Materials Chemistry
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Lecture - 5
Crystal Growth Single Crystals

In today's lecture, we will be looking at another important aspect of material synthesis, which is grouped under the title crystal growth. It is very difficult to justify the domain where crystal growth technique stands, because it involves both solution chemistry or material synthesis via wet route. At the same time the crystalline nature or the single crystalline features that emerges out of this crystal growth technique, puts it in a different perspective.

So, I have tried to discuss about the issues of crystal growth in accordance with the thin films and single crystals that we have seen in the previous lectures in module 2. We have already seen molecular beam epitaxy which is very refined physical vapuor deposition technique, where single crystalline materials can be made with different components. It can be binary, ternary or quaternary metals. But in today's lecture I will give you a glimpse of how this crystal growth can be extended not only if I am looking into it as a mere solution process, but also in terms of application we can see how this can become a indispensable technique.

Therefore, I have chosen few examples to highlight to you, the basic issues that are involved in crystal growth and fundamentals that we need to have in mind, and in the laboratory practices we have always encountered re-crystallization which is a very simple protocol. But, we can actually go to a more cumbersome and a more involved crystal growth technique, which is more expensive from the industrial point of view, but then we will we have to have a glimpse of both extremes from a lab scale synthesis to a industry scale. So, in the next few slides I will talk to you about the basics of crystal growth, and then take you through some examples of the different materials that we can prepare in different dimensions.

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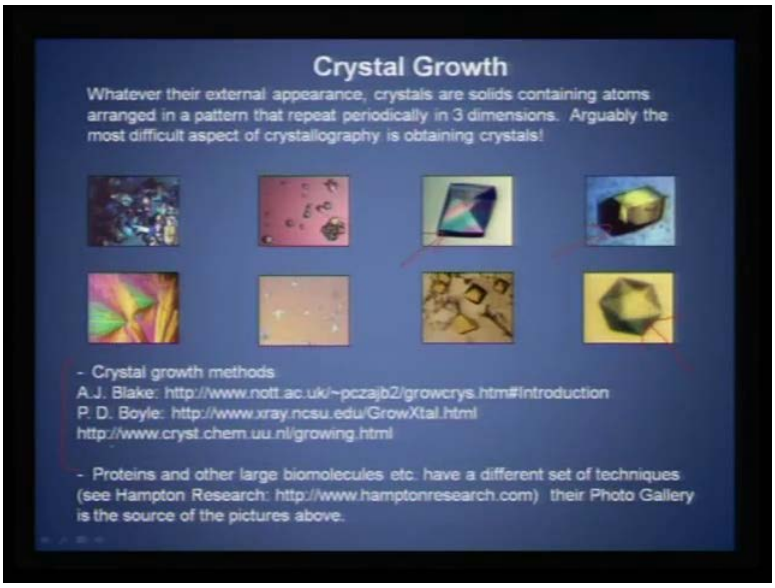

Crystal growth as we see these are all the optical images of various crystals grown from different materials, and each one is a class in itself they all order them self in a particular a way, and they grow three dimensionally. But then the facets if you look at the projections this particular crystal grows in a particular axis. And this particular crystal grows in a different axis and the shape and size of each crystal talks about the growth pattern that is involved.

So, although a growing crystal is very, very intricate, but yet it is fundamental to understanding the materials chemistry therefore, we will look at various aspects of crystal growth. For reviews we have several websites and power points from other groups, worldwide where people have discussed about crystal growth in greater detail, but I will try to give you a comprehensive picture on what are all the important techniques that are available.

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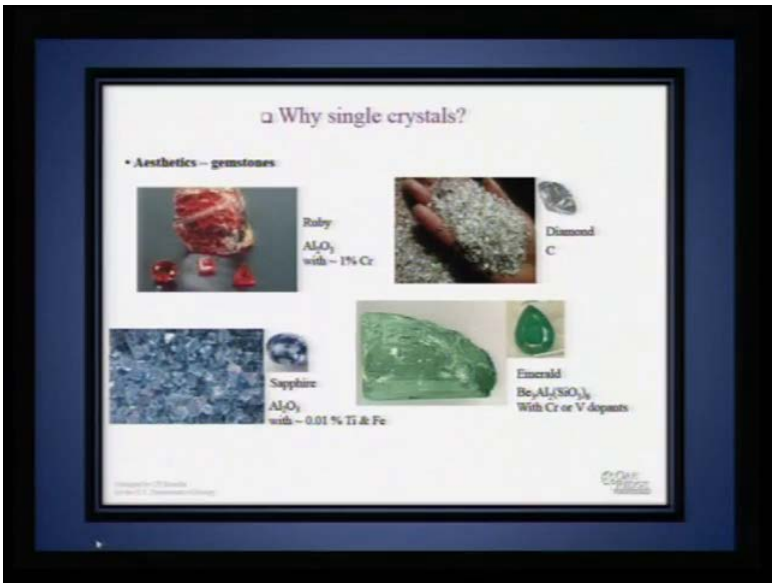

In the first place we can ask some question, why we need to prepare single crystals? As you can see here single crystal can transcend to different applications, diamond, ruby and sapphire, not only they are gem stones, but they are also extended to use in as laser materials.

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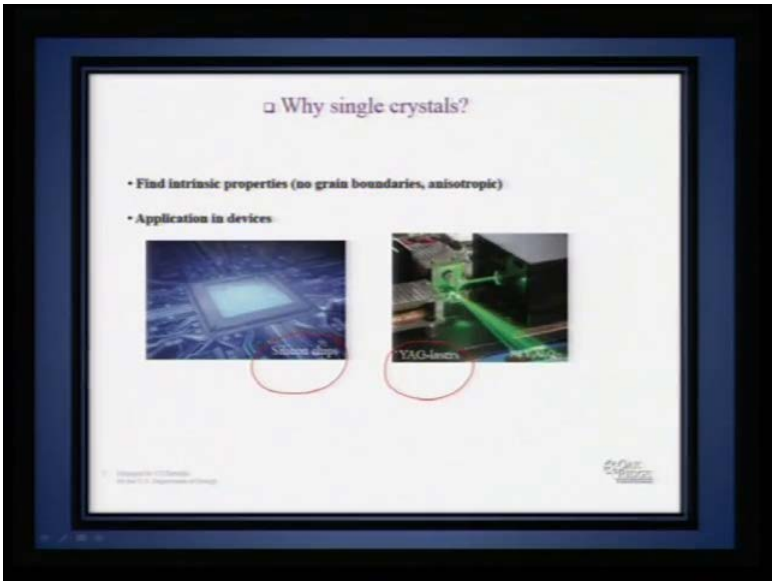

Single crystals are not just used for cosmetic uses, but also they find applications in electronic devices, one of the very important application of single crystal growth is in silicon industry, we will come to this shortly from now. So, you can see silicon chips are

actually, fabricated using the crystal growth technique, and lasers in today's chemistry is mainly pioneered by a single crystal growth.

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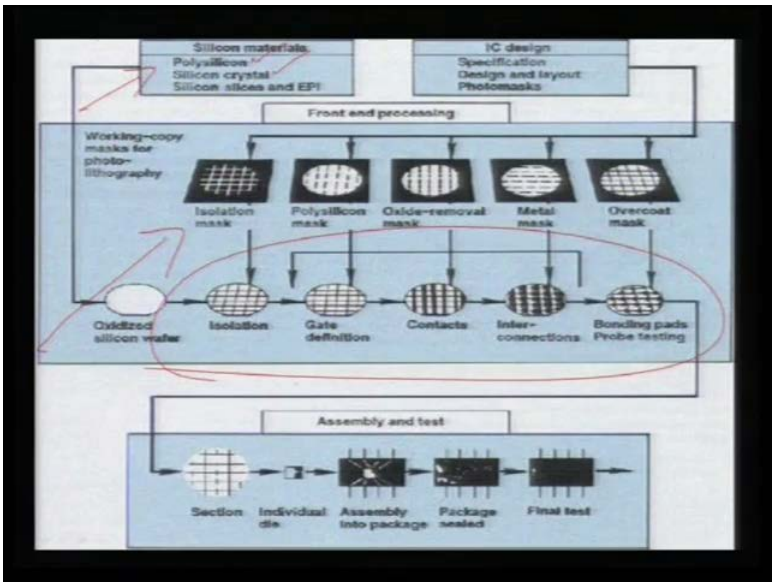

This is a map of how silicon industry is flourishing today, and it is a never dying industry and hundreds of applications have been engineered through silicon technology, and as you can see here this is one of the view graph of how silicon can be used to make devices. And the basic material that we can start is with a wafer, and there are different grades of a silicon that we can grow as wafers, as a single crystals with three dimensions or you can try to coat it in two dimension. Therefore, we can talk about silicon crystal which is oriented single crystalline, polycrystalline silicon and this is the way a most of the devices are made with a base material such as a silicon wafer. And typically the sizes that we can achieve out of this silicon wafers are 6 inch 12 inch wafers, so technology is now ribe to make such very large wafers, and if you recall this sort of wafers are the ones which really turned out to be photovoltaic cells. So, today's photovoltaic cells are mostly driven by silicon industry, and this big silicon single crystals can be made using vacuum technology.

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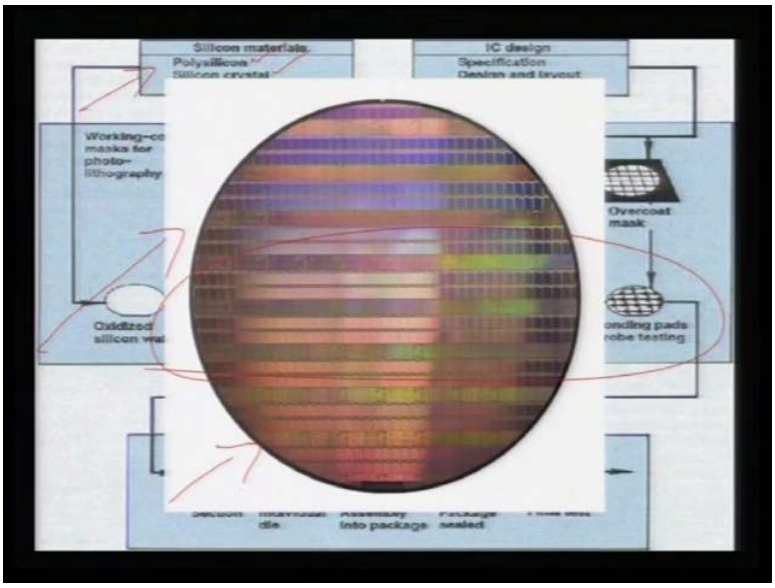

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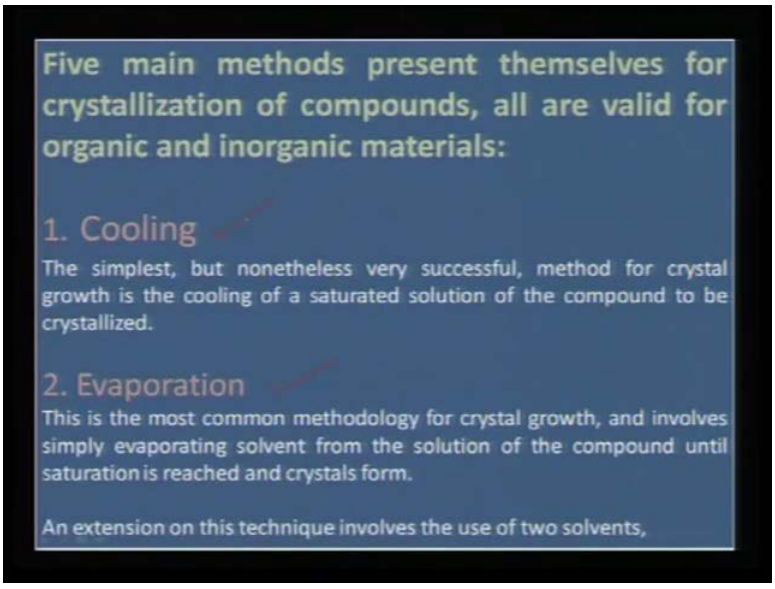

Now, let us go through some definitions and some classification before we go into specific example, from a lab point of view or for a chemist there are few things that he needs to bear in mind, when he thinks about making a crystal. So, five main methods that can put most of the organic and inorganic materials into perspective, one is cooling method, where you take a super saturated solution and then try to cool, then you can get this evaporation technique is one, cooling technique is another one.

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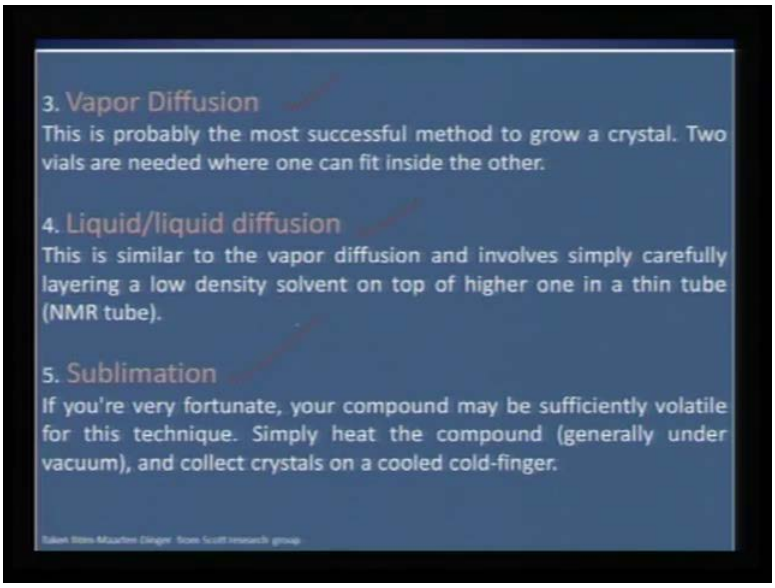

And then we can think of vapour diffusion method liquid liquid diffusion and sublimation, most of these processes are encountered in everyday's lab practices. Therefore, we have in some form have stumbled at one of this technique at some point of time, so we are not alien to the single crystal growth certainly, we have used it in some form, but this is not enough to transcend to applications we can merely be confined only to solving crystal structure, if you resort to only this sort of simple techniques.

