBr ₂	SbSeBr, BiSeBr
H ₂ S + (C ₂ H ₅) ₃ NHCl	β-Ag ₂ S
C ₂ H ₅ OH	Sr ₂ , Bi ₂
CS ₂	Monoclinic Se
CCl ₄	SeCl ₄ , TeCl ₄
C ₆ H ₆	Selenium
CH ₃ NH ₂	CH ₃ NH ₂ Li

There are also other solvent other than what I mentioned, depending on the n product that we are looking for, for example, if we are talking about amides, nitrides then ammonia's solvent is a very good option. If you are looking for sulfides or elemental compounds, then we can think of carbon disulphide or CCl₄, these are all useful materials for making a specific n product.

And if you are looking for sulfides for example, H₂S is usually the preferred solvent dissolved in a organic solvent can play a vital role, and we also have several other brominating and chlorinating agents like ethanoyl, chloride and so on which can be used for chlorinating transition metal oxides. So, apart from water and organic solvents, we can also have flexibility with other solvents such as this.

Also this list gives you an idea, what is the critical temperature of various solvents that we are using. As you see for water the critical temperature is 374 degrees centigrade where you can achieve up to 220 bar atmosphere. So, this is as far as water is concerned, one of the reason why carbon dioxide is more preferred is you do not have a such a great critical temperature. So, even very close to room temperature you should be able to get a supercritical carbon dioxide, with the very high pressure that is 73 bars. And again you can see some examples of ethanol and methanol, they have a critical temperature 243, 240 and here again, you can go for very high pressures. And in the in this whole thing you would see, for achieving high pressures water is very critical component or solvent.

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Solvent	Critical temperature [°C]	Critical pressure [bar]
H ₂ O	374.1	221.2
NH ₃	132.3	111.0
Cl ₂	144	77.1
HCl	51.4	83.2
CO ₂	31.3	73
SO ₂	157.8	78.7
H ₂ S	100.4	90.1
CS ₂	279	79
C ₂ H ₅ OH	243	63.8
CH ₃ NH ₂	156.9	40.7
CH ₃ OH	240	81
HCOOH	308	-

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Hydrothermal synthesis: dates.

Year	Name	Arrangement	Comments
1845	Schafhärdt	Papin's digester	quartz microcrystals
1848	Bunsen	thick-walled glass tubes	carbonates; transition of visual autoclaving
1851	de Sénarmont	glass ampoules in autoclave	mineral carbonates, sulfates, sulfides, fluorides; founder of hydrothermal synthesis in geological sciences
1873	von Christoff	acible metal lining	protection against corrosive solvents
1914	Moray	Moray-type autoclave	"closed" system; standard very high pressures and temperatures: 210 kbar, 21400°C
1923	Smith, Adams	internally heated autoclave	introduction of hydrothermal synthesis into solid state physics.
1943	Nacken	foundation for industrial quartz growth	external pressure regulation and measurement. More extensive working range than Moray. Standard.
1949	Turtle	"cold seal" or test tube arrangement	extremely high pressures and temperatures: >100 kbar, >1500°C
1973	Capponi	modified belt apparatus	

Started ca. 1845
 Most important for preparation of large quartz crystals.
 Piezoelectric properties of quartz discovered in 1880
 World production in 1985: ca. 1500 tons.
 Autoclaves up to 100 liter

Now, just want to take you back into little bit of the history and show some examples of the earlier work, before we go into examples hydrothermal synthesis was first explore in, 1845 by schafould was the first one to make the quartz's micro crystals. And then using glass tubes as pressure vessels, Bunsen in 1848 he made some carbonates, as crystals and then on there has been several activity. And the most important one is 1943 by nackmen nacken sorry who actually used hydrothermal synthesis for industrial production of quartz.

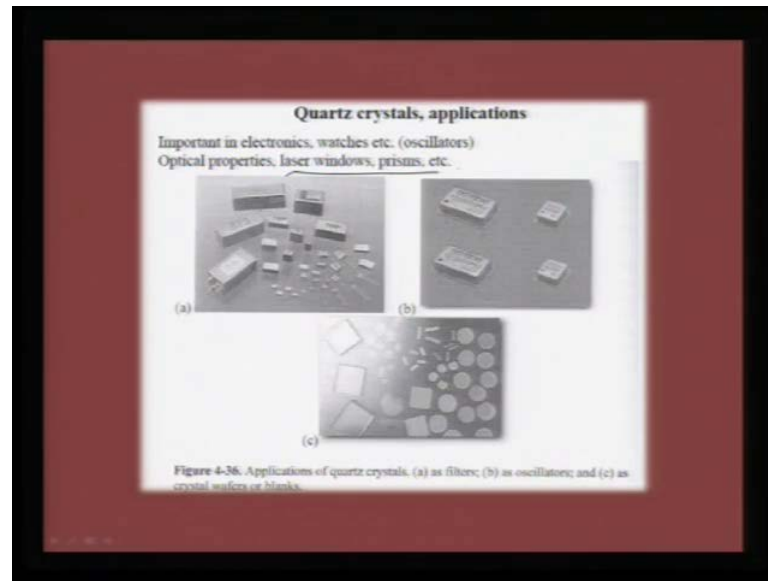
And this was the first time, the introduction of hydrothermal synthesis was taken seriously and then there has been several books written where the mechanism and the physical implications of hydrothermal synthesis has been studied. So, this was mostly a dawning point where hydrothermal synthesis was taken much more seriously, just to draw your attention this piezoelectric properties of quartz was discovered, in 1880 and world production of quartz was aimed, in 1985 and up to 1500 tons of quartz has been made using hydrothermal synthesis. Today, we do not have just small pressure vessels what I showed you now big autoclaves are there, which can help us in doing this scale up operation.

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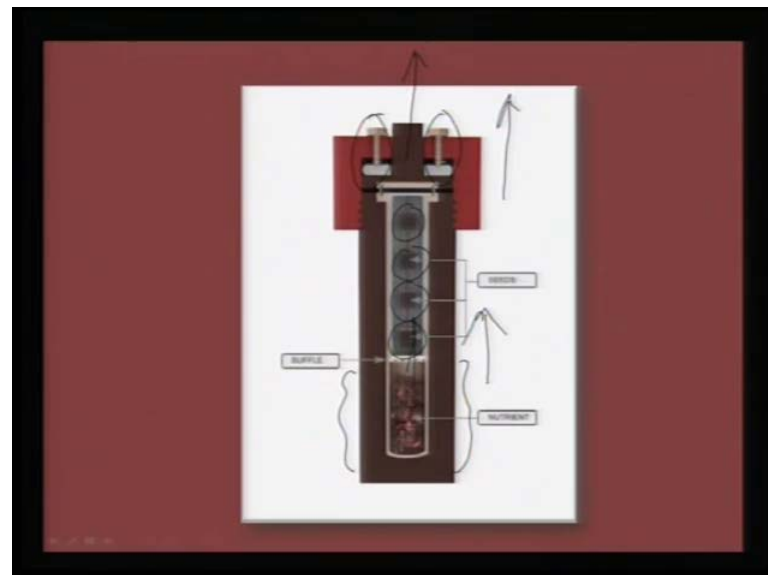
So, this is little bit of the history of this hydrothermal process and these are some of the old photographs that tells you, how big the autoclaves can be and this is not the autoclave, this is actually the seed which was inserted inside. So, the autoclave is actually housed here at the floor level, but this is the seed crystal which is actually lifted. You can see that this is hanging and all this whites labs what you are seeing is nothing but a quartz crystal. And these quartz crystal as are grown, over a period of months to grow into huge size, and this is the dimension of the seed crystal in front of a small boy, who is taking a look at it.

