Solid State Chemistry
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Lecture – 04
Synthetic Strategy

Now I will give the fourth lecture of the first week of this course. In this lecture, I will talk about the general overall Synthetic Strategy of solid state materials. I will not go too much into detail here, but I want to give the overall picture of the steps involved in a typical solid state synthesis. Now, you will see and you will learn as you learn more of these reactions that depending on the material you want to synthesize and depending on the kind of structures you want to synthesize, you use different techniques ok. But in this lecture, I will just give a brief overview of the techniques used in of some of the techniques not all the techniques used in solid state synthesis.

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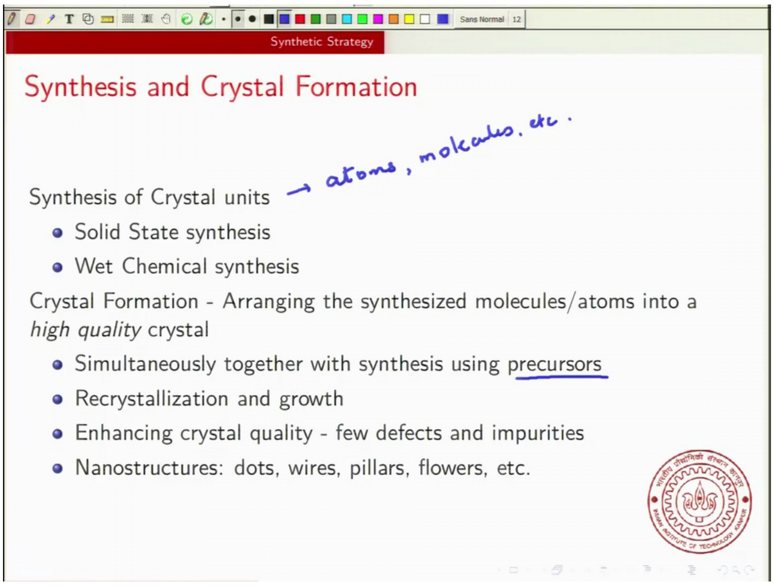

So, let us talk about, if you look at solid state synthesis, there are essentially two steps one which I am called which I am calling synthesis and the other is crystal formation. In the synthesis part, you synthesize the crystal units and this is typically accomplished in one of two ways, either through a solid state synthesis or some sort of wet chemical synthesis. So, here what is done is you synthesize the units of the crystals and when I say units of the crystal, they can be atoms, molecules etcetera ok. So, if your crystal just consists of atoms then basically we are just making sure that only the atoms are left. On the other hand if it is if it has some molecules like an oxide, then you have to synthesize the oxide ok.

So this is a step where that particular material that forms the crystal is synthesized. The second step I have called it crystal formation and here what we do is you arrange the synthesized molecules or atoms into a high quality crystals ok. So, this is where you actually take the molecules that form the solid and you arrange them into a into a very well ordered pattern that forms a high quality crystals. Sometimes this crystal formation takes place simultaneously together with synthesis. So, you start using certain things called precursors and you simultaneously accomplish both the synthesis and the crystal formation. But in many other cases, you often do the solid state synthesis and then you re crystallize your sample.

So, in your in your first step of synthesis you get a very poor quality crystal and what is done is you re crystallize it and or we use a term we grow the crystal ok. And what this does is it we use this term that it enhances the crystal quality and what we mean by this is that the crystal that has formed has very few defects and impurities. We will discuss defects and impurities later, but I just wanted to distinguish step of where you synthesize the constituents of the crystal and where you make the crystal high quality. In some cases we want to synthesize nano structures. These are essentially crystals in the shapes of dots, wires, pillars, flowers etcetera and. So, then; obviously, you have to worry about how you crystallize this, what is the substrate used and so on.

But almost any solid state synthesis can be thought of in these two as these two separate parts one is the synthesis of the crystal units and the other is the crystal formation ok.