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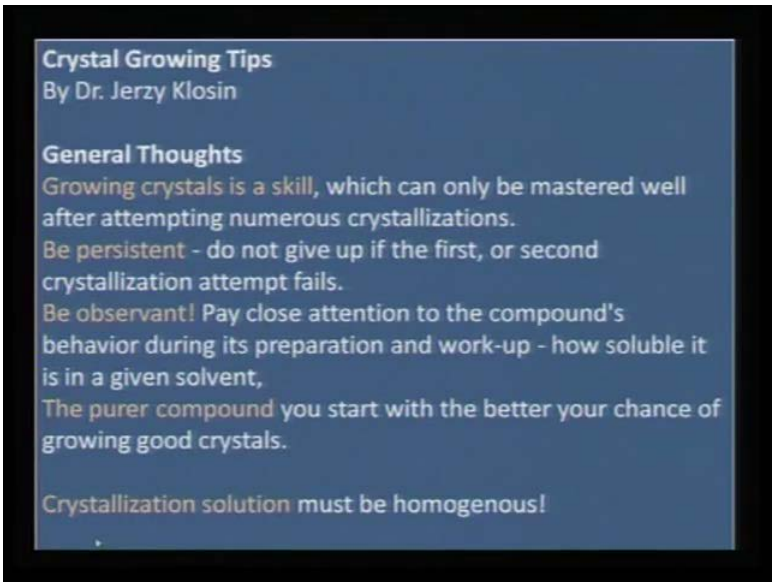

So, we will see much more involved techniques in the future slides, some crystal growth tips are given a taken from Jerzy, who has put it in a very nice way the general thoughts are growing crystals is a skill, we should not think this is a surmountable task actually it is a art. So, if you have a feel for a growing crystal, it is most likely that you will end up with very beautiful crystals and we need to be persistent, because crystal isolation is not a easy task, but at the same time we need to understand some of the fundamentals to making this crystal.

So, we need to be persistent, we need to be observant because sometimes you may be hoping for big crystals end up with a small crystal, sometimes you do not get crystal it will become a amorphous, precipitate set, and it might sediment. So, in such case you got to be careful to understand, what exactly is happening and we should also know that purer the compound that you start with then good crystals you can get.

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So, these are some of the issues that we need to think specially when you are playing with a solution route, this is the most popular crystal growth route that any organic or inorganic chemist would go for. This is a crystal growth using a controlled cooling, where you take supernatant solution, and then you start cooling in a very systematic way you do not go for a abrupt cooling, but then you do it in a phased way. And then you can see crystals are coming out of a saturated solution, so the solubility of most compounds

decreases as the temperature is lowered, thus cooling of a saturated solution often produces crystals.

So, this is one way and to make sure that this is a very gradual process you try to encapsulate this test tube, and then try to allow this to go through a very phased and systematic cooling, no abrupt cooling. And for those who are involved in organic synthesis usually you can try to re-crystallize, and then put it in a fridge even sudden cooling can bring out beautiful crystals, but these are not the sort of re-crystallization that I am talking about these are a intentionally to grow crystals.

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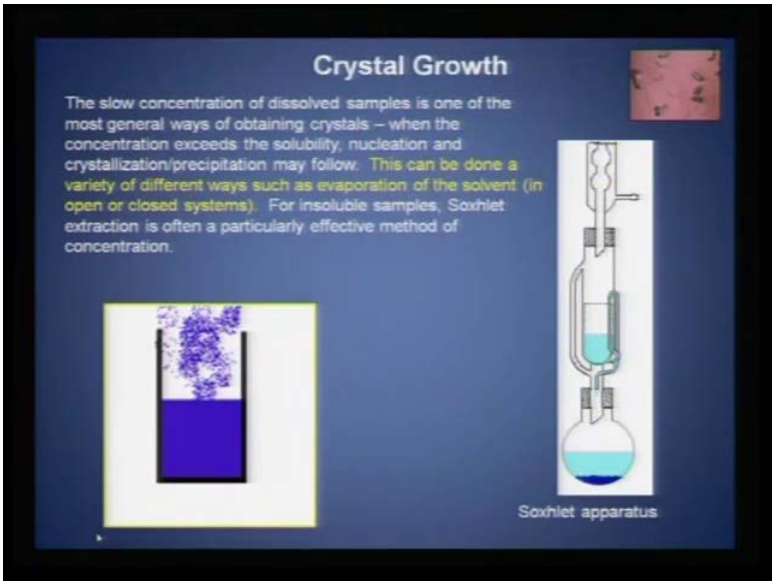

And therefore, this is one way that we can achieve, another way to achieve crystals is to reduce the concentration in order to get the crystals out. So, what you do here is carefully try to evaporate the solvent and so that you can concentrate the solution otherwise the crystals are actually soluble, so you try to exploit the solubility of your system in a given solvent. And usually you use this apparatus to preferably eliminate one or more solvents and using this apparatus, and this way you can try to concentrate the solution and once you concentrate to a particular volume then you can get the crystals down.

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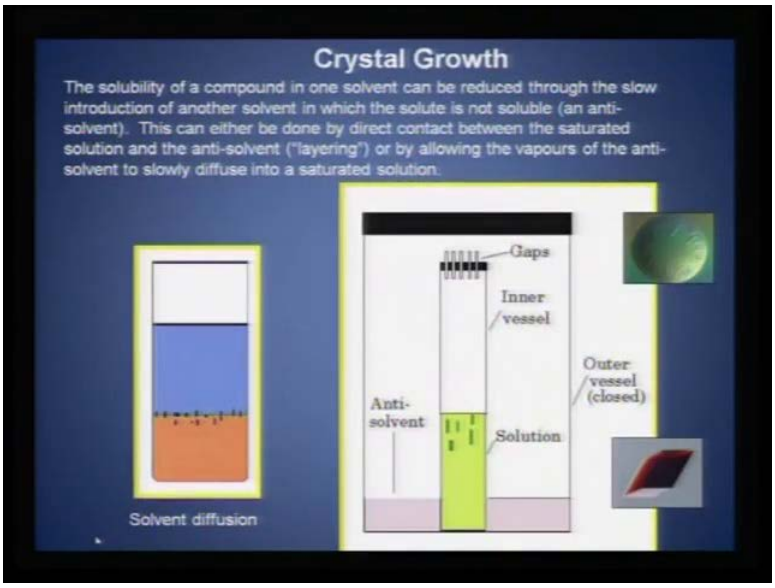

So, this is another way of doing and another approach which is very familiar in organic or inorganic practice is to take two different solutions, and they are actually not miscible therefore, they would form a layer immiscible layer. And at the interface you would actually see the crystals forming and which we call it as anti solvent, one is anti solvent therefore, there is a layer form. The other way of doing that the solvent diffusion is to take a solution, and then put it in another solution and then cover it, you can make small RFS here or small holes. So, that this anti solvent can diffuse into this one and based on this interface reactions you will get the crystals coming out, so this is another way, which is actually a slow process compared to this process, but you can definitely get crystals at the interface.

So, this is called solvent diffusion reactions and another one, which is almost a common protocol in any chemistry lab practice is sublimation, where you try to take sample and then you try to heat it in vacuum, then in the cooler you can actually have a cooling hand where this is actually chilled. So, in the cooler part of the setup you see this crystals a crystallizing or depositing, so this can be a very good and the most inexpensive way of isolating crystals, and there are other refinements to this approach in the form of this, where you try to take the sample with your solution and then you heat it, and you keep this arm of the design cooled and you can see that the crystals are actually segregating out in this fashion, so there are different ways that we can try to enforce a crystallization process using a solution approach.

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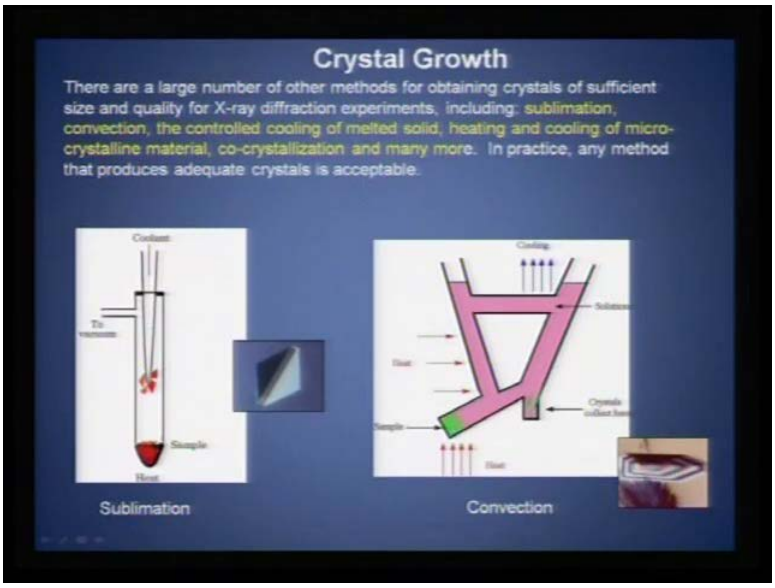

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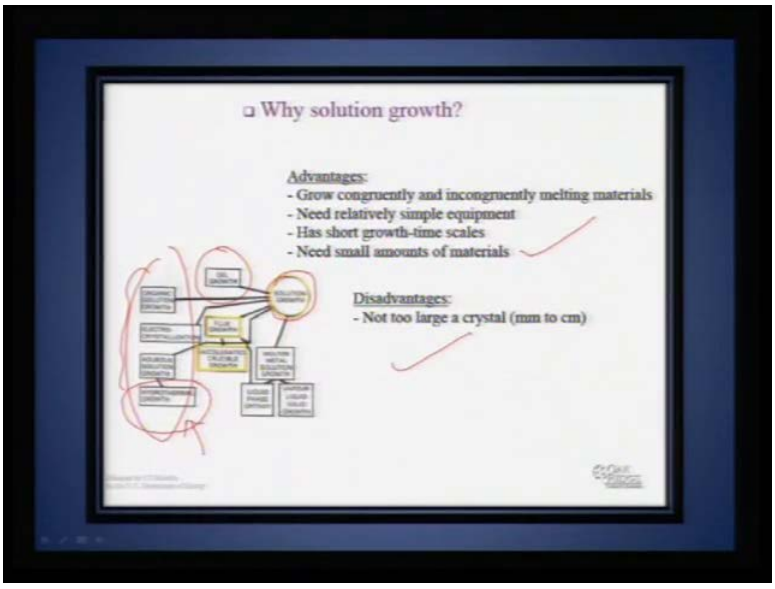

Now, why we need a solution growth, because you can grow congruently and incongruently by melting materials, we need very simple equipment. Therefore, in any chemistry lab practice you will see almost every other compound that is prepared is taken through a crystallization process, just to refine it and simple equipment is what we need. And growth time scale is also very low or very short and you need very small amount of materials, you do not have to run a batch process.

Therefore, it has its own advantage only thing in these crystals you can probably, isolate dimensions worth for single crystal X ray studies, but not for other applications, therefore, this is one of the limitations of a solution process. So, when we are talking about solution growth I want to emphasize that in module one, I had discussed in greater detail on the relevance of hydro thermal, where you take it in a autoclave. You put some pressure high pressure to it you can actually crystallize it, using a mineralizer any oxide or any other compounds can be crystallized and crystals of a preferred dimension can also be isolated, which I have already discussed in module 1. And these are the other techniques, which are usually practiced in everyday practices in a chemistry lab. So, I am not going to discuss in detail on these issues, which can be covered sol gel route also I have mentioned in module 1, but we will go into other approaches where we can try to get more inside into it.

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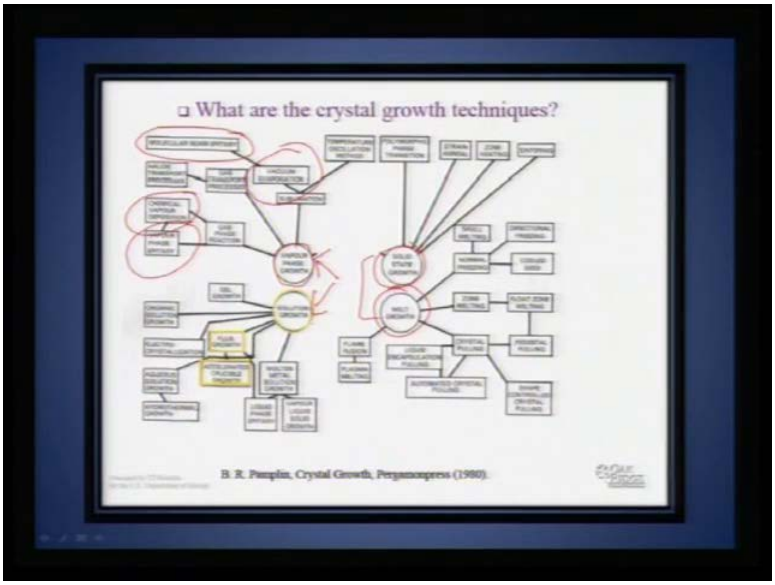

So, apart from solution growth that we have seen, so for the other important way of realizing crystal growth is through vapour phase growth, and in vapour phase growth in module 2, I have already discussed with you about this most sophisticated vapour phase technique, which is molecular beam epitaxy. And I have also mentioned to you about general vapour evaporation or chemical vapour deposition techniques or vapour phase epitaxy, all this I have discussed in the previous lectures.