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And such quality industrial grown quartz crystals have find useful applications, in many field specially in electronics in watches, in optical equipments like a laser windows prisms. All these variety of industrial applications, have been engineered with large quantity of quartz crystals.

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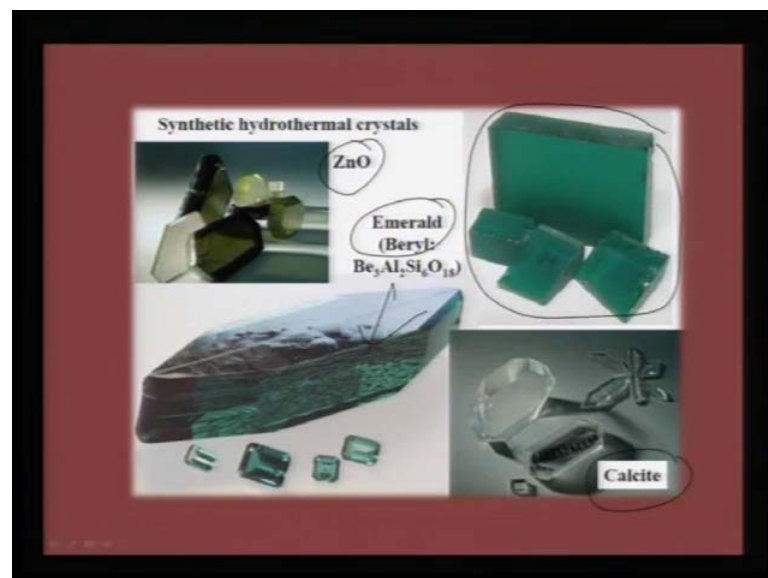


And typically the process that occurs is shown here, those big blocks of quartz are actually precipitating on this seed crystals, which is kept here. And this is being pulled upward say 1 millimeter per hour or 1 millimeter per 2 hours that is the rotation at which

it is slowly done. Therefore, it runs into several days and months, before the whole thing is actually pulled out.

So, the temperature zone is somewhere here, this the temperature zone and the this is mechanically pulled. So, it is not done manually it is mechanically pulled at a very slow rate, to our naked eye you would not see any movement at all, but that is the way it is engineered. So, once you do a slow pulling then a large crystal can be isolated from this, so to grow very be crystals you need a big loading unit also because you need, so much of starting material. Therefore, a big autoclave like this can be made and as you see here to hold the pressure this is actually done with lot of huge nuts and bolts therefore, this is a real scale up process.

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And some of the hydrothermal crystals, which have been grown in the past this is zinc crystals. And then emerald crystals have been grown, and we also have calcite calcium carbonic crystal have been grown using this procedure as you can see big size crystal can be engineered it is not just for lab scale synthesis alone.

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Advantages of hydrothermal synthesis

Usually moderate temperatures 100-300°C (subcritical) at autogenous pressure.

Some advantages of hydrothermal synthesis:

- It may be possible to synthesize materials below a transformation temperature.
 - γ -CuI (transition temperature 390°C)
 - Quartz, α - β transition temperature ca. 580°C
- Transition metal compounds may be synthesized with unusual oxidation states
 - CrO_2 hydrothermal at 350°C, 440 bar:
 - $\text{Cr}_2\text{O}_3 + \text{CrO}_3 \rightarrow 3\text{CrO}_2$
 - $\text{CrO}_3 \rightarrow \text{CrO}_2 + \frac{1}{2}\text{O}_2$
- Preparation of metastable phases
 - GeO_2 with quartz type structure using quartz seeds
- Formation of zeolites and other microporous materials

Advantages of hydrothermal synthesis, usually we are playing around with the moderate temperatures you do not need very high temperature because at this temperature you are almost achieving the super critical temperature of any of the solvents. Therefore, this is a safe range and as a result this can even be experimented in lab scale, and some advantages of hydrothermal synthesis is, it is possible to synthesize materials below a transformation temperature. For example, this is the transformation temperature of gamma copper iodide.

And because we are using temperatures below 300 we can easily stabilize this or for quartz the transition temperature alpha to beta is at 580 therefore, at low temperatures you can actually stabilize one of the phases. And again one other important aspect, I will come to this slide later, chromium dioxide is a very useful video tape material it is a ferromagnetic metal. And starting from chromium oxide you can prepare CrO_2 and as you do this synthesis, you will also release oxygen.

Therefore, there is a in built pressure that is released during this hydrothermal synthesis, what is peculiar here is chromium is usually stabled in chromium 6 or chromium 3. But, in hydrothermal synthesis you can actually get chromium 4 as a metastable phase, so CrO_2 is not easy to prepare by any other technique other than, hydrothermal. In fact, large scale synthesis of chromium dioxide, has only been achieved using the only technique that is hydrothermal, no other technique has given such precise control over the

oxidation state. And then preparation of metastable phases we can do, we can try to achieve and one of the other very useful parameter or very useful implication of hydrothermal synthesis it is control of the zeolite morphology, we can make cage structures using a hydrothermal approach.

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Comparing zeolite synthesis with biological processes

Table 4-5. Technical and biological synthesis of SiO₂-materials.

	Zeolites	Unicellular algae
Reaction time	days	shell formation within hours
Concentration of the inorganic precursor	>1 M	<0.001 M
pH	6 – 14	6 – 8
Temperature	125 – 200 °C	4 – 25 °C
Pressure	1 – 100 bar	1 bar
Structural description	compact translatorial repetitive microporous with uniform pores (typical: 0.3 – 2 nm)	shell hierarchical micro- and macroporous (pore diameters 5 nm to μm)

Comparing zeolites synthesis with biological process, we should understand how much we are blessed with the mother nature, because we tend to realize this with sophisticated cage structures of alumina silicates, using hydrothermal process. But, a simple comparison between how this can be easily done biologically will give us some clue, what the biological process means in material synthesis. For example, take the case of zeolites it will take days together, if you are going to use hydrothermal process.

Whereas, this will just happen in few hours concentration of this inorganic precursors very harsh environment whereas, very dilute concentration is enough. And p H conditions although comparable, now you can achieve using biological process at room temperature the same zeolites can be formed. So, we are trying a very hard way to synthesize some unusual inorganic structures, but at the same time mother nature has gifted with lot bacterial based or enzymatic based reactions, which can actually stabilize such very naval motives of metal oxides in a very fast way.

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Hydrothermal leaching

The Bayer process (patent 1888): Industrially important large-scale process for extracting high-grade aluminium hydroxide from bauxite ore.

