Materials Chemistry
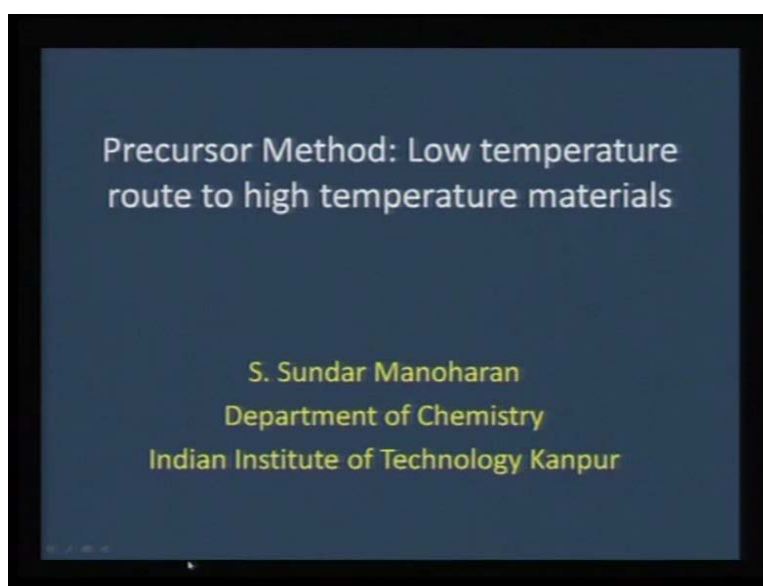**Prof. S. Sundar Manoharan**
Department of Chemistry
Indian Institute of Technology, Kanpur

Lecture - 02
**Preparative Routes Conventional Precursor Technique-I**

In the past few lectures, we have being looking at the number of different synthetic approaches that are possible to make solid state materials. So, in materials chemistry.

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We have both conventional methods of preparation as well as non-conventional methods of preparation. So, it is very useful to look at some of the orthodox methods which is very typical of chemical routes. In chemical routes, we can talk about many approaches; one of the approach is called precursor method. And in today's lecture I will be talking more about the principle of precursors, why precursor methods are still the most coveted as far as chemical approaches are concerned? So, I will outline few examples of what this precursor chemistry means and what are the advantages and what are the new approaches that we can make using precursor technique.