Therefore, we will not look into this vapour phase growth either, so in today's talk mainly we will look at some of the solid state growth or we will look at some examples of melt growth technique. So, in perspective when you think about crystal growth you need to understand there are several ways and the magnitude of each effort varies, and the simplest of it of course, is the most orthodox chemical route that we call it as solution route, so let us go a little bit more and try to see what are all the different phases of melt growth and solid state growth techniques.

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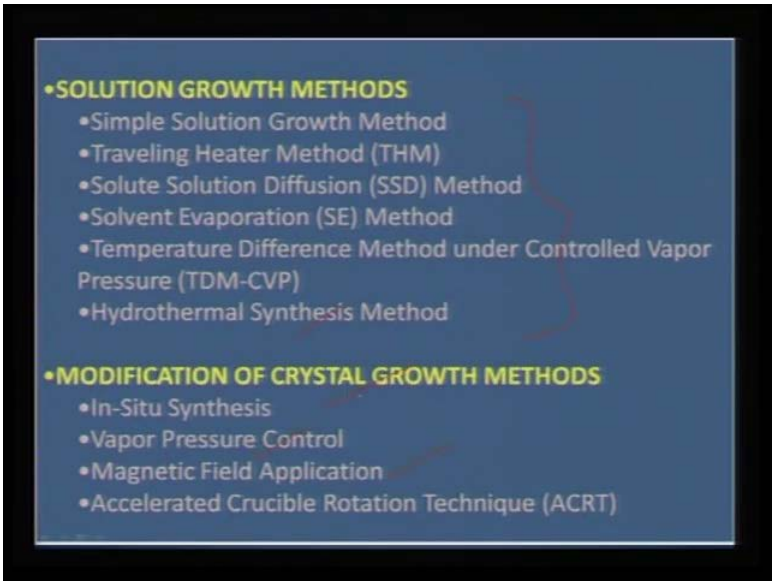

As, I have already told you these are the different categories of solution growth technique, so I do not want to go through this list again, and then there are several modifications to this a solution growth technique, you can do that even with magnetic field and you can try to bring about a pressure control all this are a different facets to the solution growth technique. And vapour phase growth method as I have told you is chemical vapour phase or molecular beam epitaxy, so this again I will try to skip and take you more into the details of melt growth technique.

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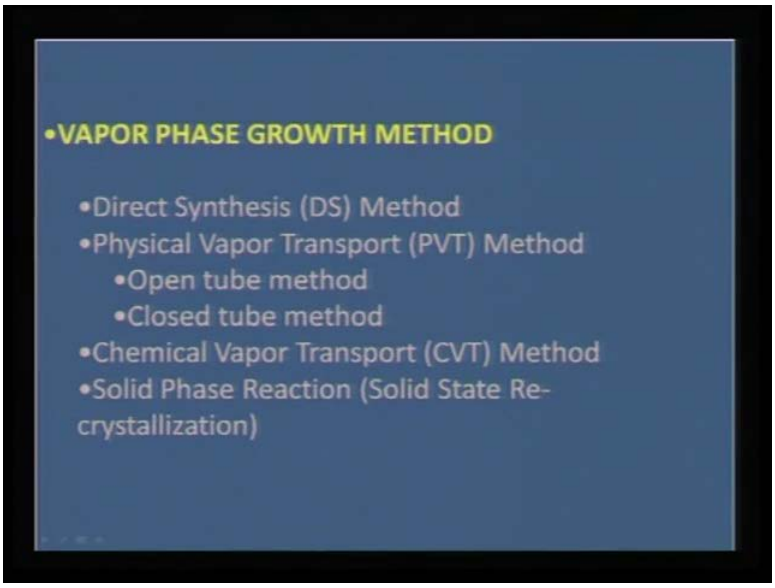

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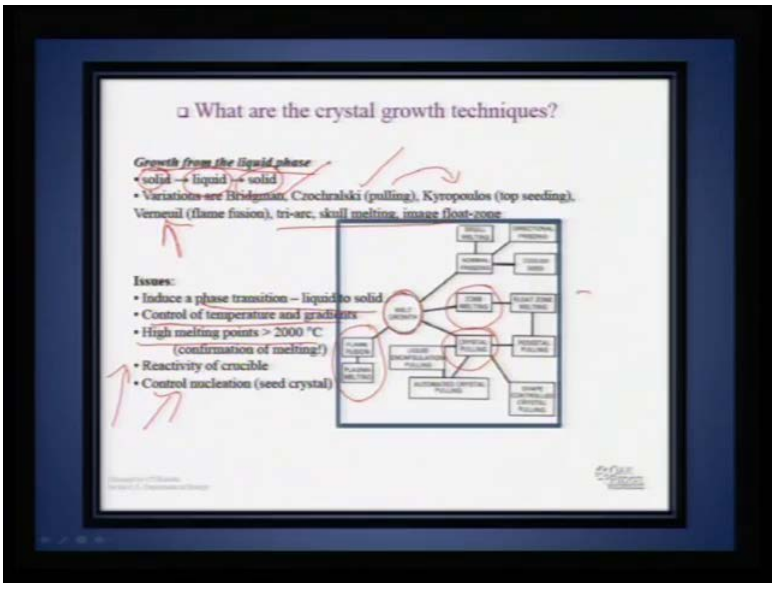

So, this is nothing but growth from liquid phase and it involves a two stage phase transition, one is you start with solid and then end up with the liquid, and then again you grow a solid. So, this is a two step phase transition solid to liquid, liquid to solid which we call it as a melt growth, and in this two or three popular methods are there and historically, there are at least 30 to 40 years old and we have never found any other alternate route, other than improvising on this good old techniques.

And what are they one is Bridgman technique and the other one is Czochralski technique, and same to do with that a closely related is Kyropoulos technique, and then another different one is Verneuil's technique, and these are closely related to Verneuil's method. So, we can take actually few examples to identify, what this techniques are and what are the minimum requirements for it, issues that we need to understand here is there is a phase transition liquid to solid and then we need to have a precise control of temperature, and the temperature gradients.

As, we grow this crystals and we may have to heat at very high melting point, because you are taking a solid to a liquid state and then again transforming it therefore, you need a way to melt this solids. Usually, inorganic solids are having very high temperature therefore, you bring in a additional requirements such as heating methods before you optimize on the cooling issues.

And then another important issue is that when you are actually taking from a solid to liquid, you need a container which will not react with your material and therefore, the reactivity of the crucible, becomes or the crucible design material issues become a very crucial point. And then the control nucleation all this become important, so in melt growth technique, we will be looking at zone melting which is one of a very popular route and another one is crystal pulling.

So, you actually try to initiate a crystal growth using a pulling technique, it can be it can either be initiated in a horizontal way or you can pull the growing crystal in a top way, but in nevertheless you need to actually start with a seed crystal, and that seed crystal will initiate a larger crystal growth. So, in all this techniques you actually initiate the nucleation process and from that is front it will start growing in a periodic way, so these two are more involved because it is very it is a time consuming process. But, flame fusion, which is Verneuil's method is a rapid growth method, you just melt all the stuff and then you immediately cool it, this is quite different from the zone and crystal pool technique.

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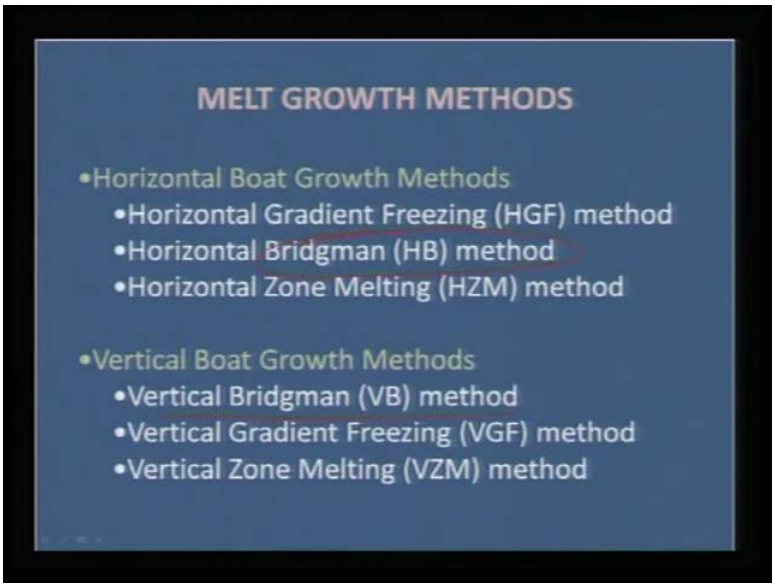

In melt growth method the most important one is a Bridgman technique, and this has a different way of realizing it, so you can actually go for a vertical Bridgman technique or you can go for a horizontal Bridgman technique. So, the assembly of your technique actually matters, but by and large the principle of Bridgman technique remains the same, we can also have the other one that is zone melting technique can either be in horizontal mode or it can be in a vertical mode.

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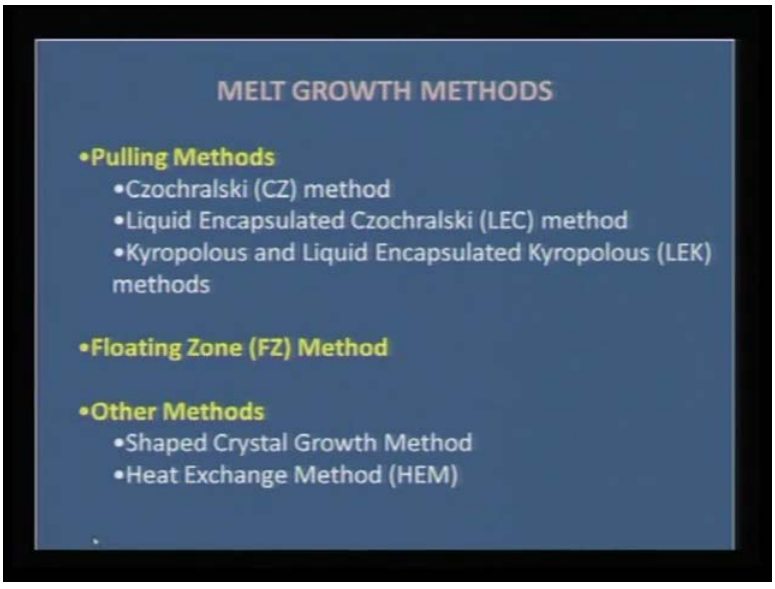

We will come to this schematically, then we can understand what exactly we mean by that, and then we have pulling techniques which is usually Czochralski method, and then floating zone methods are there we will look at this one by one.

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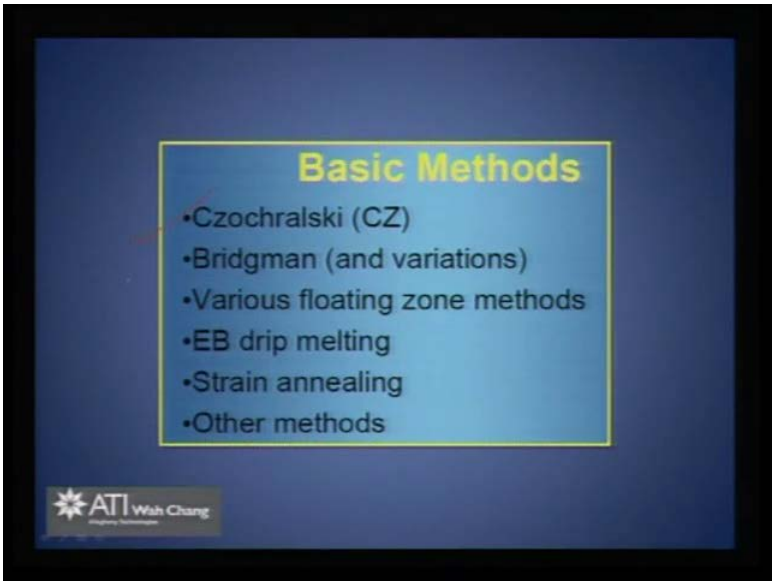

So, the basic methods that we are talking about is Czochralski method Bridgman method Floating Zone method and we also have other methods, which are a combination of two, we will shortly see from there.

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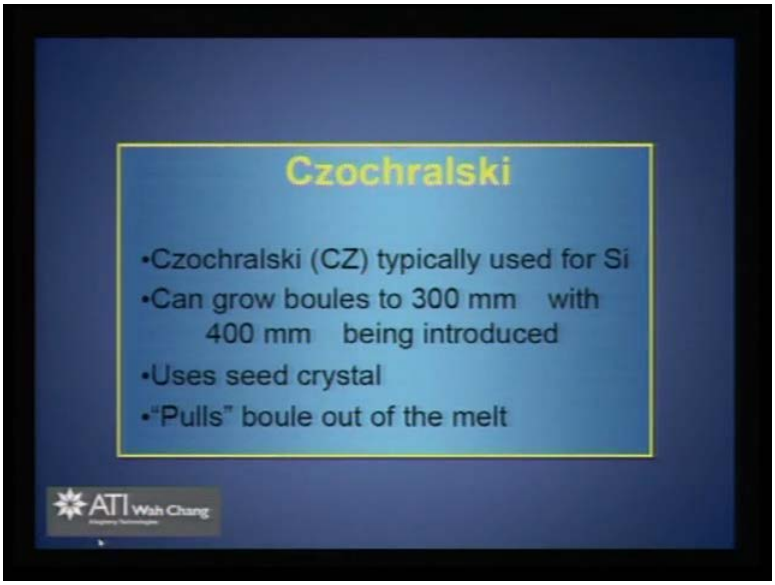

What is this Czochralski method this is a most industrially used method, because you can get very high qualities crystals, specially for silicon and basically this Czochralski method is even till now it is a sustained process, because the use of silicon is very important. Therefore, this is one of the established way to grow the crystal and you can see if you have a feed you can realize single crystal, successfully for three fourth of the batch that you are feeding.