Bauxite: Mixture of $\text{Al}(\text{OH})_3$ and $\text{AlOOH} + +$ (silica, $\text{Fe}_2\text{O}_3, \dots$)

Hydrothermal extraction (with concentrated sodium hydroxide solution) via reaction to a soluble aluminate complex:

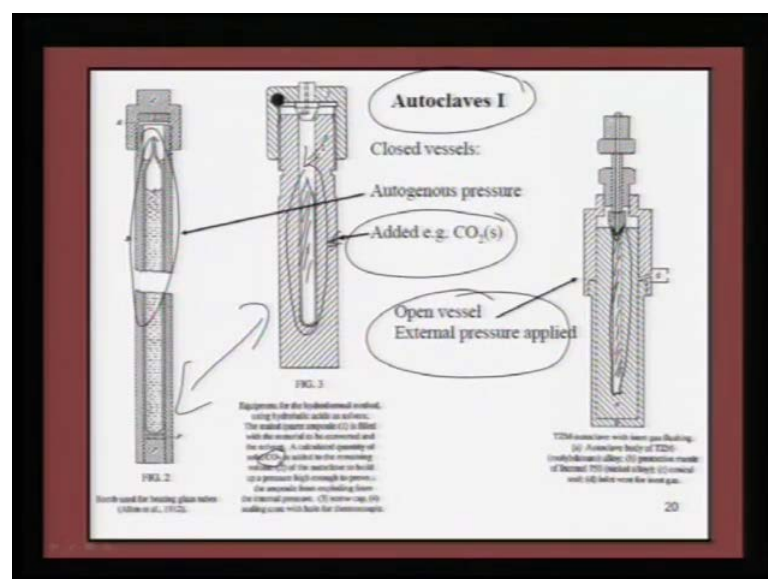
$$\text{Al}(\text{OH})_3 + \text{NaOH} \rightarrow \text{NaAl}(\text{OH})_4(\text{aq})$$
$$\text{AlOOH} + \text{NaOH} + \text{H}_2\text{O} \rightarrow \text{NaAl}(\text{OH})_4(\text{aq})$$

$\text{Al}(\text{OH})_3$ is precipitated by cooling, diluting and seeding

Heated to corundum (for aluminium metal production) $\rightarrow \alpha\text{-Al}_2\text{O}_3$

Hydrothermal leaching as I told you is done, by taking bauxite ore which is nothing but aluminum hydroxide and aluminum oxy hydroxide. So, you can treat this with sodium hydroxide concentrated solution, and they form the respective the sodium aluminum hydroxide, precipitates and this can be heated to get corundum structure. So, starting with a crude ore, we can go for highly pure alpha alumina phase by hydrothermal leaching.

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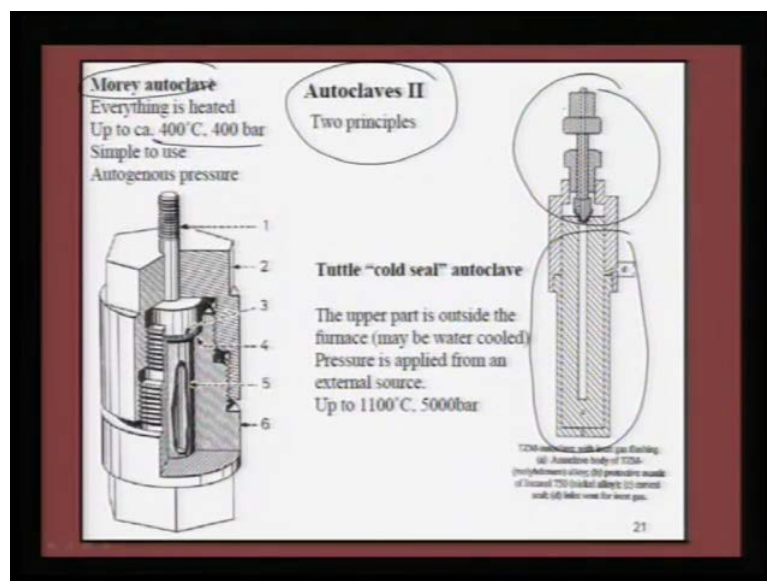


So, this is one of the important applications I will also show you different phases of the autoclaves that are used, this is one range of autoclave where you have this sort of quartz tube, which is sealed tubes. And these sealed tubes are actually kept inside a bomb or a autoclave, where you can use a secondary system like carbon dioxide in this case, we can actually use carbon dioxide and during heating this will also grow in pressure. And this pressure will try to confine the internal pressure otherwise this internal pressure that is generated in the sealed tube will actually explode.

Therefore, a comprise has to be made in the close vessel. So, you actually use a external influence like carbon dioxide in this case, to restrict the internal pressure from blowing up. So, this is usually done in a closed vessel system, we can also have a open vessel system, where you do not use a shield tube this is again shield tube, do not use a shield tube you just use a open vessel like this, but you can actually block the opening with the bomb.

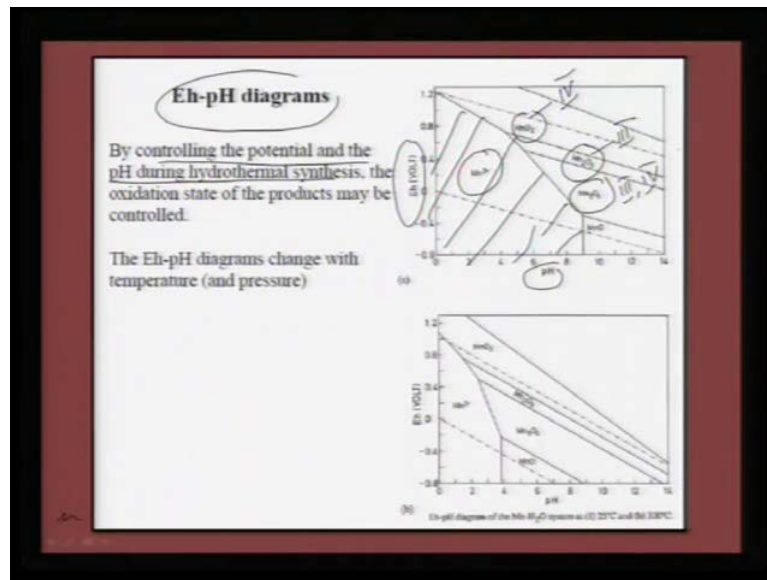
So, that the pressure is actually built only here and this is another way of generating very pressure. So, this is called a open vessel external pressure based autoclave, and in this case you are actually using a sealed capsule and trying to generate high pressure, but at the same time you count track that high pressure from putting another solvent to combat with the internal pressure.

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This is another autoclave which is morey autoclave which is nothing but a bomb which is made where the whole thing is heated, the whole bomb is actually heated to high pressures to and to high temperature. And this is one way of doing that or we can actually try to heat the vessel here, with the open vessel we can try to block this opening. And then heat the vessel here, but the top portion can be actually used for cooling therefore, a very high pressures can be avoided. So, there are two types of autoclave that you can use for making materials, and that also depends on what sort of material that, we are looking for and what is this scale up operation that we require. There are other issues also, which are connected to hydrothermal synthesis.

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This particular cartoon tells about E h p H phase diagram, which gives a clue what sort of other governing parameters, which we can try to operate with during the hydrothermal synthesis, by controlling the potential and the p H during hydrothermal synthesis it is possible to specially control the oxidation state. For example, in the E h versus p H diagram here, you can clearly see that if you are planning to stabilize manganese in two plus, then we need to change the potential of the reaction mixture. As well as the p H within this range, and beyond this we can encounter many other phases. For example, this is M n O 2 in plus 4 and M n 2 O 3 in plus 3, M n 3 O 4 in 3 and 4 states all these are possible, when we go to very high p H. Therefore, if we need a finer control on the oxidation state, then we need take into consideration both the p H as well as the potential that we engaged.