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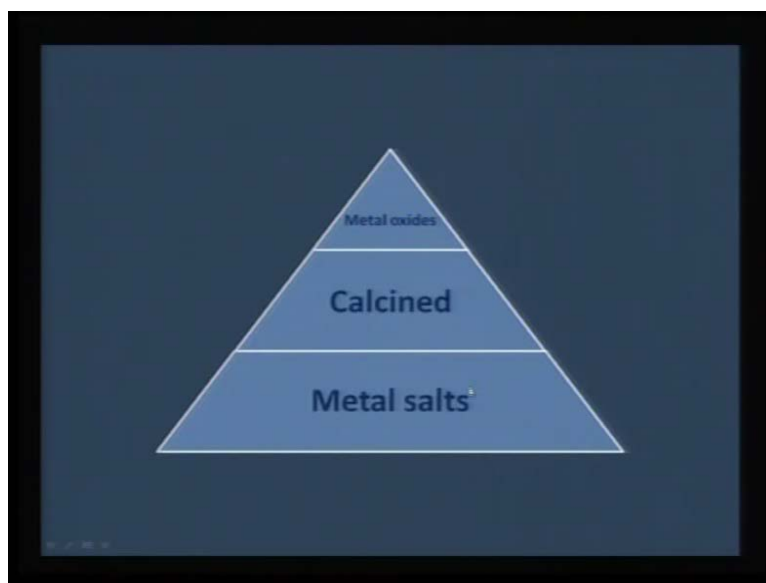
In principle, any metal salt can actually be converted to the corresponding metal oxides for example, if you start with a nitrate salt let us say copper nitrate. And if you are going to calcine it, then on calcination it is going to give the corresponding metal oxide. So, copper oxide, you will get if you make a mixture of 2 different metal salts. Then you will get a mixture of 2 different mixed metal oxides. But when we are trying to look for a final composition which is a single phase then the choice of your metal salt has to become vital. And it is important for us to know, how this precursors can be tailored and what sort of measures we need to take in order to arrive at the final compound that is metal oxide. So, we will learn in this lecture, what sort of principles that we should have in mind.
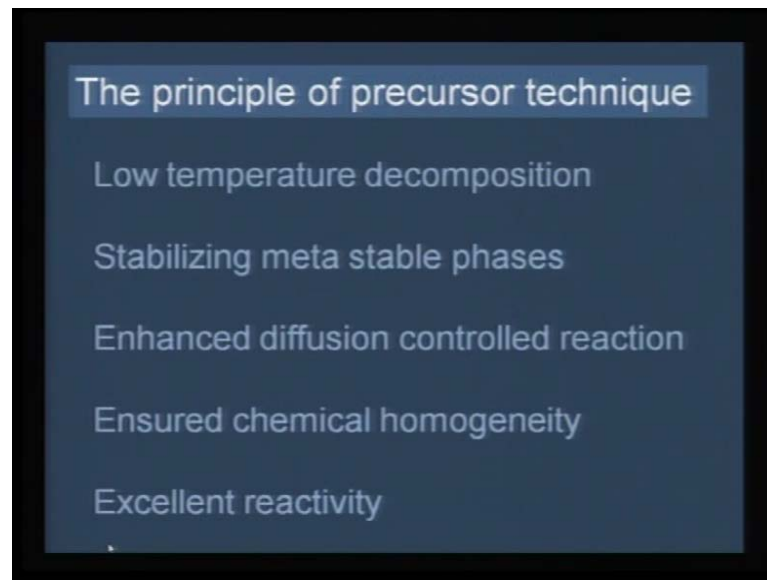
The principle of precursor technique a first of all is concerned with low temperature decomposition if it is not going to have a low temperature decomposition then it does not stand out compared to solid state methods. So, one of the primary aim is to look for low temperature decomposition. And second when you are trying to do a low temperature route you often end up with stabilizing unusual oxidation states what is not possible a at high temperature may become possible at low temperature. So, you are essentially trying to see whether you can stabilize a meta stable phase which means a phase which is only stable at a very high temperature on cooling will revert back to a different phase. But because of this solid solution route, you are stabilizing a meta stable phase at room temperature.

Enhanced diffusion controlled reactions are possible as I told you if you bring 2 metal ions in the precursor form then you are enhancing the diffusion. And by that way you are trying to increase the reactivity and then ensured chemical homogeneity is another thing. Because when you are bringing them into atomic distances you can guarantee a pure or stoichiometric oxide which is your final product. And thirdly it is excellent reactivity because you are doing a low temperature preparation. Suppose 2 metal oxides are combining to form a final compound, because they are released or liberated at low temperature. The general reactivity of this powders will be very high as a result any diffusion control processes can be enhanced, because of this low temperature approach.
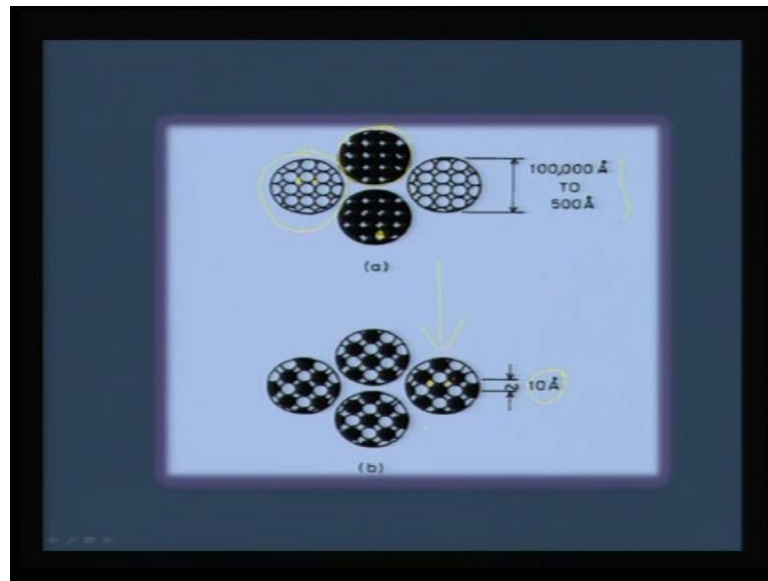
Now, this is a cartoon which has been used for more than 30 years now to drive home the point about a precursor technique for example, if you have a precursor like this with metal ions in this interstices. And if you are going to bring it with these metal ions which are of a different size and these may be different element. So, if you have going to bring these together in solid state form. Then the distances between them is of the order of 50 nanometer to 10000, or even 110000 nanometer. So, the distance between these metal oxides are going to be very very large, but when you are going to bring them into a precursor situation, where you are trying to atomically bring them into closer proximity. Then you can see that the picture has changed as a result the distance between 1 metal and the other metal actually be 10 Armstrong. So, you are reducing the distance between 2 metal atoms from orders by orders of magnitude. As a result you are enhancing the reactivity and that is the strength of precursor technique. So, if you are able to stabilize good precursors then you are actually trying to affect the atomic level doping atomic level composition and subsequently its reactivity.