Therefore, you do not loose on the starting material, because the silicon powder itself to get it is very costly therefore, to grow a crystal, where half of it becomes waste cannot be a viable process, but Czochralski method you can actually translate three fourth of the feed, that you are giving during melting can be realized as a single crystal therefore, this is a very popular method.

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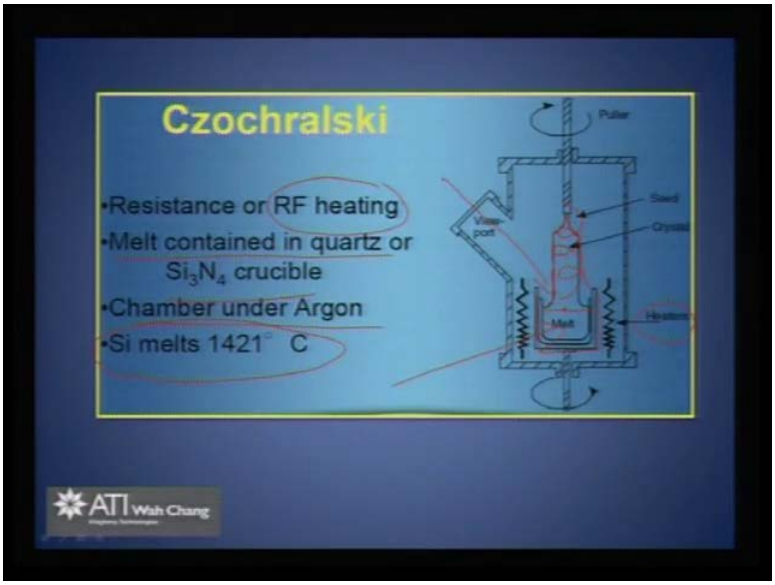

And the design of a Czochralski method is like this, you have the feed which is actually transformed into a melt using a heater and this heater can be a resistance involved or it can be radio frequency involved heating. So, you can actually see the whole growth process through this view port, and what you do here is that you have a pulling machine and this rod is actually suspended with a seed here and this is actually kept here at the beginning at the start of the process, where the seed crystal is touching the melt.

And then you can keep on rotating, this in a fashion that it will actually grow into a larger crystal, so this is actually pulling from bottom up. And what are the requirements

you need the melt is actually contained in quartz or in silicon nitrate crucible, because otherwise it will react and then the it has to be confined in a chambers therefore, the whole thing is kept in a atmosphere of argon. And what we need to achieve is the silicon which is the feed has to be melted the melting temperature is of the order of 1400 degree C.

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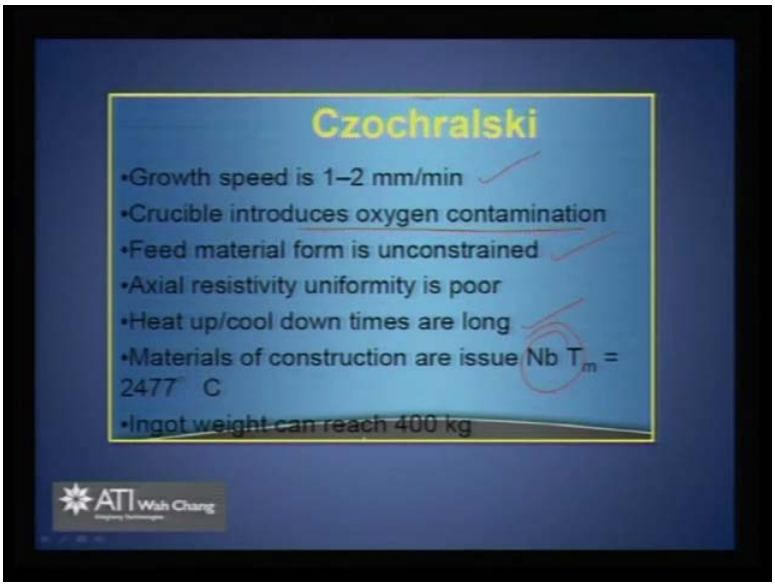

Therefore, the whole assembly has to withstand such high temperatures and then you can realize such single crystals, and the other parameters in Czochralski synthesis is the growth speed. Typically, you would not see the rotator moving because it is actually making an R P M very slow, so to your naked eye you would not even see anything moving, because you are actually going through 1 to 2 millimeters per minute.

Therefore, it is a very, very slow process and it might take even days to grow almost a half a feet long crystal, so a crucible introduces oxygen contamination, which is a problem, which is often combated. And then feed material form is unconstrained and then heat up and cool down times are long, and usually we worry about the assembly, which has to be made to withstand such temperature and niobium and the construction of this whole system becomes a issue.

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Czochralski method can also be modified and this is one such system, where you can see this is they use a tri arc furnace to quickly melt the feed, and melting is accomplished by three arcs then you can actually do a rotating water cooled copper crucible. And we can do this in vacuum, we can achieve up to 3000 degree C using this sort of tri arc furnace.

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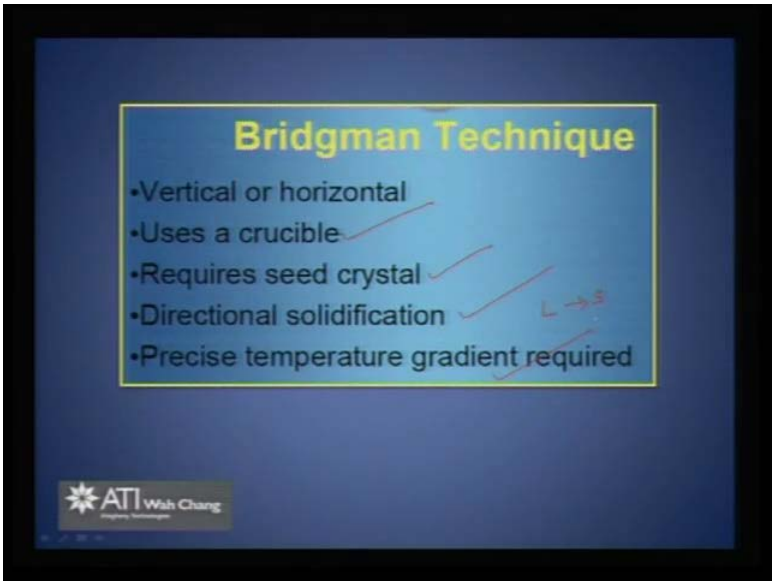

The next one is actually a Bridgman technique and in Bridgman technique we can try to mount your crucible or your feed it can be loaded in a horizontal way or we can have it in a vertical way, and mainly we use a crucible for this pulling technique. You also

require a seed crystal in this Bridgman technique, and this is a process where you actually have a direct solidification, because we are talking about liquid to solid and in this pulling technique, you are actually pulling it with a temperature gradient, so that this will become a solid. So, what is required here in this pulling technique is that you need a precise temperature gradient and this is the way Bridgman technique is realized, you have a heater, which will actually melt your feed.

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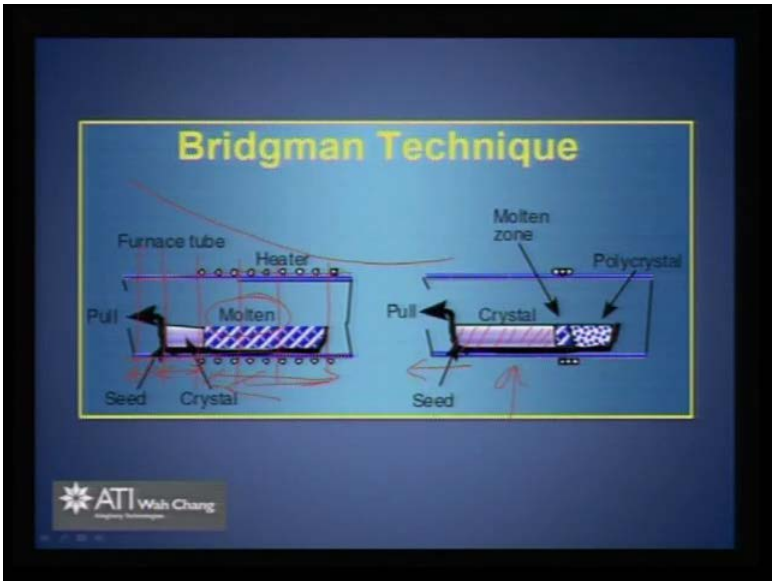

And therefore, what you see here is a molten a substance of any material that you want to grow as a crystal, and you actually pull it in one direction and this is actually kept in a furnace, and this furnace can actually be divided into different zones. Therefore, you need to keep this area in one temperature gradient, and this one in another temperature gradient and this one, so you need a very gradual temperature gradient like this, so that as you come a come out you will be able to grow a defect free one.

Suppose, you just pull it out which you call it as quenching then there will lot of imperfections in the crystal that is grown, because definitely it will solidify, when you pull a melt, but that is not the way you grow a crystal. So, this is a technique by itself which is very costly although it looks simple, but you what you see here you can grow very large crystals to the dimension of crucible and volume of your melt.

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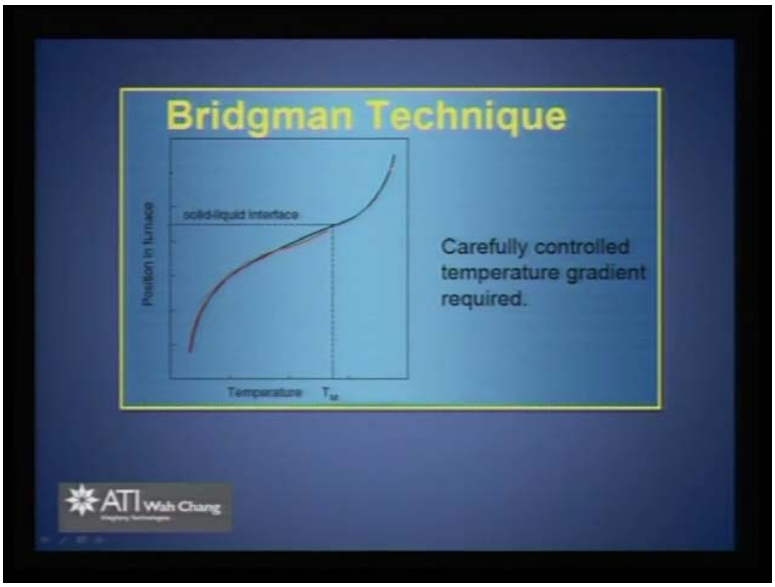

Therefore, this is a very a good technique compared to even Czochralski and much more easier all you need to optimize is this pulling time has to be optimized, and the temperature gradient has to be standardized. And typical position versus temperature is a curve for a Bridgman technique is like this, where initially you can pull it fast, but then when you try to solidify it when you try to form the crystal you should actually go through a platter which is much more slower. Therefore, you need to go through a temperature gradient like this before you realize your crystal, so this is the type of a profile or the temperature position graph that you should optimize for your Bridgman technique.

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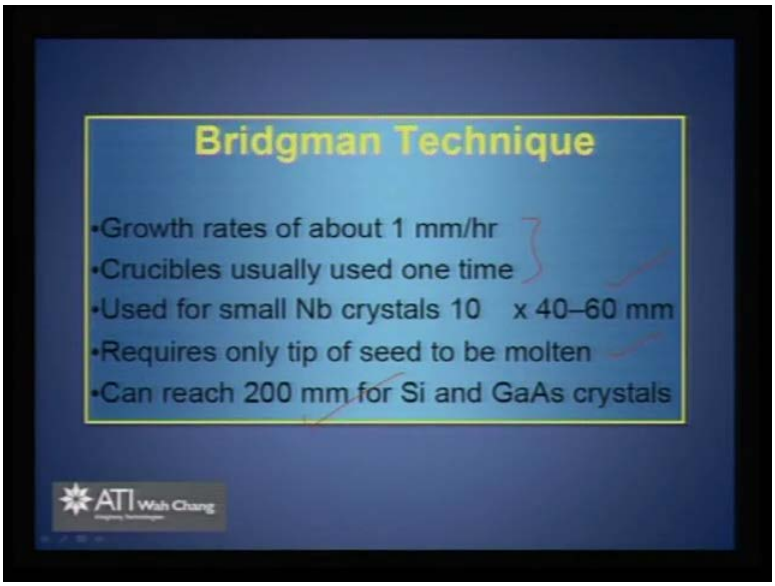

What you can achieve here is that crystals of dimension 10 to 40 millimeters can be realized, and it requires only tip of seed to be molten, which means a very small tip is needed, so that on that it can start growing. And you can also reach up to 200 millimeter for silicon and gallium arsenide crystals and this again is actually kept in a inert atmosphere, and some of the other issues from the economy point of view you cannot keep on using the same one.