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Hydrothermal buffer systems

By using a buffer system and e.g. hydrogen permeable membranes, the potential during hydrothermal synthesis may be controlled.

TABLE 2 Buffers	
Oxygen (H ₂ O) O ₂ /H ₂	Acid - Base
MnO/Mn ₂ O ₃	Ag-AgCl
Mn ₂ O ₃ /Mn ₂ O ₄	Ag-AgBr
Mn ₂ O ₃ /Mn ₂ O ₇	Ag-AgI
Pt/Pt ₂ O ₃	Ni/Ni(OH) ₂
Pt/Pt ₂ O ₄	Cu/Cu ₂ O
Pt ₂ O ₃ /Pt ₂ O ₄	Sulfur (H ₂ S)
Cu ₂ O/Cu ₂ O ₂	Ag-Ag ₂ S
NO/NO ₂	Pt ₂ S ₇ /Pt ₂ S ₈
Co-Co ₂ O ₃	
Fluorine (HF)	
CaSiO ₃ + 2HF = CaF ₂ + SiO ₂ + H ₂ O	
CaAl ₂ Si ₂ O ₈ + 2HF = CaF ₂ + Al ₂ Si ₂ O ₇ + SiO ₂ + H ₂ O	

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For this reason, a hydrothermal buffer system are also used and there are several buffers which can be used for making a precise control. For example, arrangement for the growth of magnetic ferrite crystal, these are lanthanum ferrites, lanthanum is the rare earth here, and Fe has to be in 3 plus oxidation state and for this reason actually a copper oxide buffer is used. So, that the formation of the Fe 2 plus can be prevented, so hydrothermal buffer systems are also play very vital role.

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Mechanism for HT reaction

- Usually follows a liquid nucleation model
- Differs from solid-state- reaction mechanism from diffusion of atoms or ions between reactants
- Due to enhanced solubility:
 - Solubility of water increases with temperature, but alkaline solubility increases dramatically with temperature

Barrett, R.M. *Hydrothermal Chemistry of Zeolites*; Academic Press: London, 1982

Now, when we come to the high temperature reaction in hydrothermal process, what really happens and how does the whole transformation occurs. Because, we are operating at a very low temperature, to prepare high temperature phases, but we are operating at a very high pressure. So, what really happens usually it is a liquid nucleation model that is suggested, and this model differs from solid state reaction because in solid state synthesis it is mostly a diffusion controlled reaction where, atoms do migrate between solid, solid interface.

But, this is usually a liquid nucleation method that is responsible for the growth of oxides, due to enhanced solubility, solubility of water increases with temperature. And if you are going to add alkaline solvent, like hydroxide then the solubility will dramatically increase with temperature, and thereby this nucleation process can be enhanced or moderated.

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Solubility

• Solubility of SiO₂ (quartz)

T (°C)	Sol (g/L)	T (°C)	NaOH wt%	Sol (g/L)
100	-	300	1	20
150	0.0030	3	5	115
200	0.024	15	15	514
250	0.049	350	1	25
300	0.068	5	5	152
350	0.070	15	15	515
374	0.025	400	1	35
		5	5	135
		15	15	560
		450	1	35
		5	5	143
		15	15	560

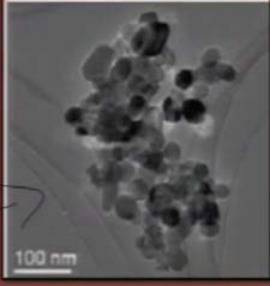
Barrett, R.M. Hydrothermal Chemistry of Zeolites; Academic Press: London, 1982

If you take the case of silica, and it is solubility in water as you see here, when you increase the temperature, the solubility very marginally increases and maximum solubility is aimed at 350 degree C for silica in the growth of quartz crystals. Whereas, the moment you put 1, 2, 3 percent of ammonia into it, then the solubility of the same silica enhances to 560 or 515 grams per liter. So, solubility can be enhanced with this sort of additives.

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BaTiO₃ Nanoparticles

- $\text{Ba(OH)}_2 + \text{TiO}_2 \rightarrow \text{BaTiO}_3$ nanoparticles
- 300 - 450°C, HT
- Two proposed mechanisms:
 - Dissolution-recrystallization
 - In situ crystallization



Hakuta, R., Ura, H., Hayashi, H., and Arai, K. Ind. Eng. Chem. Res. 2005, 44, 840-846

So, this is mostly a nucleation method now if you take the case of barium titanates as an example, barium titanate is formed by the reaction of barium hydroxide and TiO_2 . And this gives BaTiO_3 at optimum temperature of 300 to 450 degree C in hydrothermal condition. But, the proposed mechanism for barium titanate formation can either be viewed in two ways, one is in situ crystallization or dissolution re crystallization.

Dissolution re crystallization is, where you have barium hydroxide and titania has gone into one single homogeneous phase, and from their re crystallization occurs which comes out as barium titanate or it could be a in situ crystallization, one of this is getting crystallized and over which the other can form into a barium titanate. So, we need to know the proof of what sort of process that is occurring, which gives you very nice barium titanate morphology. And this is the TEM picture of those barium titanates which are formed.

But, what we see is there are three important things that happen, which is weighing or which proves as indicator for dissolution re crystallization. Now, one thing is when varying the water isopropanol ratio in the synthesis, the grain size of barium titanate decreases when amounts of alcohol increases. So, this is one clue that tells that something is happening when the solvent is changed.

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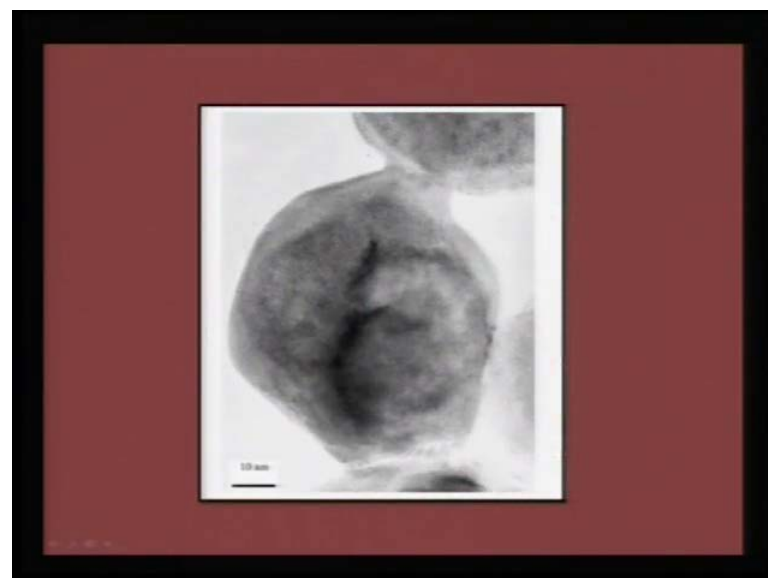
Dissolution-Recrystallization

- BaTiO₃ formation at 150°C
- Stated:
 - “when varying the water/isopropanol ratio in synthesis at 150°C, the grain size of barium titanate decreases when the amount of alcohol increases, i.e. when the solubility of the precursors decreases”
 - “TEM observations of incompletely reacted powders showed that the grains are either amorphous or entirely crystalline BaTiO₃, which means that homogeneous nucleation and growth is occurring instead of heterogeneous nucleation
 - “high resolution TEM observations of fully reacted powders revealed the presence of necks between particles. These three experimental observations in the same reaction system provide strong evidence of dissolution-precipitation as the primary reaction mechanism.”