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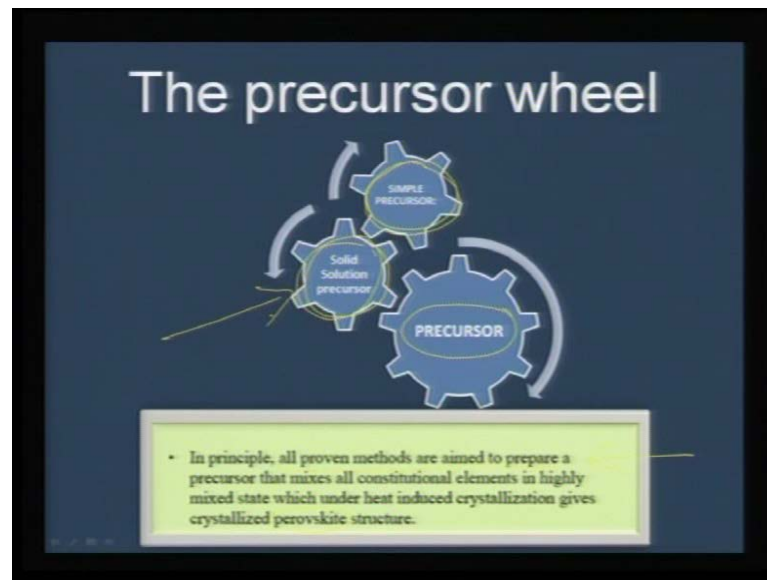
 I call this as a precursor wheel, because this precursor chemistry can be actually activated by 2 approaches; one is called solid solution precursors. And the other one is called simple precursors, you can take any sort of salt metal salt. And you decompose you will get a corresponding oxide or chalcogenide if it is a sulphide based salt. Then you will get sulphide metal sulphide if it is any other organic ligands then you would on decomposition get the corresponding oxide. So, precursor can be defined in 2 ways in principle all proven methods are aimed to prepare a precursor that mixes all constitutional elements in highly mixed state which under heat induced crystallization. And they give crystalline phases not necessarily a perovskite structure it can be a simple cubic or complex metal oxides. So, in today's lecture, we will look at the issue of simple precursor and solid solution precursor. Now, when we talk about these two then we need to understand one question what is a solid solution, because both are precursors. But how does a solid solution vary from a simple precursor route? Therefore, the understanding of solid solution is a important issue.

So, what is a solid solution? A homogeneous crystalline structure in which one or more types of atoms or molecules may be partly substituted for the original atoms or molecules without changing the structure. So, the important point is you do any sort of substitution, but do not disturb the structure. So, as long as you retain the structure you can either dope a atom or you can put a molecule and you can partially substitute substitute the original crystalline structure. Now, the word solid solution still need not be very very obvious to hearers. So, we need to understand what other solutions are known in our common day language solid solution is there liquid solution is there gaseous solution is there.