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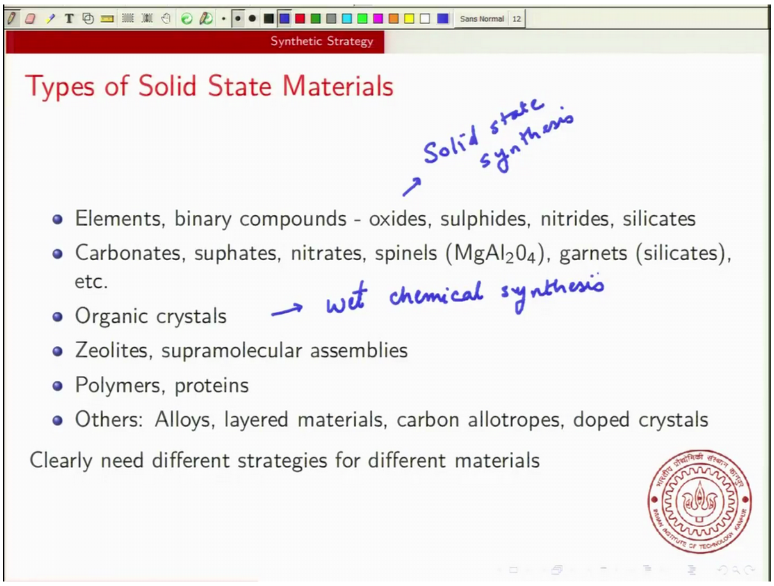

So, now; obviously, because there are so many different kinds of solid state materials you require different strategies for crystallizing them. So, you could have solid state materials such as just simple elements or binary compounds, you could have oxides, sulfides, nitride, silicates. You could have slightly more complicated compounds like carbonate, sulfates, nitrates or you could have things like spinels. So, an example of a spinel is MgAl 2 O 4. You could have garnets which are essentially silicates ok.

So, you could have such compounds which are not very complicated, you could have organic molecules forming a crystal, you could have zeolites which are again some sort of silicates or you could have supramolecular assemblies which form crystals. You could have crystals of polymers, crystals of proteins and some other things you could have you could have alloys, you could have layered materials where you have where you have one crystal deposited on top of another. You could have allotropes of carbon you could have crystals that are doped that are intentionally doped ok. So, it is clear that each of these would require a completely different method of synthesis.

For example, typically oxides are synthesized using solid state synthesis ok. Typically they are synthesized using solid state synthesis, you can synthesize them sometimes from using soft wet chemical methods. But typically they are synthesized using solid state synthesis and some of the other compounds are often especially organic crystals will be you will use wet chemical methods of synthesis. And I will come to, I will come to describing these two different synthetic strategies, I would not talk so much about arranging the constituents into crystals. There is a whole array of techniques for doing that, but I will not be discussing that in this lecture.

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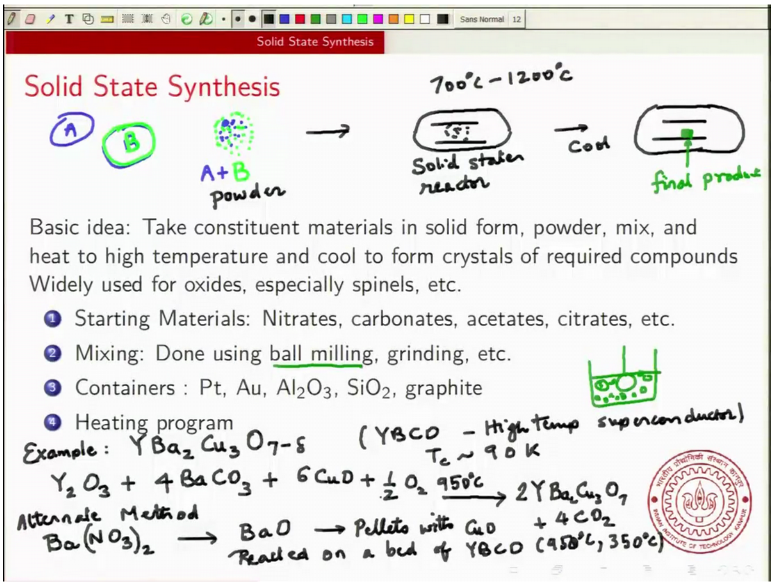

So, let us look at solid state synthesis ok. So, the basic idea is that you take the constituent materials in a solid form ok, you powder them, you mix them and heat it heat the whole thing to high temperature and then you heat it to a high temperature. So, they react to form your compound of interest and then it is cooled to form crystals of the required compounds. This is widely used for oxides especially spinels.

So, what do you do? Let me just depict it pictorially. So, you start with your solids solid materials; let us say A and B. These are the solid materials that you take, you powder them mix them and you powder them. Let me show B in a slightly different color; let me show B in green. So, then you have this finely mixed powder of A and B. These are still in. This is A plus B powder ok. Then what is done is this whole thing is introduced into a reaction chamber. So, it is introduced into some sort of a tube and I am just showing it this way, this is a typical solid state reaction chamber. So, this material is right somewhere here and usually you heat it state reactor and this is heated to maybe anywhere between 700 degree centigrade to 1200 degree centigrade depending on the material that you want to synthesize. And when you heat this to a very high temperature, then A and B react they mix, they often they give out or they disintegrate sometimes to various components.