Pinceloup, R., Courtois, C., Vicemb, J., Leriche, A., and Thierry, B. J. Eur. Ceram. Soc. Res. 1999, 19, 973-977.

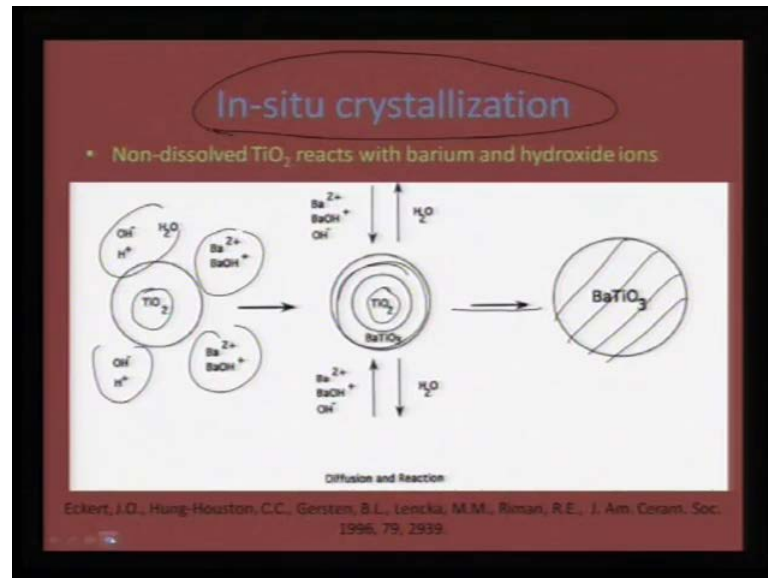
Another thing is TEM observation of incompletely reacted powders, show that there is show that either it is a amorphous barium titanate phase or it is entirely a crystalline phase, you do not get to see both the cases in TEM. And then in high resolution TEM, we also see that there is a presence of necks between particles, these three experimental observations suggest there is a strong evidence for dissolution controlled, re crystallization process which is occurring.

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If you take the case of silica can be seen here, and this is the necking area between two particles, which gives more indication that this is a dissolution induced recrystallization otherwise these two will be separated.

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And if it is in situ crystallization, then the model is you would not see titania going into the solution, where the titania solubility is much less than barium hydroxide because barium hydroxide can easily dissolve into water. So, in that case what you expect is the once a seed crystal of titania is formed, then you have barium and other components coming and joining. And then overall it will transform into a barium titanate process, but what is seen, is that this is not a hydrogenous crystallization process whereas, it is a complete dissolution.

So, for in situ transformation what you would require is just a porous product, which will act like a nucleation site and from there the whole thing can evolve. But, for dissolution precipitation what you would see is a dissolution, should be much fast to ensure a steady flow of reactants. So, by enlarge when we are trying to make oxides the solubility of the starting materials, the mineralizers that you add will decide whether this process would go by, the dissolution precipitation mechanism.

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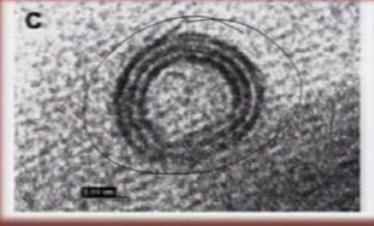
- For **in-situ transformation**, formation of a porous product facilitates the transfer of the reacting species, leading to a facile reaction
- For **dissolution-precipitation reaction**, **dissolution (and subsequent precipitation) must be fast to ensure a steady flow of reactants**

Eckert, J.O., Hung-Houston, C.C., Gersten, B.L., Lencka, M.M., Riman, R.E., J. Am. Ceram. Soc. 1996, 79, 2939.

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Tube/wire Formation

- $\text{TiO}_2 + \text{NaOH} \rightarrow$ titanate nanomaterial
- **Crystal flakes rolled along [001] direction**

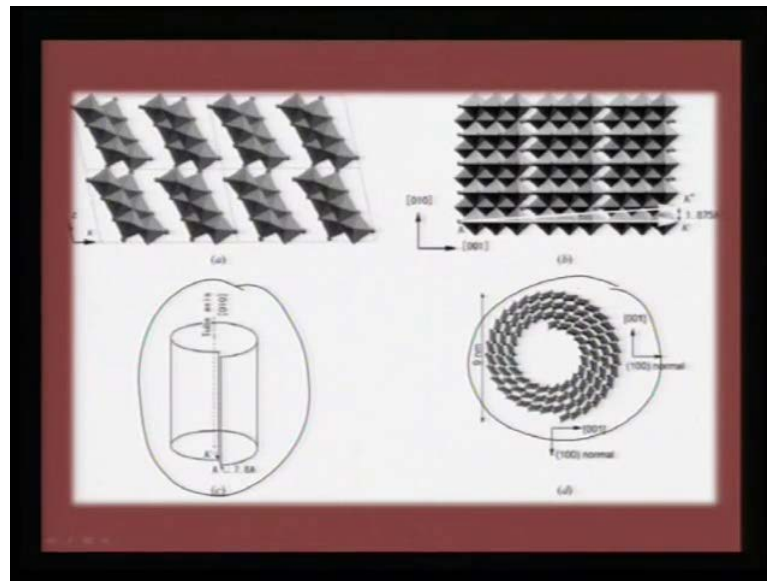


The image is a transmission electron micrograph (TEM) showing a single, multi-layered nanotube. The nanotube has a circular cross-section with several concentric rings, indicating a hollow structure. The layers are separated by small gaps, and the overall structure is cylindrical. The image is labeled with a 'C' in the top left corner and a scale bar at the bottom.

Chen, Q., Du, G.H., Zhang, S., Peng, L.M. Acta Cryst. 2002, B58, 587-593.

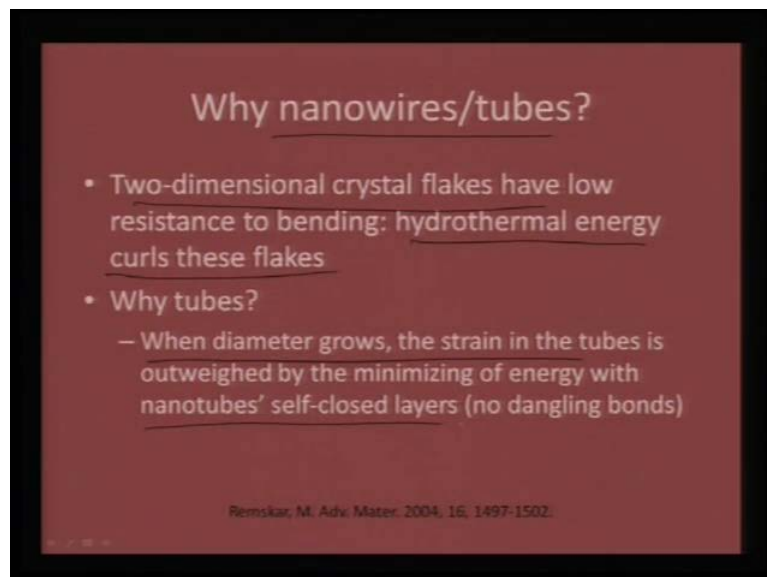
Again there are other useful insights that we can draw from hydrothermal process for example, this is a TEM graph which clearly shows that TiO_2 wires or tubes can be formed. So, this is the way we do it take TiO_2 dissolve it in sodium hydroxide in hydrothermal condition, actually the crystals get rolled up into a tube or into a flake.