If you talk about gaseous solution the excellent example is air And if you talk about liquid solution you try to mix H C L and water Then you get this sort of coloured solutions, but they are actually liquid solutions, But when you talk about solid solutions you talk about for example, brass as a good example one going into the other And they are forming immersible alloy where you cannot really retract any of the individual elements they are mixed together mainly because of its structure and it is ionic size they blend such a way that they produce a new alloy. So, a alloy is a good example of a solid solution. Now, how can this alloys form or how can such oxides form? We will look at few examples to understand the technique of solid solution. Then we can go back to understanding what a solid solution.
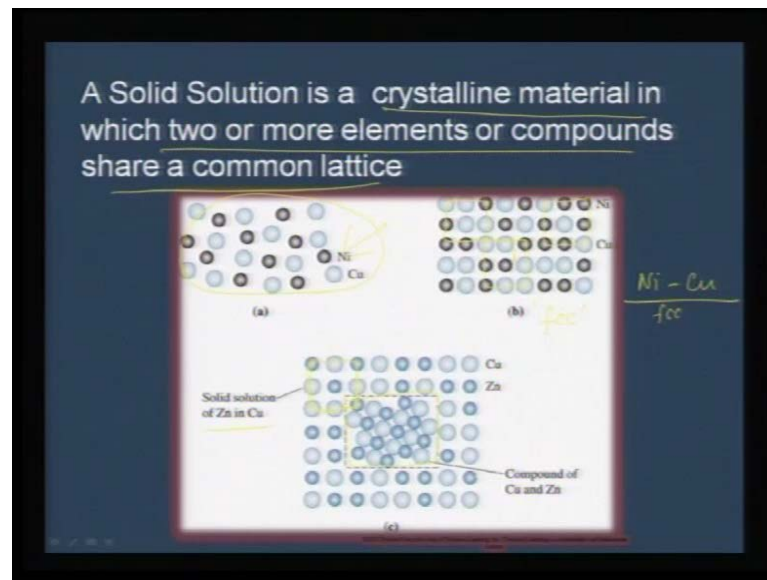
Precursor is a solid solution as we saw from the previous line is a crystalline material in which 2 or more elements or compounds share the same common lattice. For example, nickel and copper if you look at nickel and copper this is in liquid state when the metal is melted. Then in the liquid they excellently mixed together you can just mix it over the entire range of doping. But in the solid actually you can see they can distribute themself in any periodic way or in any random way they can occupy each other side. For example, if you take the case of copper with nickel and copper, both they form f c c structure. As a result over the entire range of doping, it is possible for you to keep doping nickel into copper or copper into nickel. As a result you can see a f c c pattern is always there but only thing in every f c c unit cell you would see the random distribution of copper or nickel.

But when you take zinc in copper for example, zinc has a different crystal structure compared to copper. And as you can see two things can happen one to some extent zinc can go into copper. Therefore, it is a solid solution because they are arranging in a periodic way only thing the distribution of zinc in copper is random. But along with that there is also a region where it is not solid solution. But some compound of copper and zinc are precipitating out which means there is a restriction I cannot go beyond a particular solubility limit where I can retain the f c c structure of copper. In other words it is lost therefore, you get a mixed phase there and you do not call that as a solid solution. So, solid solution in this case is only up to a minimum amount not like the

nickel copper case where throughout the entire range compositional range they exist only in f c c. But in this case there is a problem because zinc has a different crystal structure compared to copper.