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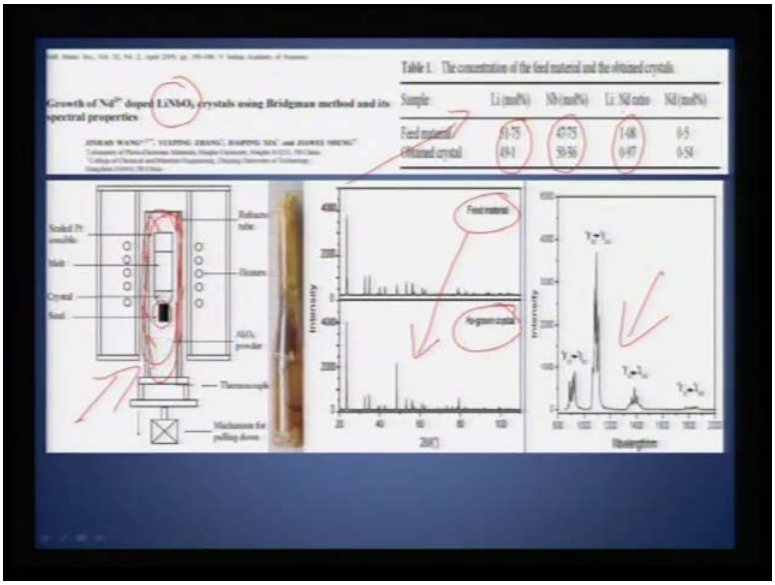

Therefore, it becomes Bit more expensive on those lines, one of the well-known compound that is lithium niobate it is a optical material, lithium niobate it is a perovskite and doped with a neodymium lanthanide ion, this can actually be a filter for your Nd-yag lasers. And how to prepare this, you can take lithium niobate and we can try to melt it and then cool this stuff, this is actually a vertical process what you do here the feed is kept here.

And we can try to use the seed crystal to keep pulling it, but this is also kept in a in a surrounding, which is packed with alumina because they there will be a temperature gradient if you are directly exposing this to a heater. So, in order to avoid a temperature gradient in a drastic way you try to pack this whole assembly in a alumina matrix. So, that it is a isothermal effect, there will be uniform distribution of this temperature throughout, otherwise there will be a very serious a temperature gradient, and this is the assembly and you can see here the X ray pattern of the lithium niobate that is grown.

This is the feed material which is the bulk before it is melted, and then the ash grown crystal both shows a very clear match in the X ray pattern, and lithium niobate which is doped with neodymium as I told you is a very good material optical material and shows PL at around 1200 nanometers. If you look at the purity of the crystals that we get you can see a very good agreement between the feed material and the obtained crystal, you can see here not much of change in the lithium content niobium content has a slightly larger mismatch, but lithium to neodymium ratio is absolutely in a agreeable limit. So, this is a very, very important and the most preferred route for ferroelectric crystals therefore, Bridgman technique is still being used for growing ferroelectrics.

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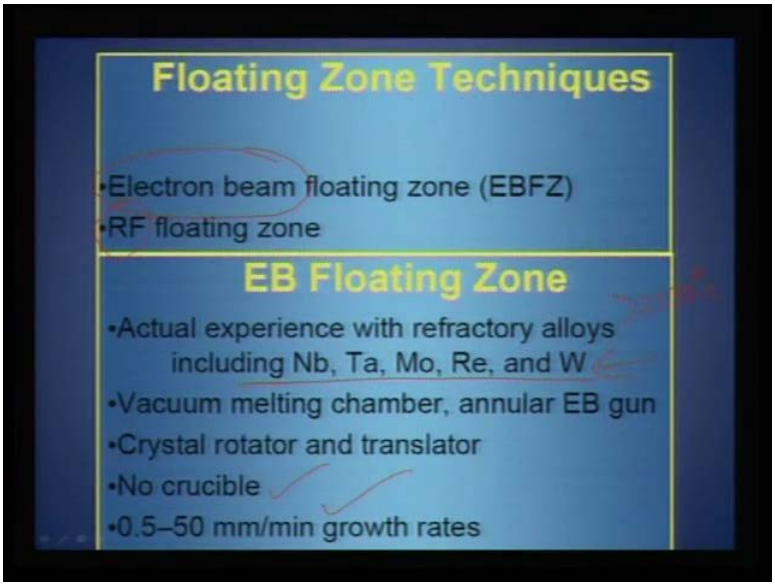

The next technique is a floating zone technique and here floating zone means you try to bring out a zone, which will divide between the feed and the crystal and the intermediate necking region is actually melted. So, how do you melt that you can use radio frequency to melt that region or you can use a electron beam to melt that region therefore, it is called EB floating zone a method.

And actually, we can make a several alloys or metals using floating zone to mention niobium, tantalum, molybdenum, rhenium, tungsten the reason why a floating zone method is very popular is all this alloys or metals which are mentioned here they are having very, very high melting points above 2500 degree C. Therefore, it is very difficult

to use other methods what I have discussed, so E beam floating zone method is still the most preferred one for simple metals like a molybdenum, rhenium and tungsten.

And there are several issues that are related to that one important thing, that you should understand between the Bridgman and Czochralski method and this is here you do not need a crucible. So, you just have a feed and then you have the seed and in between the feed and the seed you create a zone, and that will actually melt and start growing as a crystal. So, growth rates of a 50 millimeter per minute can also be realized therefore, these are comparatively a fast crystal growing technique compared to Bridgman method.

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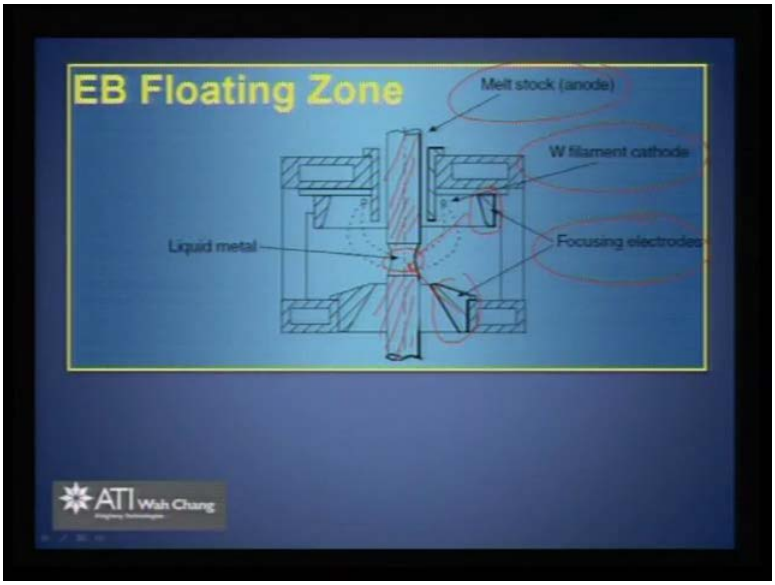

This is the typical assembly for this EB floating zone, where you can see here the tungsten filament cathode is there this is the melt stock which is nothing but your anode, so this has to be conducting in order to make this as a anode. So, this is your feed what we call and this is your seed with a interface and in between you can see the liquid melt which is actually melted using a filament, but in order to focus it only on this region otherwise the whole feed can melt.

So, in order to do that you also introduce some optics here which we call it as focusing electrodes, so you try to bring such a way that the focus is only on a very small interface. So, that we call it as a floating zone, so it will not actually melt the growing seed neither it will melt the feed fully it will only concentrate on a very small region therefore, the there are different ways that you can realize, such a preferential melting.

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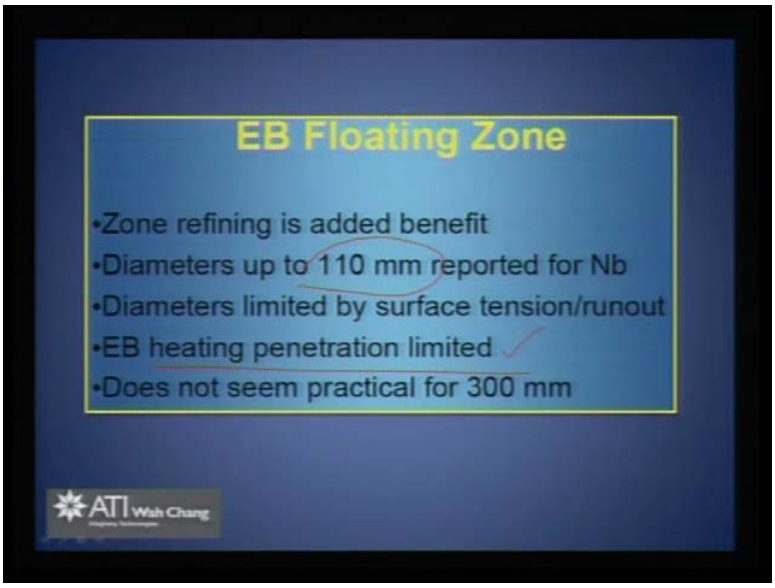

So, in EB floating zone you can get crystals of diameter up to 100 millimeter and then one problem that we face here is the penetration, it is not possible to actually run through the bulk especially when you have a feed, in EB what happens the surface melts, but then it does not really go into the bulk. Therefore, there are some practical problems which needs to be sorted out, when we go for this floating zone method.

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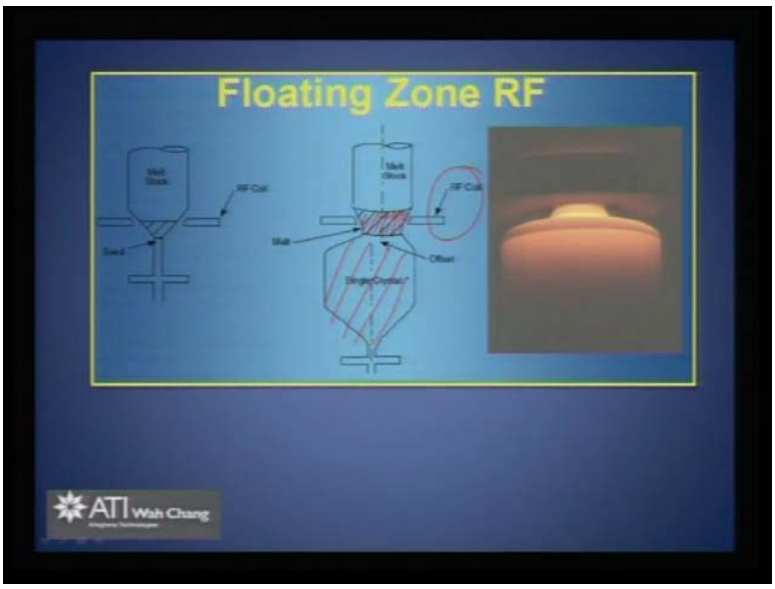

Here, is another picture of a floating zone apparatus where you are actually using a RF coil to melt this interface and here, again you can see the single crystal can be grown into a bigger dimension and that is one of the advantage of using a floating zone method.

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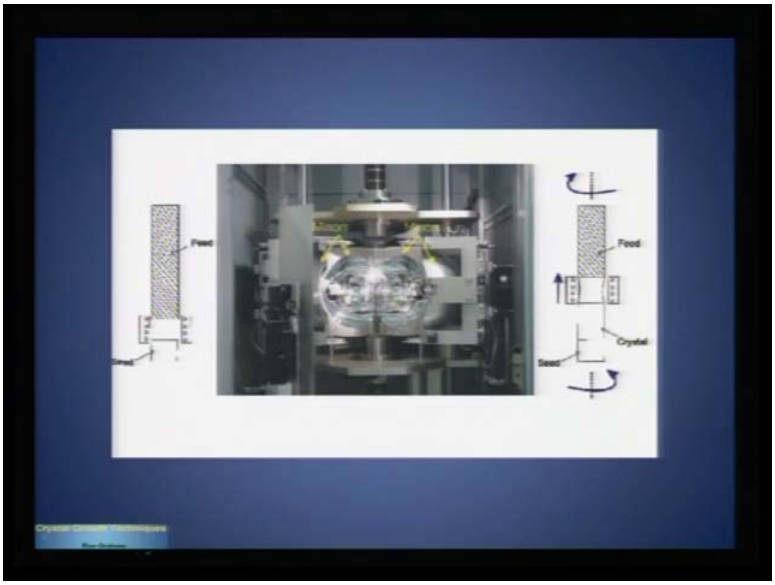

Typically, you can realize such sophisticated instruments for a floating zone these are commercially available, so this is an industry in itself where such apparatus refined ones are already commercially available, so we can go for such expensive techniques also.

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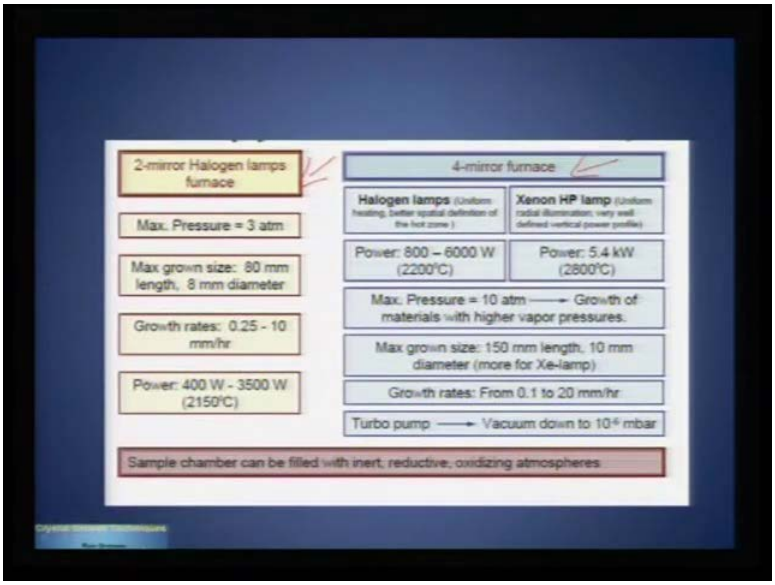

Now, to bring about a proper melting at the interface, there are different arrangements that are possible one is called two mirror a halogen lamp furnace, you can also have a four mirror halogen lamp furnace. And the whole idea in this floating zone technique is to make sure that it is really melting the zone in a very, very precise way without creating any temperature gradient over a large area, so lot of refinement has come into picture in this floating zone technique.