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And how does that happen you can see this sort of two dimensional sheet is evolving, but under a hydrothermal condition, they get wrapped up into tube like structure or like a wire like a structure. Instead of going into a three dimensional network, they get rolled up into cylindrical compacts.

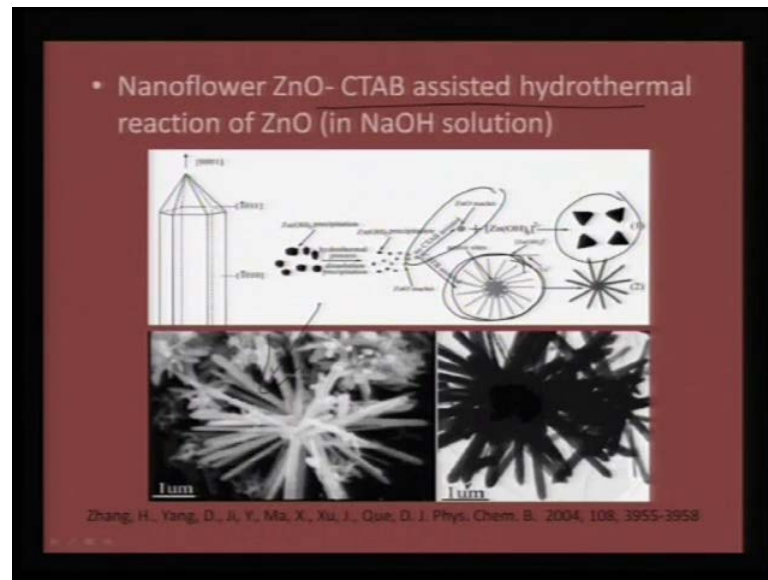
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And the reason, is the two dimensional crystal flakes have low resistance to bending in a normal approach or using a conventional approach. Whereas, hydrothermal energy actually curls these flakes into a tube therefore, usually when we try to prepare oxides,

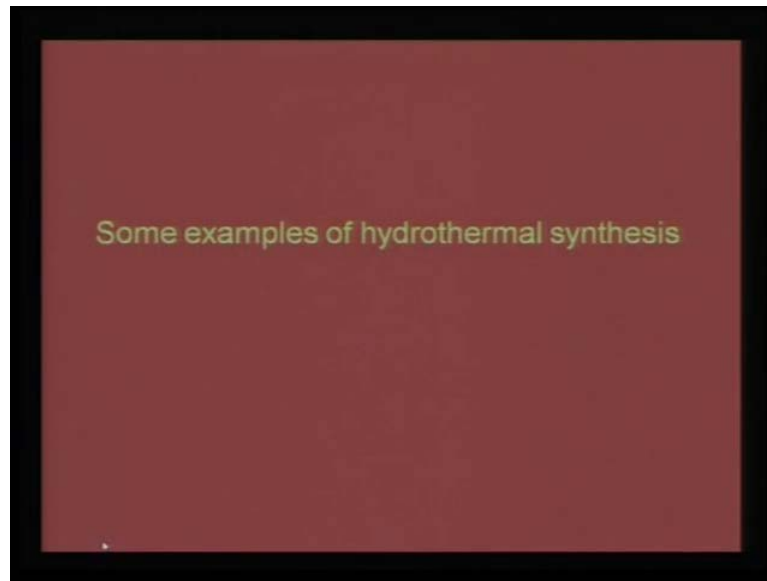
we either end up with nano wires or rods or tubes. And this is mainly because this resistance for bending is actually overcome by the high pressure. And why tubes because when diameter grows the strain of the tubes is outweighed, by minimizing the energy and therefore, you actually get nano tubes with these under hydrothermal conditions.

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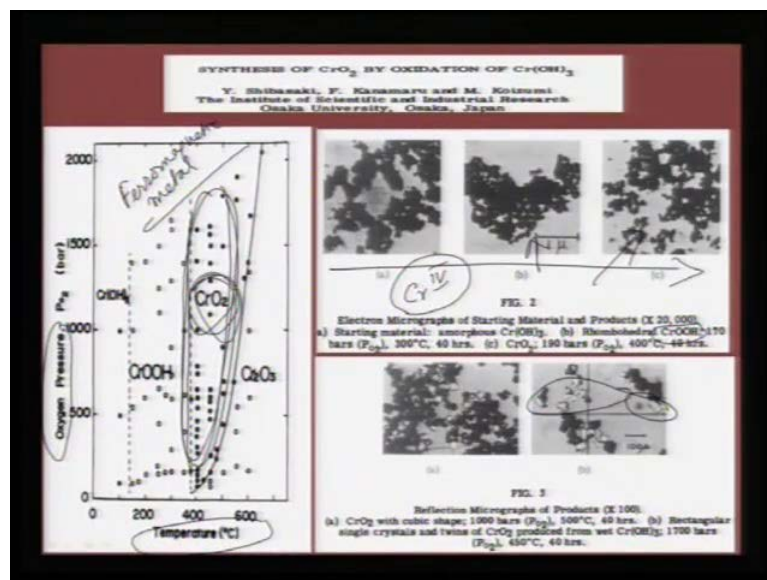
And also we get very different morphologies for example, nano flower type of a morphology is observed for zinc oxides, and why this nano flower type is coming because of the CTAB assisted hydrothermal reaction. CTAB is nothing but a ammonium bromide with a long alkali chain, and if you are going to put CTAB then we see this sort of floweral pattern coming where, you get a nano flower like zinc oxide rod coming, whereas if there is no mineralizer that is added then you get separate individual particles of zinc oxide. So, this is one of the clue that along with zinc hydroxide and water, if you are going to put some mineralizers then we can get this sort of pattern emerging. And this is the SEM view graph of such nano flowers, and this is the TEM view graph clearly showing the such nano rods can be made.

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I will just stop with a few examples of some of the noted oxides, which can be selectively prepared using hydrothermal synthesis. One is chromium dioxide as I already pointed out to you.

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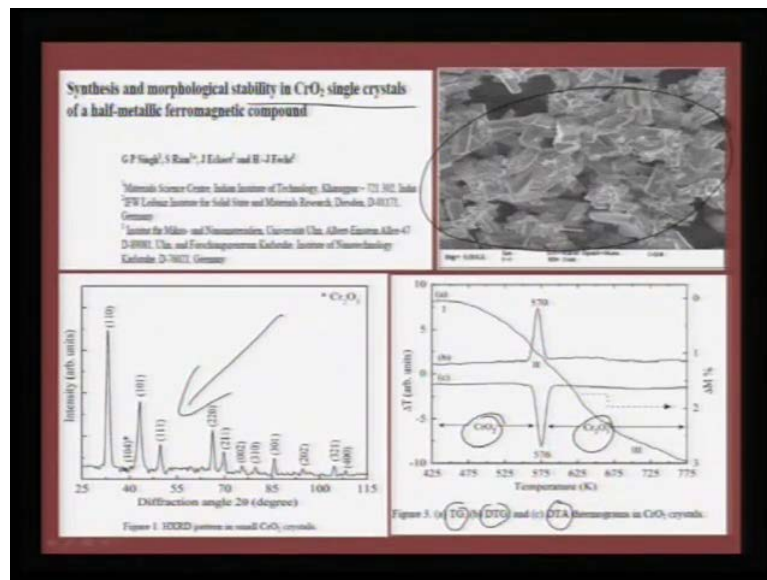
Chromium hydroxide is actually in 4 plus which is very difficult to prepare, there are many reports now a days where thin films have been, thin film technology has been used to stabilize chromium 4 plus. But, again there is a lack of clarity in the oxidation state of chromium, why chromium four is very difficult to prepare, if you look at the temperature

versus pressure phase diagram. You would see, chromium oxide is actually coming in this region and it is actually happening slightly above 400, and this is stabilized at very high pressures.