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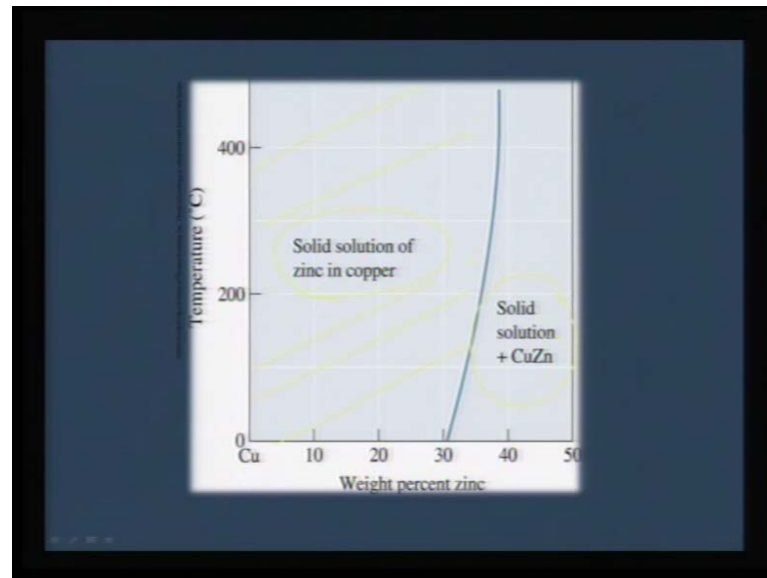
So, this is what we see in this viewgraph solid solution of zinc in copper is possible only in this range where the limiting composition is 30 percent beyond this. It is not to be a solid solution, because it deviates from the f c c pattern of the parent copper. Whereas above 30 percent, we cannot completely exclude the possibility of a solid solution there is going to be solid solution plus some other alloy phase of copper and zinc. Therefore, not all systems can form solid solution over the entire range. But there are certain systems which can form solid solution only in a limited solubility limit.
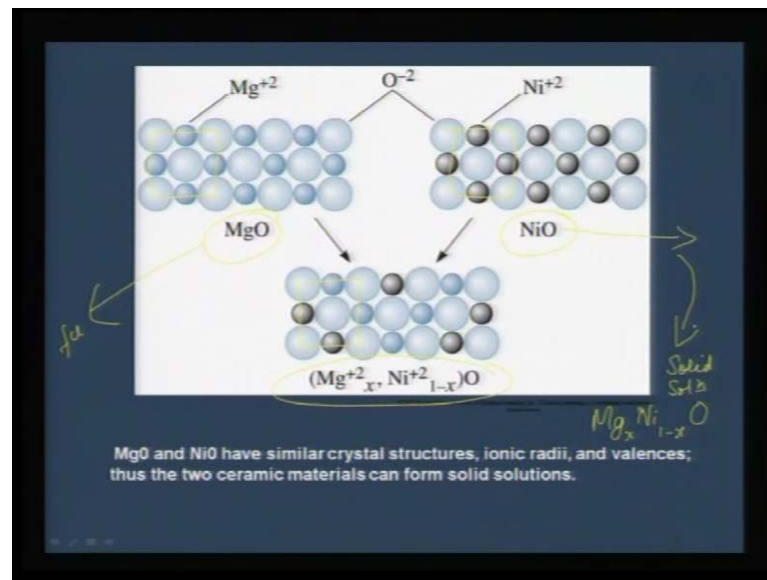
Take another example of Magnesium oxide and nickel oxide both are cubic and you would see the this is the oxygen array f c c oxygen is simple cubic array. And here again you see a f c c pattern of nickel oxide both when they are mixed together in some form either you mix and grind it. Or you can use a precursor technique in both ways; because of the structural similarity it is possible to create a solid solution of magnesium in nickel oxide. So, if it is a solid solution then we can confidently write in this form what you say? You can say this is M g x nickel 1 minus x oxygen. So, in nickel oxide I can keep on putting magnesium and it goes into the crystal lattice. Therefore, this is a best representation of solid solution suppose nickel oxide is a different class. And magnesium oxide is a different class suppose this is f c c and this is not f c c suppose if it is not f c c. Then this is not possible, but fortunately both are same therefore, we can call this as f c c. So, because of the structural similarity it is possible to make a solid solution of magnesium nickel oxide.