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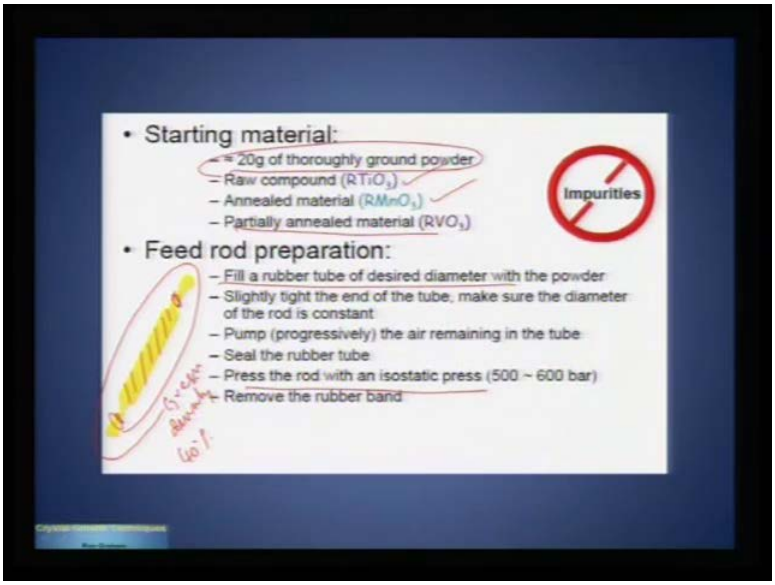

How do we go about this floating zone, simply we can start with an example roughly what you would need is about 20 gram of a powder, you can if it is a tight net you do not have to worry about it you can take the raw powder as it is. In case of manganites you need to actually anneal it little bit mainly, because manganites take carbondioxide or water it since it is reactive you need to activate the surface.

Therefore, if you are going to grow a manganite crystal, you may have to do a annealing before you take it or you may have to partially anneal it for vanadates, so this is just to prepare your sample. And how do you go about it you actually fill it in a rubber tube, you can even do it in a ballon and you can stack this 20 gram in a ballon and tie it in this fashion, and you can tie this ends and you can put this in a isostatic press. Isostatic press is nothing but you put it in a container with oil and then you apply pressure from all sides, then what happens this stuff which is contained in the ballon or rubber will actually become a rod by itself.

In other words if you start with a compaction or a green density of say a 40 percent; that means, you just tapped it and took away all the air sacs, in between then using isostatic pressing you should be able to get upto 60 or 70 percent density, and that will be a very good feed for your floating zone method. So, what you do after isostatic pressing you can try to remove this rubber or you can tear of the ballon, then you get a rod which is nothing, but a simple compact, but good enough to hold it as a rod and then you try to put that as your feed here.

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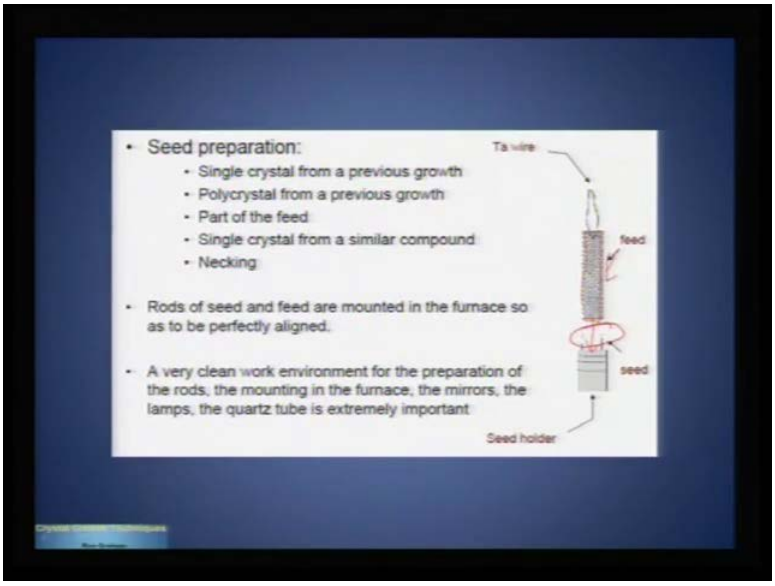

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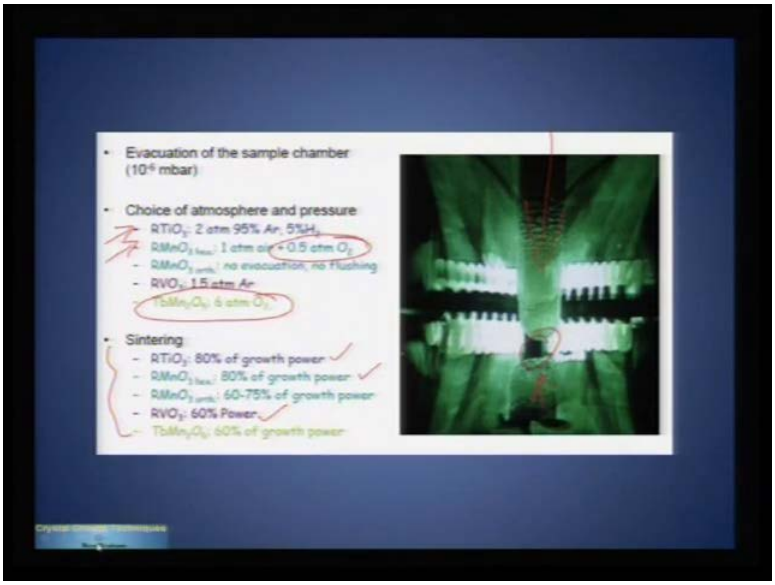

And then we can, so this is nothing, but the dimension of what I have shown in the previous slide, so this we can use it for using as a feed in order to grow the seed. So, this feed is actually mounted, and we can start melting it in this interface or in the necking region then we can try to grow the cryatal.

And this particular cartoon gives you a real time image of how this growth process occurs, you can see this is your feed and then how the necking region is here, and then the seed cryatal is actually growing. In there are different conditions that are required when you are growing different materials for example, for titanate you have a preferred choice 95 percent argon and 5 percent hydrogen is needed.

In case of manganese because it is a oxide with a different valency of manganese you got to be careful therefore, you need to have a mixture of air and more amount of oxygen to it. And similarly, other a rare earth manganese can be used what you can see here is this the amount of sintering that has also to be accompanied with this sort of floating zone method, for titanates you can achieve upto 80 percent of growth and again manganite 80 percent then we can look for a vanadate 60 percent.

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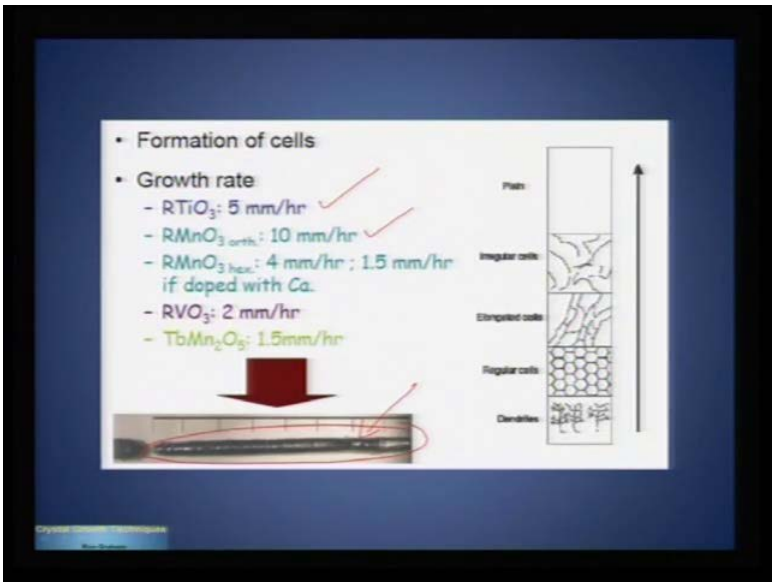

So, the compaction melting all these are very crucial for different oxides that we are using and usually we try to standardize this by a trial and error method, typically the growth process also involves the way you try to grow it the in terms of growth rate. Manganites are much more faster we can try to grow at a much faster speed, but titanates

are usually are time consuming one, the sort of rods that we can grow a single crystal manganites or venadates typically looks like this. You can grow such long ones and then those are nearly 99.9 percent dense, so this sort of single crystal rods can be usually achieved using this floating zone method.

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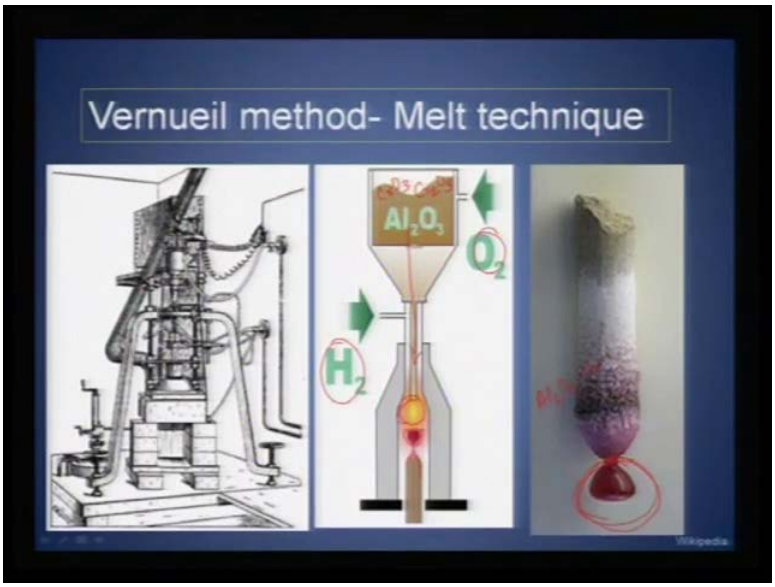

This is another technique that stands out compared to all the other techniques that we have discussed, this is called Vernueil method. And vernueil method is a melt technique where you are actually going to feed alumina as a powder and you are going to send hydrogen oxygen flame, and this hydrogen oxygen flame will actually melt this feed, which is coming from here. And at this point if you have a seed here this will nicely grow and what you are seeing here is nothing, but a ruby crystal which is a Al 2 O 3 doped with chromium.

And if you are going to grow ruby all you need to do is take some Cr 2 O 3 or Cr O 3 whichever is possible and try to melt it along with alumina in a desired quantity, then you should be able to get a single crystalline, ruby crystal. And this is basically a melt process which is very different from the other stuff, because the melting is actually carried out by a flame which is composed of hydrogen and oxygen which can actually heat flame temperatures upto 20 to 100. So, it is more like a welding protocol, you try to use a very high flame to melt the compound and grow the crystal.

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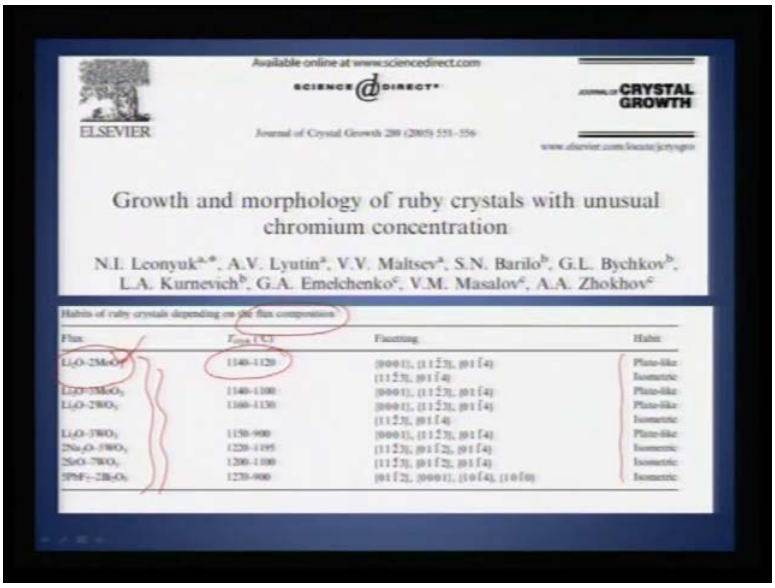

Ruby crystals actually can be made using Vernueil's method, but we can also use another important technique, which I will be discussing in the next few slides which is called as flux method. And in this cartoon you can see there are several flux that are mentioned and this is one of the very distinguish chemical technique by which we can prepare single crystal rubies. You can see here lithium oxide, molybdenum oxide mixture in 1 is to 2 mole ratio if you take, and put it in a furnace in a crucible.

You can actually melt it between 1120 to 1140 degree C. Then this lithium oxide, molybdenum oxide will form a melt and in this melt, if you drop some alumina with chromium oxide then what you will get is ultimately a ruby crystal in a melt and this lithium oxide, molybdenum oxide is actually water soluble. Therefore when the crystals are formed all you need to do is just dump it in a hot water, then all this things gets dissolved into water and what is remaining as a residue is nothing, but the crystals that are formed.