So, this can only be achieved by hydrothermal process and under ambient conditions it is not possible at all, in lab scale people have tried to use sealed tubes to prepare chromium dioxide, but with great difficulty. So, to prepare chromium dioxide which is a ferromagnetic metal, it is a big challenge and hydrothermal reaction is one way that we can do it. And these are the SCM micrographs, which clearly tells, how the formation of the CrO_2 happens starting with the chromium oxy-hydroxide CrOH .

And then when you heat it for a long time under pressure then it transforms into CrO_2 like this, and we can also try to isolate rod shaped CrO_2 which is actually needed. Now, if we prepare this CrO_2 in lab, you would usually get platelet or spherical shaped one which is actually not useful for your recording media, what you need is this sort of acicular shaped crystals, which is possible only through hydrothermal route.

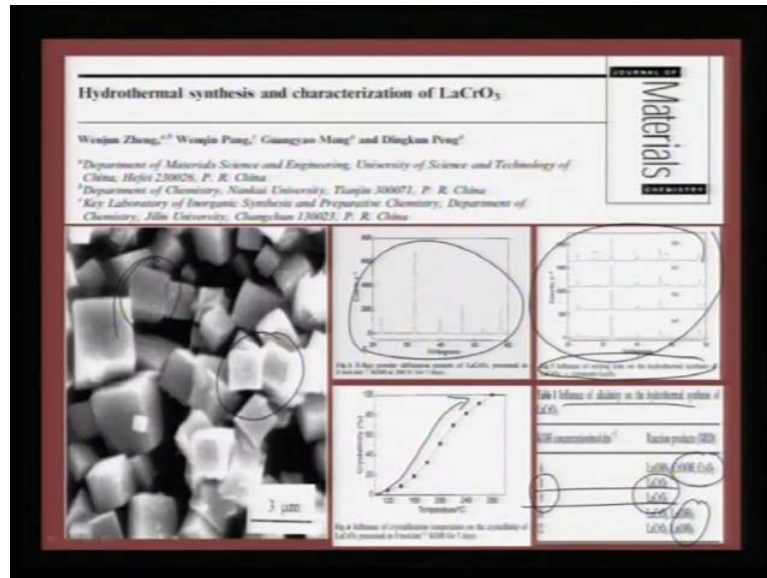
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And here again another group has also prepared chromium oxide single crystals, and you can see this shape and size selectivity that you can achieve using hydrothermal synthesis. This is typical a x r d pattern of CrO_2 , where you almost see a very small negligible percentage of Cr_2O_3 are sitting other ways a very clean compound can be made, and TG, DTA clearly shows that these are indeed CrO_2 crystals. The TG, DTG and DTA

thermo grams are indicative that this CrO_2 to Cr_2O_3 conversion occurs somewhere around 577 Kelvin.

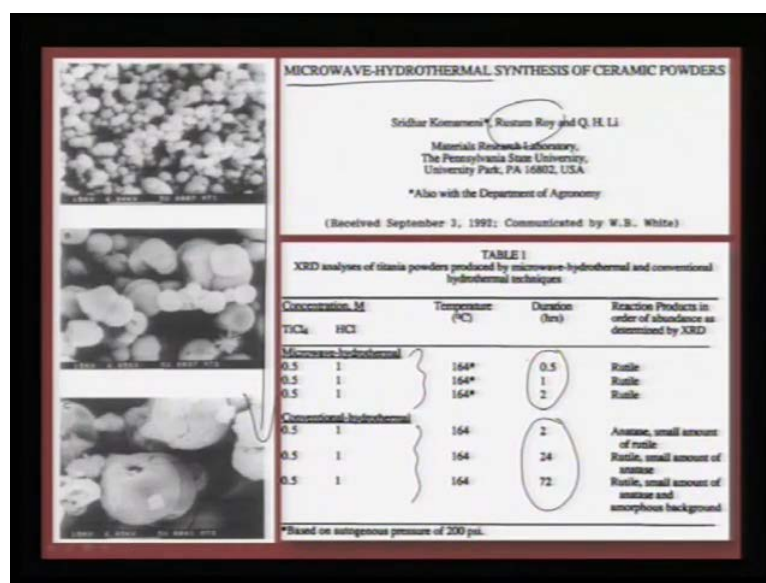
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There is another report where LaCrO_3 is made, this is the a perovskite compound and this is a very good heating element, lanthanum chromite doped with strontium is a very good heating element. And you can make this sort of nice shaped crystals, and single crystalline using hydrothermal process, but as you would see here, in this case there is a influence of stirring, when you are trying to take aluminum hydroxide chromium, hydroxide and heat it in hydrothermal condition, with stirring you can see the crystallinity improves.

So, each system holds some surprise and again if you the influence of alkalinity, if you are going to take potassium hydroxide mineralizer. You would see the critical composition where p H is 8 to 9 is the place where you would really get LaCrO_3 in single phase, in other cases other compounds do precipitate. So, p H is governing issue and then stirring improves the crystallinity and also the temperature seems to improve the crystallinity to a greater extent for LaCrO_3 .

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And then we also have a hybrid model where, you use microwave hydrothermal this was actually pioneered by rustam Roy's group, in pen state. As early as late eighties this is paper published in material research in bulletin, showing how with different duration of microwave exposure, titania particles can be prepared. And there is also a comparison made between microwave assisted hydrothermal process, and conventional one. You can see here, conventional hydrothermal process it requires days or hours together whereas, in microwave engineered hydrothermal process you can speed up the hold reaction. So, this is a very useful way where you can replace conventional heating times, using microwave to speed up the reactions.

And this is another example of how zirconia can be made, microwave route you just hours and conventional route, and then we can make comparison between microwave prepared and a conventional hydrothermal process. You can clearly see the, particle size distribution is distinctly different between these two.

And not only that the most important or useful, application of hydrothermal synthesis is preparing cage like structures, because for host list guest chemistry, where you can put selectively some reactions or even cracking of alkenes or some alcohols into gasoline zeolites are used. And specially creating such cage like structures, hydrothermal synthesis has been used by enlarge, and not only simple oxides, complex oxides can also be prepared using hydrothermal routes.

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TABLE 3
XRD analyses of zirconia powders produced by microwave-hydrothermal and conventional hydrothermal techniques.