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Now, is there any other oxides that are solid solutions that can be made by substituting with magnesium oxide? And what other ceramic systems are likely to exhibit 100 percent solid solubility with magnesium oxide. The governing principle is the ionic radii if you look at the ionic radii of cadmium in cadmium oxide calcium in calcium oxide cobalt 2 plus in cobalt oxide. Then the corresponding divalent ionic radii of these metals are given here. So, based on this particular composition or this formula where you can substitute this value and calculate the percentage ionic capability or compatibility. Then you would arrive at some numbers these are the numbers which will tell you whether substitution of such metals are possible.

For example, you would see the error inward is only 9 percent for cobalt substituted in magnesium oxide or 12 percent for ion 2 plus substitution in magnesium oxide. Therefore, in this whole list you can actually single out that these two can actually go into the lattice comfortably. So, the percent difference in ionic radii actually suggest that F e O m M g o system and cobalt oxide system can actually be substituted very comfortably into M g o. Therefore, you need to have a knowledge of what sort of ionic radii is your dopant ion and how much of percentage iconicity difference is there. So, based on this you should be able to even map what sort of reaction that you can carry and how the solid solutions can be made.

So, there are conditions for unlimited solids solubility. And Hume-Rothery rule is one guiding principle which will tell us how much of this solid solution capability can be achieved between 2 metals. And the rule actually suggests that size factor the corresponding parent crystal structure, valence and electro negativity. All this play a important role in fine tuning a solid solution for example.
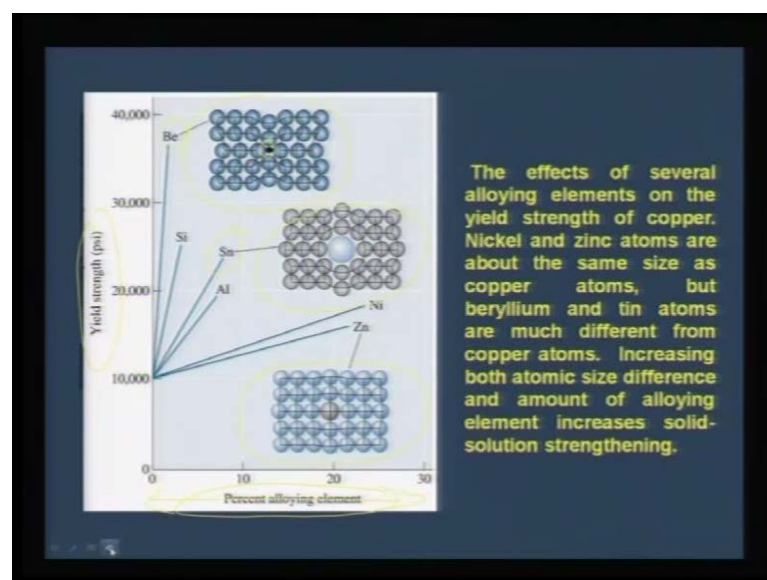
If you take the case of copper in copper, if you are going to substitute various metal. You would find out that zinc all though it can form a solid solution the, because of the ionic

radii the crystal symmetry change or the expansion in their, a crystal lattice can be viewed using this cartoon. Whereas, if you are going for a bigger cation like tin and you are going to substitute in the same copper f c c you will see a lattice elongation of that type. Or if you are going to put beryllium a small cation in a copper then you would see a compressive strain. So, the strain that it would induce into the lattice will bring about different properties.

For example, even though there is a lattice expansion or lattice contraction you would see as a function of yield strength of this alloys beryllium doped copper system seems to have a better yield strength or a very high yield strength compared to tin compared to zinc. So, even though we have a good solubility limit up to 30 percent for tin in copper or zinc in copper based on the nature of the metal the size of the metal you can actually see the yield strength is differing considerably. So, this is the solubility limit for all these three compounds, but you can get a maximum yield strength for beryllium only around this composition may be up to 20 for tin we can extend up to 30. So, this also determines the architecture of your solid solution.