So, this is a simple protocol of a flux method and this flux method is very, very common in all solid state chemistry laboratories, where you just need a oven not even a furnace, you just need oven because most of the flux can be melted at 200 or 300 degree C. So, this is a very, very easy way to realize single crystals of any compound only thing, you do not get a control over the large size that you can grow, but in a lab scale you can get very oriented and good quality crystals for even tricky composition like ruby. So, this is

one way you can realize as you can see here depending on the flux ratio, you can also try to affect the a growth process and the shape of the ruby crystals.

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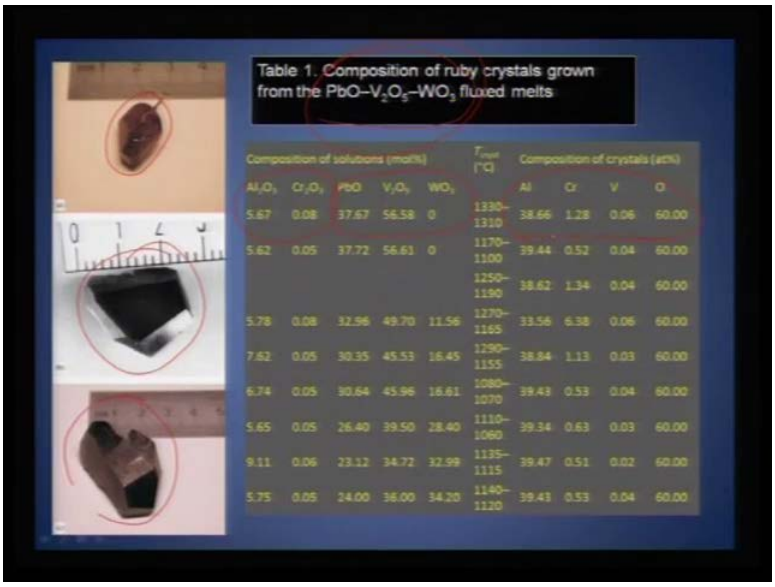

And here is another one which is usually used a lead oxide, vanadium oxide and tungsten oxide as a flux melt, and if you have different compositions of this you can take aluminum chromium ratio. You will be able to get different qualities or different varieties of a single ruby, single crystals and here you can see all this pictures of ruby crystal.

Although, they do not look like pink color the characteristic color, the surface is actually contaminated with the coating of the melt, now once you polish this you will be able to get a real quality rubies, and depending on the melt you can see the shape and dimension of the crystals that you can isolate. And you can also see this melt does not really affect the composition of your ruby, it will be in trace amounts.

So, one can use a variety of combination of a flux for growing ruby crystals in for flux growth, there are some essential things that we need to bear in mind. One is the advantages, that you can have play around with a very low melting temperature, because you are actually melting a flux and that will actually bring about the melting temperature of your target compound. So, you low down the melting temperature of the desired compound, we can also easily separate the melt from the product and therefore, this has advantages, what are the needs or what we really need for a flux growth method, you

need tubes and you need crucibles, tubes in order to seal your material and then crucible because that is where you let the crystals grow.

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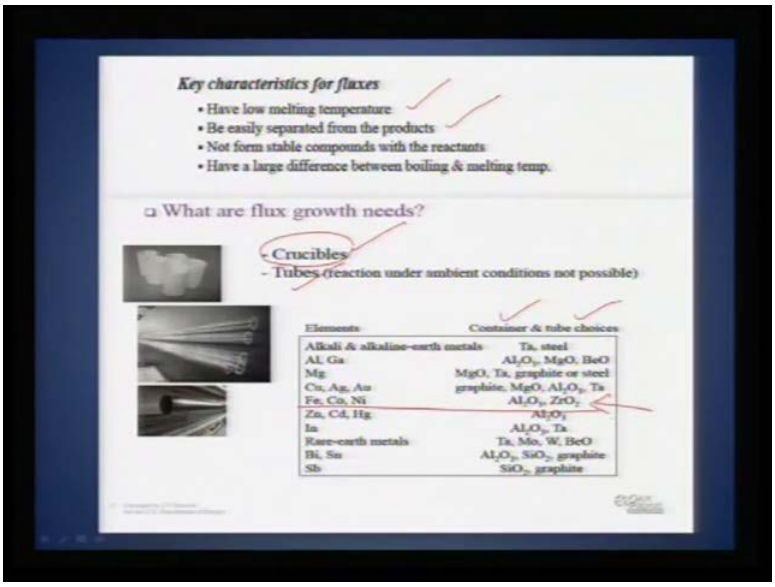

So, typically the container and tube choices are given here just I want to single out for example, I if I want to prepare a single crystals of iron cobalt, nickel, ferromagnetic metals, then I usually use a high temperature crucible like alumina or zirconia, which does not react with any of this metals therefore, I can get that.

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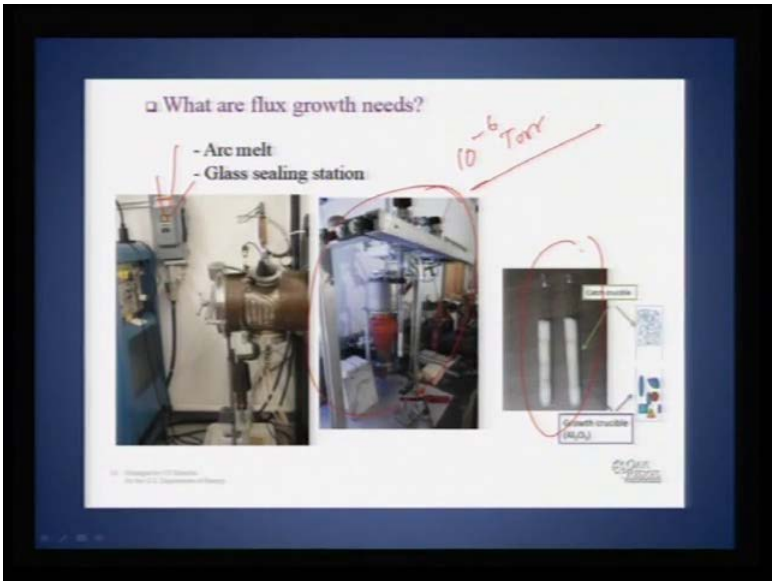

The assembly for making flux growth also can be as involved as this, although you can even use a simple oven and here is one case where you can actually arc melt the flux, because you immediately get it. And then you certainly require a glass ceiling station which means you need to achieve upto 10 power minus 6 torr atmosphere, and once you achieve this then you should be able to seal this.

And this is typically the capsules that you get before you go for flux growth, what you see here are the alumina crucibles which are the which is called as growth crucibles and then you have catch crucibles which are usually quartz. So, quartz is actually used for sealing the crucible, and inside the quartz you can actually have alumina crucibles with your materials.

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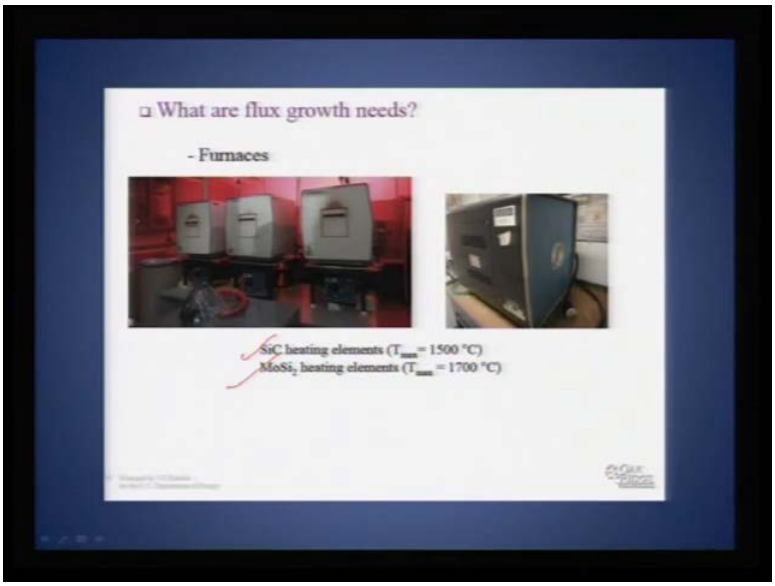

So, this is the way you do it and typically you need furnace to grow this flux grown crystals, so these are typical dimensions of the furnaces that you need to have, you can actually use high temperature furnaces, mostly molybdenum disilicide which can give you upto a 1700 degree C or you can use silicon carbide furnaces, which can achieve upto 1500.

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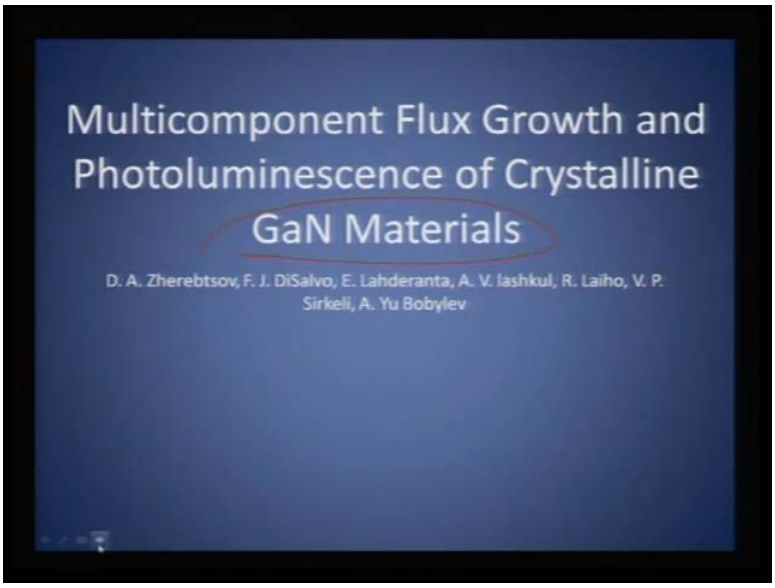

One of the main advantage of flux grown method is to prepare photo luminesent gallium nitride materials, which is actually published by this group and just want to show you some glimpse of how costly the gallium nitride is and how we can achieve using flux grown method.

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Gallium nitride as you know is a well known LED Light Emitting Diode and typically this is also used in read, write laser diodes and it these are all very costly products, which are in market today. And to grow this gallium nitride main problem is you do not have a

gallium to nitrogen ratio which is 1 is to 1. Usually, when you grow by other methods including thin film methods, the ratio of gallium to nitride is always different, so you end up getting gallium nitrogen 1 minus x always. The nitrogen composition will be very critical to control, and as a result it can actually induce lot of defects in your gallium nitride diodes.

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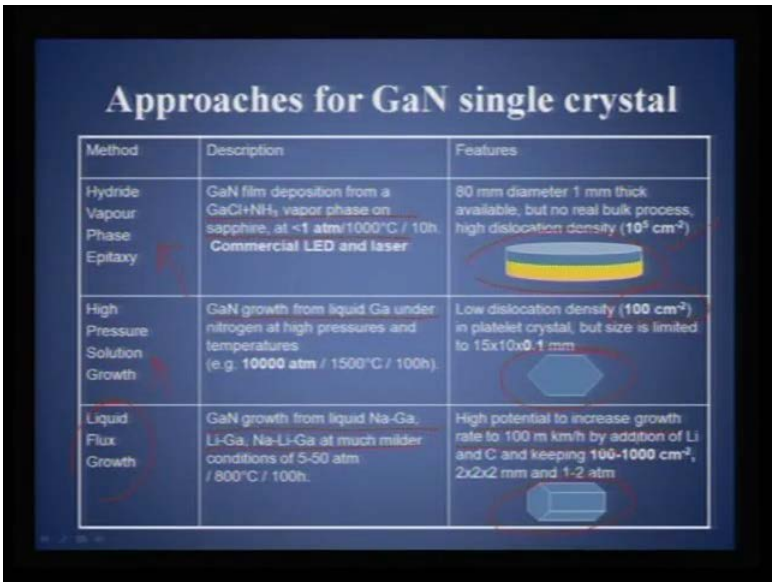

So, flux method can give you a very refined growth, and as you see here this is a comparative slide, which tells you how important flux grown method can be these gallium nitride single crystals can be grown in a larger disc like this, using physical vapour deposition routes. And what you do here you take gallium chloride and ammonia is passed as a wafer and you can try to deposit in a sapphire crystal, and you can get dimensions of this order only thing when you grow as a thin film, then the disc location density is very high.

So, in order to beat that you can actually go for a high pressure solution growth, where you can try to grow it using liquid gallium and nitrogen at high pressures, in such case you can realize very less dislocation density, which means the quality of the single crystal is very good, only thing you get very small dimensions of gallium nitride crystals. Flux grown method is another easy route where you can achieve comprehensively a larger a diameter with less defects, and how do you go about with a flux method gallium nitride we can grow with a liquid sodium gallium melt. And we can try to also add

lithium and other additives to enrich on the nitrogen content, and this has a high potential to increase the growth rate even to 100 kilometers per hour you can grow such large crystals at a faster rate.