Concentration of $ZrOCl_2 \cdot 8H_2O$ (M)	Temperature ($^{\circ}C$)	Duration (hrs)	Reaction products in order of abundance as determined by XRD
Microwave-hydrothermal			
0.5	164	0.5	Poorly crystalline monoclinic ZrO_2 (m- ZrO_2)
0.5	164	2.0	Same as above
1.0	164	2.0	Very poorly crystalline m- ZrO_2
1.0	194	2.0	m- ZrO_2
Conventional hydrothermal			
1.0	195	2.0	

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New Materials in Hydrothermal Synthesis
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Received April 17, 2000; Accepted April 17, 2000

Table 1. List of Hydrothermally Synthesized Complex Oxides and Fluorides

Sample	Reaction	
	T/°C	t/days
Al_2O_3	180	5/30
Ca_2SiO_5	240	3/41
$Ca_3M_2Si_2O_{14}$ (M = Ca, Sr, Ba)	240	3/27
$M_2Si_2O_7$ (M = Na, Li, Ag)	240	7/30
$La_2M_2Si_2O_{14}$ (M = Ca, Sr, Ba)	240	1/9
$NaM_2Si_2O_7$ (M = Na, Cs)	240	3/36
$M_2Si_2O_7$ (M = Ca, Sr, Ba)	240	3/36
$BaM_2Si_2O_7$ (M = Na, K)	180	5/42
$Ba_2Si_2O_7$	240	1/43
Ph_2SiO_2	180	1/38
$M_2Si_2O_7$ (M = La, Pr, Y, Gd)	240	3/7
$AlPO_4$ (A = Li, K, Rb = Ba, Mg)	140	5/8
$AlPO_4$ (A = Li, K, Rb = Y, Sr, Ba)	220	3/39

FIGURE 7. View of the structure units (top) of (a) Ph_2SiO_2 (10) and (b) $AlPO_4$ (11) and (c) $AlPO_4$ (12). Reprinted with permission from ref. 11. Copyright 1999 American Chemical Society.

And lastly I would like to show that hydrothermal synthesis is still the most proven method for zeolite chemistry. And zeolite chemistry has gone into a big industry, now most of the catalysis in automobile exhaust is mainly using, zeolites removing hardness of water is achieved using zeolites. Usually starting with simple SiO_4 tetrahedral, we can try to make cage like a cuboid structures, which has typical cage cavities which is useful for taking selectively some gases, effluent gases or some solvents, where chemical reactions can be achieved.

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The Hydrothermal Synthesis of Zeolites: History and Development from the Earliest Days to the Present Time
 Colin S. Cundy
 Centre for Molecular Materials, Department of Chemistry, 10007, P.O. Box 46, Manchester M13 9PL, United Kingdom
 Paul A. Cox
 School of Pharmacy and Biomedical Sciences, University of Portsmouth, Saint Michael's Building, White Swan Road, Portsmouth PO1 2DT, United Kingdom

A. ZSM-5
 The original patent on ZSM-5 disclosed a molar ratio of composition:
 $0.9 \pm 0.2 M_xO \cdot W_2O_3 \cdot 5 - 100 YO_2 \cdot 44 H_2O$
 where M is a cation of valence \pm , W is Al or Ga, Y is Si or Ge, and $x = 0-40$.

amorphous solid \leftrightarrow solution species \leftrightarrow crystalline zeolite
 —————
 progress of reaction

And these are two people, barrer and Milton who are considered to be fathers of zeolites, who first experimented the usefulness of zeolites in, industrial processes. And these zeolites can actually be made using a simple progression of reaction, where you take amorphous product, dissolve convert it into solutions pieces, and over a period of time it will come out as a crystalline zeolite.

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Hydrothermal synthesis of fine oxide powders
 SHIGEYUKI SATOYKA and RITSUM ROY

2.2 Hydrothermal metal oxides
 2.2a Zr metal (SatoYka et al. 1984) 15-50 g Zr metal powder was reacted with water to form the oxide.
 $Zr + H_2O \xrightarrow{300^\circ C} ZrO_2 + 2H_2$
 At 300°C under 10 MPa, ZrO₂ and ZrH₂ appeared. Above

Oxide	Temperature (°C)	Average crystallite size (nm)	
		Temperature (°C)	Time (min)
ZrO ₂ (2 wt%)	200	Not detected	10
ZrO ₂ (5 wt%)	200	Not detected	20
TiO ₂ (20 wt%)	200	Not detected	40
SnO ₂	200	12	17
La ₂ O ₃ (20 wt%)	200	13	19
SrO (20 wt%)	200	10	13

Figure 3. TEM of zirconia powder by hydrothermal oxidation (100 MPa, 300°C, 3 h, Zr:O = 0.15).

Figure 4. Schematic illustration of hydrothermal oxidation of zirconia powder.

So, one of the notable zeolite even now which is used in automobile exhaust is ZSM catalyst which is nothing but aluminum or gallium oxide doped with silicon or

germanium. So, this is still proven to be one of the most powerful catalyst, running into billions of dollars, so such cage like molecules can be prepared using hydrothermal process. And here is another example of how zirconia can be made using, hydrothermal route and the various parameters that are involved which affects the structure of this zirconia, is also studied using hydrothermal route.

(Refer Slide Time: 55:43)

Table 5. Typical characteristics of ZrO₂ powders by hydrothermal homogeneous precipitation.

Powder	ZY30	ZY80	ZP20
Chemical composition			
ZrO ₂ (wt%)	94.7	86.0	> 99.9
Y ₂ O ₃	5.2	13.9	—
Al ₂ O ₃	0.010	0.010	0.005
SiO ₂	0.010	0.010	0.005
Fe ₂ O ₃	0.005	0.005	0.005
Na ₂ O	0.001	0.001	0.001
Cl ⁻	< 0.01	< 0.01	< 0.01
Ignition loss	1.5	1.5	8.0
Crystallite size (nm)	22	22	20
Average particle size ^a (μm)	0.5	0.5	1.5
Specific surface area ^b (m ² /g)	20	25	95
Sintered specimens:	1400°C × 2 h	1500°C × 2 h	
Bulk density (g/cm ³)	6.05	5.85	
Bending strength ^c (MPa)	1000	300	
Fracture toughness ^d (MPa ^{1/2})	6.0	2.5	
Vicker's hardness (GPa)	12.5	11.0	
Thermal expansion	11.0	10.6	
	20 ~ 1000°C (× 10 ⁻⁶ /°C)		

^aPhoto sedimentation method; ^bB.E.T. method (N₂); ^c3-Point bending method; and ^dMI method.

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Hydrothermal Route

- Pros:
 - New materials ✓
 - Easy, relatively cheap ✓
- Cons:
 - Difficult to control morphology, size ✓
 - Not for all materials ✓
 - May obtain variation in size ✓

And the toughening of zirconia can be modified with addition of yttria or alumina and so on. And the fracture toughness of these zirconia's have been, evaluated hydrothermal

process. Lastly I just want to conclude by saying, the pros and cons of hydrothermal synthesis, what are the advantage one is you can discover many range of new materials because every particular reaction will bring about a new metastable phase. Easy and relatively cheap which can be experimental in a lab scale, and the difficulties are we need to understand the chemistry that is operating it is not just, generating very high pressure. But, we need to understand before a hand, the nature of the components additives that you are using.

Therefore, we need to have a knowledge of how to control this morphology in size, this although ranges very big, but still limited to only few materials and it is impossible to attain variation in size with these. Therefore, the critical parameters that are involved are more than two therefore, a knowledge of the starting materials, the reaction conditions like p H pressure, temperature, volume all these forms important ingredients in hydrothermal reaction.