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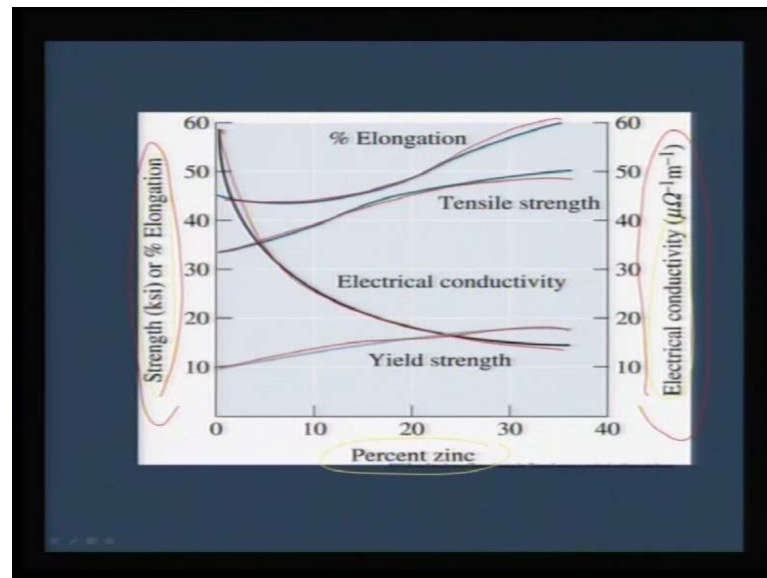
So, if you look at the same viewgraph in a different way percentage of zinc plotted versus electrical conductivity and a strength or elongation then you would find out. So, if you take this viewgraph where percentage zinc is plotted against the physical properties. One would see that the elongation curve is increasing with increasing zinc percentage.

So, is the tensile strength? So, is the yield strength whereas, if you look at the electrical resistivity for this solid solution it is exponentially decreasing. So, the solid solution not necessarily have to aid all the physical properties it can influence one when it is losing on the other. But we need to understand what is the property that we are able to fine tune.