But finally, you get your product and when you cool it, then you will get in your in your reaction chamber, there will be some amount of your final product. Let me show this in this dark green color ok. So, this is your final product and I should mention that a lot of gases are eliminated during this process ok, I am not showing all those things, but this is the basic idea. So, let us look again what we did. We started with A and B and we mix them and we powdered them and then we put them in this reactor and we which is heated to 700 to 1200 degree centigrade. And at this high temperature A and B will react to form your product and when you cool it you get nice crystals of your product. This is the basic idea of a solid state synthesis.

Now there are several questions that are required to be addressed and which are different for each solid state material that you want to synthesize. So, some of the questions are, what should be the starting materials that are used ok? So, you can use nitrates, carbonates, acetate, citrate etcetera ok. If you are if you are making oxides, then typically you use one of these and then you heat them. So, suppose you take a nitrate and heat it and then no two gases is evolved and you get the oxide ok. But basically you decide which one of these precursors to use and again that is very specific to the to the material that is being synthesized.

Then there is a process of mixing, how is this done? You can just use a usual mortar and pestle grinder and grind with hand. Alternatively you can use a more sophisticated mixing technique called ball milling where essentially you have some sort of ball made of which is there in these in your starting materials and essentially this ball is spun around at for a long time maybe one day or so ok. And when this when the spins around for a day or day or so, then you get very fine powder. So, ball milling is one very popular technique that is used in order to mix the two premix the starting materials before introducing them into the reactor ok.

Then you have to decide what should be the container of the reactor. So, the container of the reactor is typically because it has to withstand very high temperatures, it should be inert, it should not contaminate your final crystal ok. So, typically noble metals like platinum, gold are used, but you can also use alumina, quads, silica in the form of quads or you can even use graphite crucibles for this purpose.

And then the last thing is I have called it the heating program and I mean so usually you raise the temperature you keep hold it for some time at one temperature, then you might hold it for under for some more time at a different temperature, then you will cool at a certain rate; all those things have to be decided. So, now, let us take one very specific example ok. So, suppose you want to look at synthesis of so this is an example. You want to synthesize yttrium, barium 7 minus delta ok; yttrium, cuprate. This is commonly called as YBCO, this is a high temperature superconductor and the height it has a T c around 90 Kelvin, of 90 Kelvin and this was the first superconductor that had a that was super. So, it is superconducting below 90 Kelvin ok. So, if you use liquid nitrogen, you can see this will become a superconductor ok.

Now you can this can be prepared using the following reaction Y 2 O 3 plus ok. So, yttrium and barium are reacted and in the presence of copper oxide and some oxygen. This if you heat it at 950; if I carry out this reaction at 950 degree centigrade, then I can get 2 Y B a 2 C u 3 O 7 and plus 4 CO 2 ok. So, the carbon dioxide is a gas that is produced in this reaction and you can get and if you at 950 degree centigrade this reaction takes place and if you cool it down, then the carbon dioxide will escape is leaving you crystals of YBCO ok.

Now the problem with this reaction is that barium carbonate is very stable on heating. So, you have to carry out this reaction at very high temperature and this can actually cause contamination ok.

So, at this very high temperature this copper oxide can react with the sides of the of the container. Also at height also this carbon dioxide it might not fully escape and if it is not escape, then it leads to the backward reaction taking place ok. So, an alternate method an alternate method is to not use carbon dioxide, to make sure that carbon dioxide is not produced and this can be done by using a nitrate as a starting material.

So, so you can take barium nitrate ok, you powder it and you heat it and you will get barium oxide ok. So, barium nitrate when heated will give you a barium oxide and it will give you nitrogen dioxide gas ok. And what is done is you make barium nitrate is converted to barium oxide which is combined with which is made into pellets with C u O and then this is reacted on reacted on a bed of already prepared YBCO.