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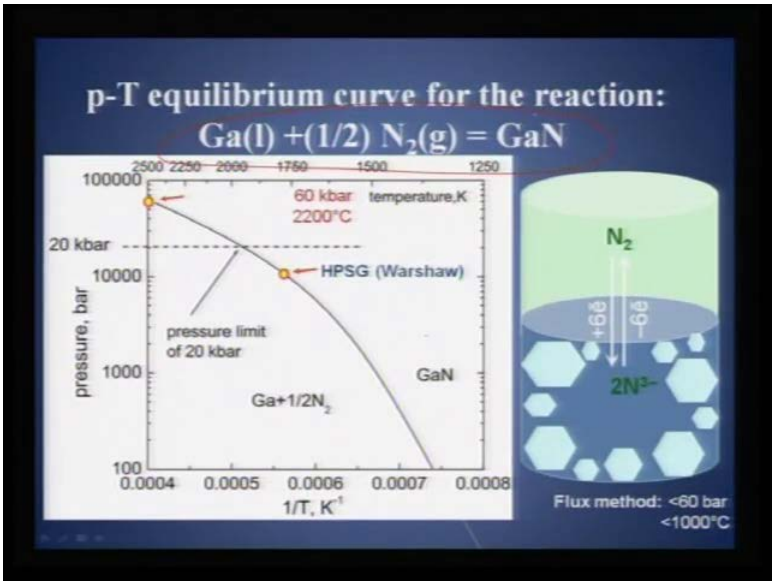

So, this is a typical profile of your pressure a temperature graph, which is required for achieving a gallium nitride formation using flux growth.

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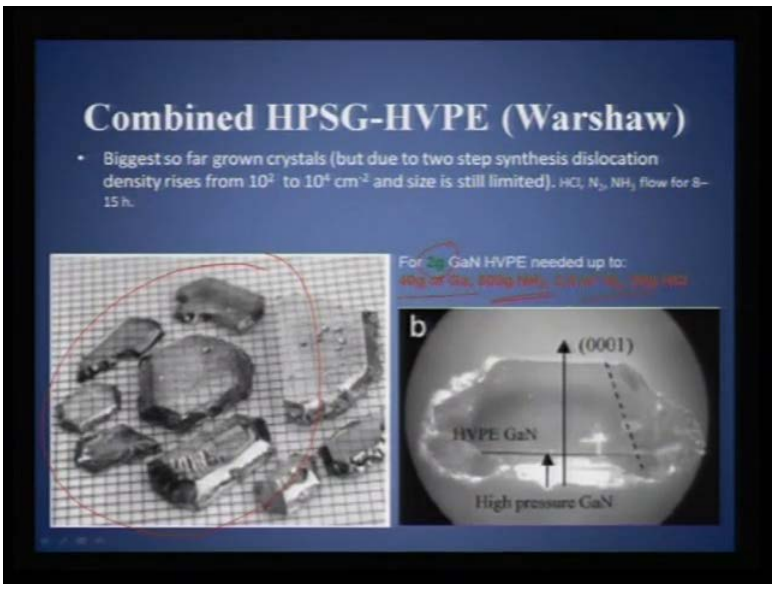

And typically the size of the crystals can be as large as this, so this is achievable if you you can get a gallium nitride of say two gram quantity if you are going to start with 40

grams of gallium and 600 grams of ammonia and hydrogen. So, this is typically the the the level in which you need to start in order to get 2 gram quantity of gallium nitride.

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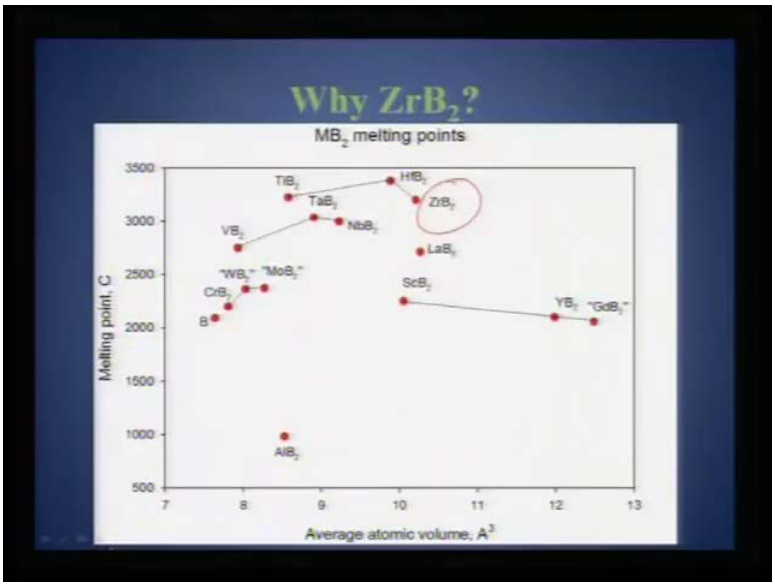

Main issue as far as gallium nitride growth is concerned is the container in which you are growing, because it should not diffuse or it should not react with your melt, and in that case usually borides are used. So, any flux growth method all that you should remember is borides, metal borides are the most important ones, which which needs to be used therefore, most of this crucibles are very, very expensive a zirconium bromide is one which is often used. And there are several ways to improve on this gallium nitride growth, specially addition of carbon seems to increase the solubility of gallium nitride in the melt. So, lot of improvisation can be achieved using this.

And this is one view graph which tells what sort of growth that you achieve out of gallium nitride, typically gives the characteristic P L property for the flux grown crystals. And I have to also mention that this although looks like a simple technique this is one of a billion dollar industry in today's materials world, crystal growth can never be substituted with any thing. And therefore, there are several companies across the globe which is producing several varities of single crystals.

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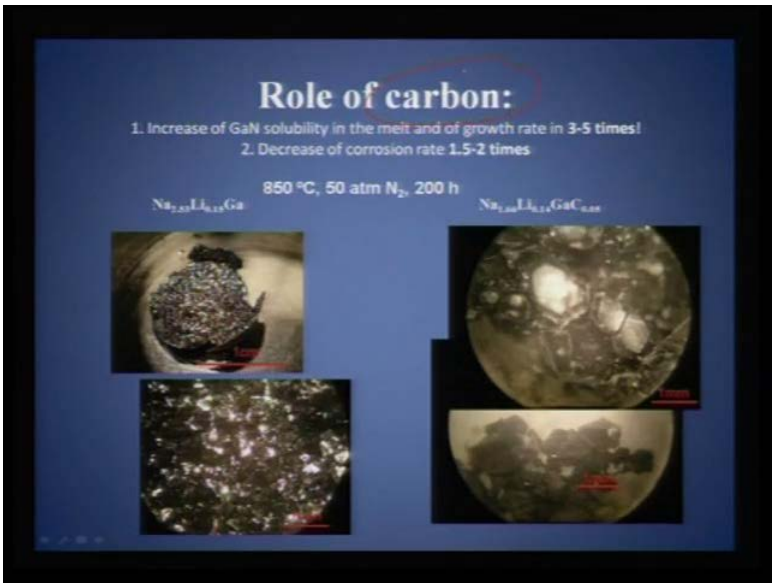

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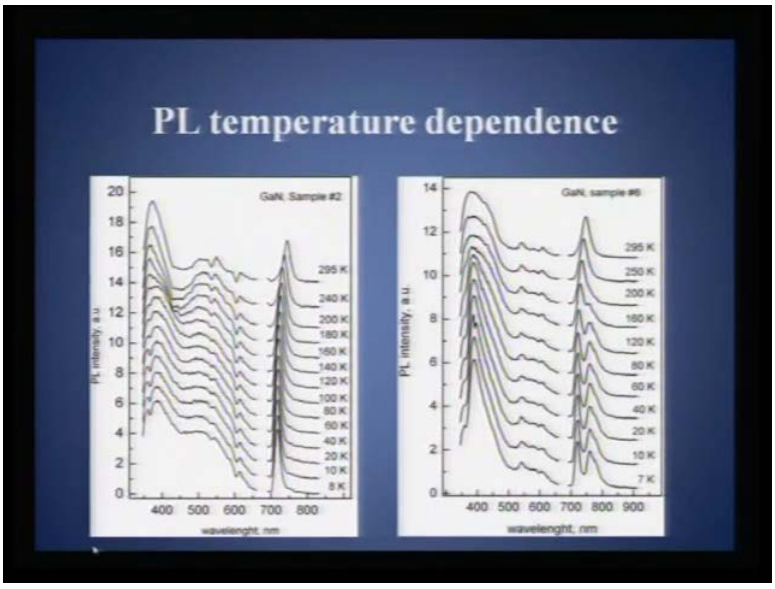

I am not particularly inclined to promote this, but then these are some of a the companies which are found in the websites for example, I am just quoting this particular company, just to highlight what sort of single crystals are been marketed. Almost, you name any element in the periodic table they seem to be making a single crystal out of it, so it is a big business used for several applications as monochromators they use all sort of methods that we have discussed for making a wide range of compounds. And for sophisticated or for preferred single crystals like sapphire or Nd-Yag or for silicon wafers all this can also be made.

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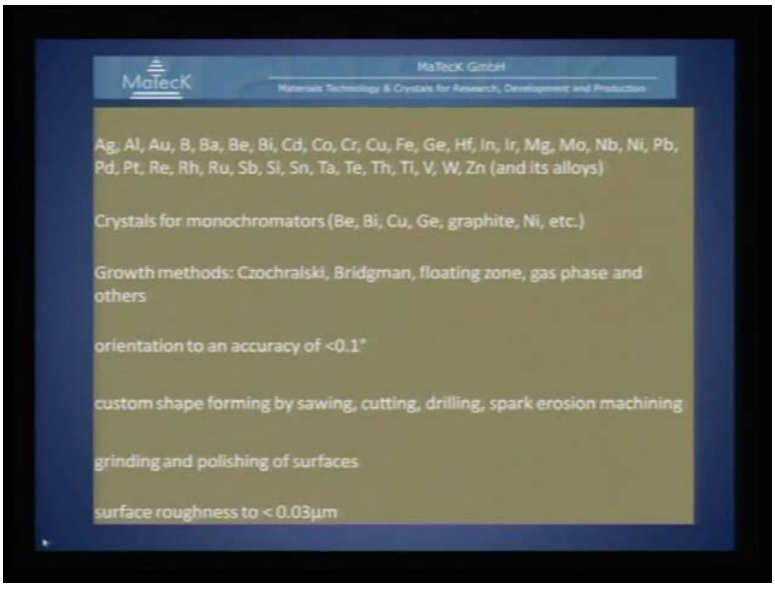

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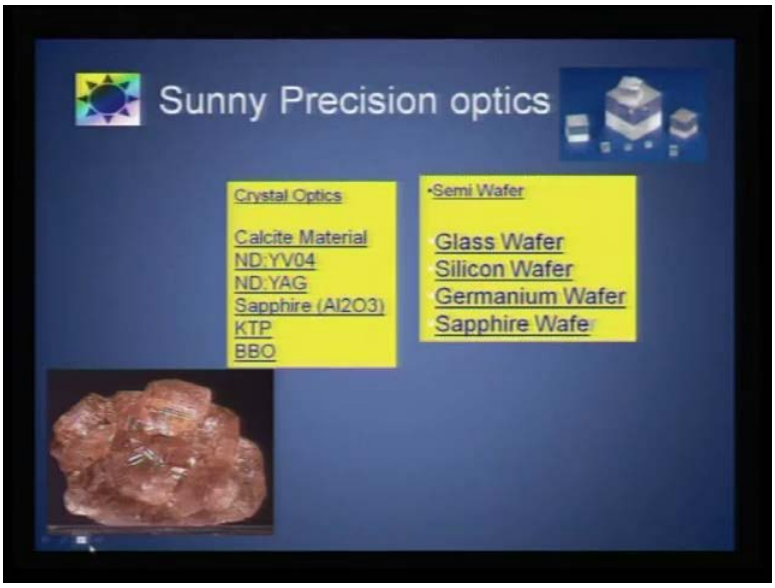

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And there are several companies working or specializing on particular materials also, I should also say that a single crystal growth is not a just an other one, it is a field in itself it is a research field and several publications have also floated in today's literature. And just to show you how this area has grown has bloomed into a major area, you can see several journals are also floated exclusively on crystal growth.

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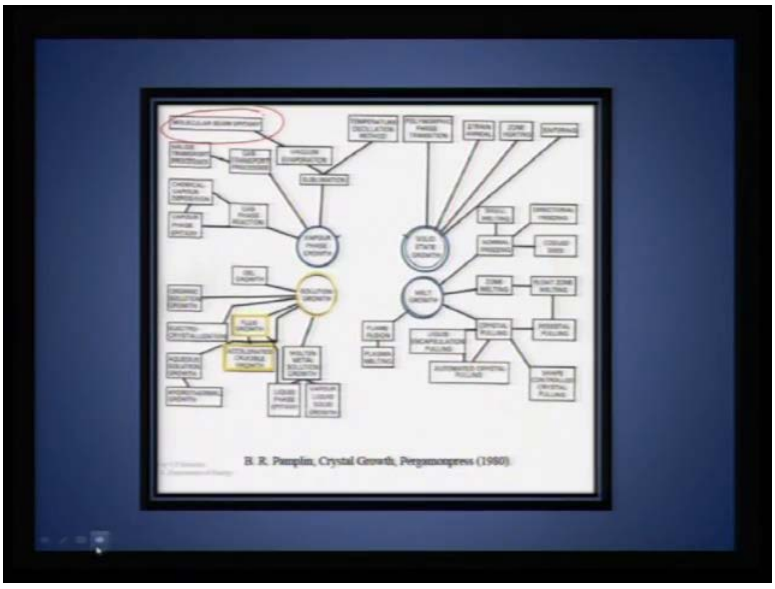

So, just to conclude I have to tell you that we first looked at the principles of solution growth, which we are already familiar with and then we looked at the vapour phase growth. And notabily the molecular beam epitaxy which stands out as the best single crystal growth method and then we also looked at some examples of solid state growth. And lastly, we have seen the various combinations of melt growth techniques, which are used even today for making a fine quality single crystals.