So, you first synthesized some YBCO and then you make these pellets of barium oxide and copper oxide and then you carry out this reaction on this bed of YBCO and this is first done at high temperature and then it is done at lower temperature ok. So, what is done is you first do at 950 degree centigrade and then you do at 350 degree centigrade and this second heating at 350 degree centigrade. It actually gives you the right value of delta so that your T c is about 90 k. So, it turns out that for this material based on the value of delta your Tc varies ok. So, and delta is typically some fraction ok, it is much less than one and so, this delta is essentially varied till you get the optimum curie temperature, optimum T c for superconductivity ok.

So, again this is an example of a sort of a typical solid state synthesis ok. So, here we started with a precursor that had barium nitrate and you will have again you will have copper oxide and you react it on a bed of already prepared YBCO ok. So, you can see that there are a lot of things you can do, even within this general framework of solid state synthesis.

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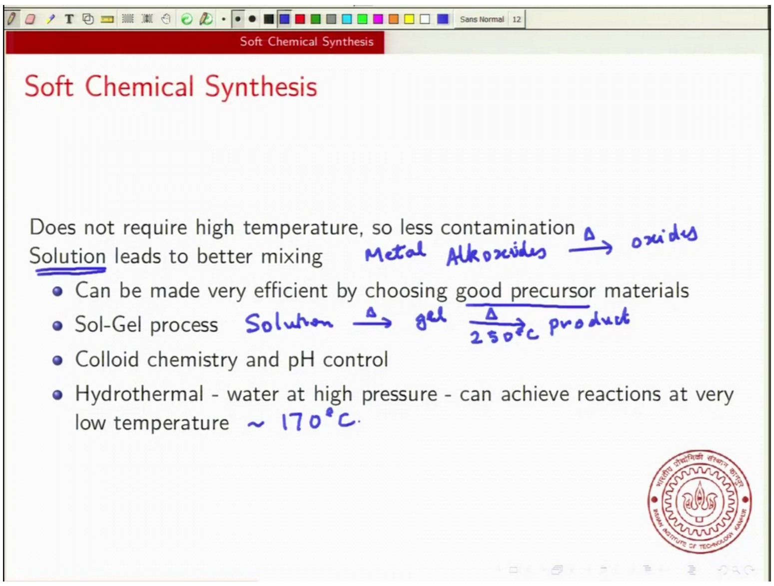

Now, the alternate synthetic method is the soft chemical synthesis ok. So, in soft chemical synthesis, you do not require such high temperatures ok. What is done is you use chemistry to make sure that you that the reaction takes place at much lower temperature, and the basic idea is that you use good precursor materials ok.

So, for example, if you want to make an oxide ok, you can just use. So, like Alkoxides can be used as precursors when you heat them you get oxides ok. So, you can start with alkoxide as a precursor of whichever metal you have ok. So, you so you have your metal alkoxide you heat it and you get oxides. So, this is one very simple example of using a good precursor material and you do not have to heat to very high temperatures to get your oxide ok. Another procedure that is used quite often is what is called a solid gel process ok.

So, one of the characteristics of these soft chemical synthesis is that we use solutions and when your initial mixing of your materials is done in a solution form ok, then that leads to much better mixing ok. So, what is done is you take your solution and then you essentially evaporate it slowly ok. So, then it forms it forms a colloidal salt ok, then you keep evaporating it forms a gel ok. So, so you go to solution by slowly heating you get gel and this gel is taken. So, this gel is heated at high temperature heated at high temperature to get your product ok. So, this is called a Sol-Gel method so, where the mixing is done using a solution and then you condense it to form a gel and then this gel is what is introduced in your solid state reaction and here the temperature is typically much lower.

For example, you can get spinel will just 250 degrees centigrade. In this procedure, you can get spinel by using a temperature of just 250 degree centigrade and there are a lot of other things in this in this process. For example, you can use colloid chemistry and control the nature of the products using pH, I am not going to discuss these in detail. There is another variant of this called a hydrothermal method, where you use water at very high pressures and this can achieve reactions at very low temperatures. For example, you can get reactions the same spinel can be prepared at 170 degree centigrade using a hydrothermal method, where basically you use water at very high pressures to make the reaction faster ok. Now again I am just showing you some of the soft chemical synthesis methods ok, I am not showing you all the methods and the basic idea is that you have to choose a method based on the quality of crystal you want based on the on the material you are trying to synthesize ok.

So this is the overall strategy of solid state synthesis. Again I emphasize that every material requires unique strategies, every material presents different set of challenges ok. And so, there are several techniques within that fall within the class of solid state synthesis and I I will not be talking about all of them ok, but I just wanted to give the overall strategy of solid state synthesis. So, with this I will end this lecture.

Thank you.