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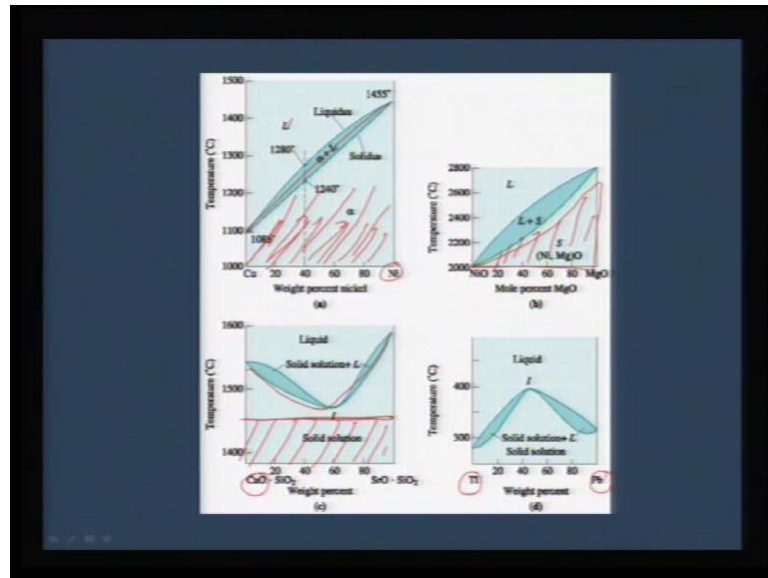
So, if you actually have a variety of a pairs the solid solution notion is all about trying to find out a region where you can put any amount of the doping cation. For example, nickel up to 100 percent I can dope freely only beyond this limit I see a liquidus compound coming. So, this is my solid solution limit. So, without any restriction I can play around in this whole domain. Whereas, in this case you see it is constrained therefore, nickel and magnesium oxide; this is the region where I can happily dope solid solution or get a solid. In case of calcium oxide silicate and strontium oxide silicate, you can see here the liquidus curve is of this nature. Therefore, below 1500 we can actually have any sort of composition I can vary between strontium oxide and calcium oxide in a very phenomenal way. So, is the other case of lead and thallium again I can actually dope any amount of thallium for lead.
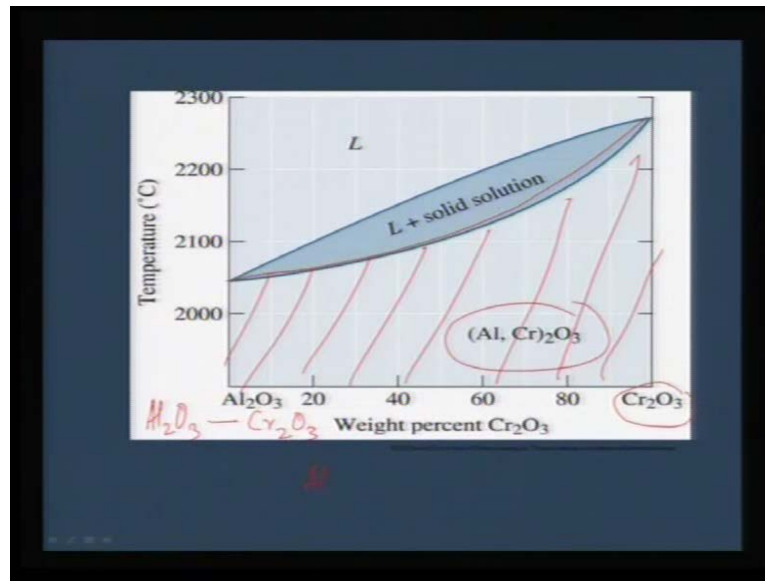
If you take aluminum oxide say A l 2 O 3 and C r 2 O 3 these are good examples of a corundum based oxides. I can dope chromium oxide to any level, because it forms a liquidus phase plus solid solution only around this region. Therefore below this liquidus curve I actually have a very free hand to dope any amount of chromium in to l 2 O 3. So, if I have a good precursor or if I know how to start with a proper choice of my starting material then it is possible for me to dope any amount of chromium into alumina because they both form the solid solution over the entire range. Now, having understood little bit on what the solid solution means then we can extend the same analogy now to what a solid solution precursor is.
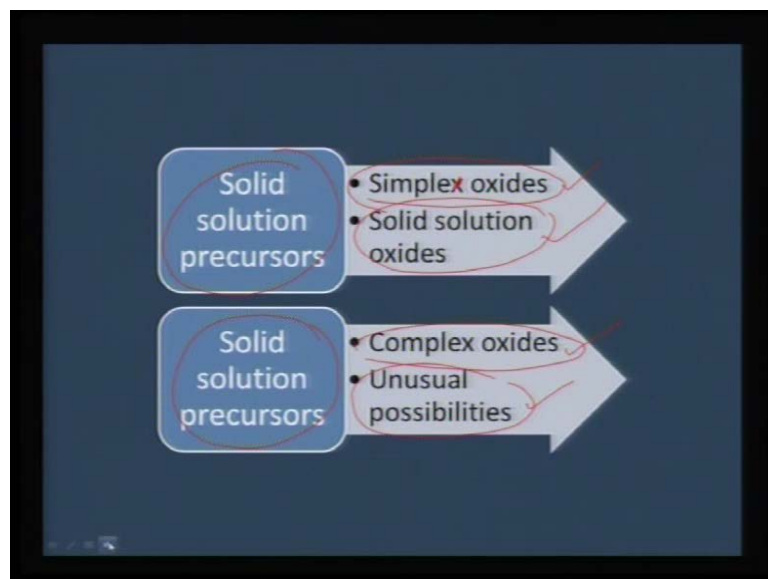
So, coming back to the precursor wheel we are having a precursor. And my aim is to translate this into a metal oxide. So, this precursor is nothing but a complex. And if I can aim for a solid solution precursor; that means, I have a particular oxide in mind. And if I want to get that oxide then I tried to exercise the solid solution notion in the precursor itself. So, that the final compound will exactly be the final oxide without going through any subsequent intermediate steps of reaction in the simple precursor. You may have to go through one or two more steps, but nevertheless it still has the advantage of a precursor method.
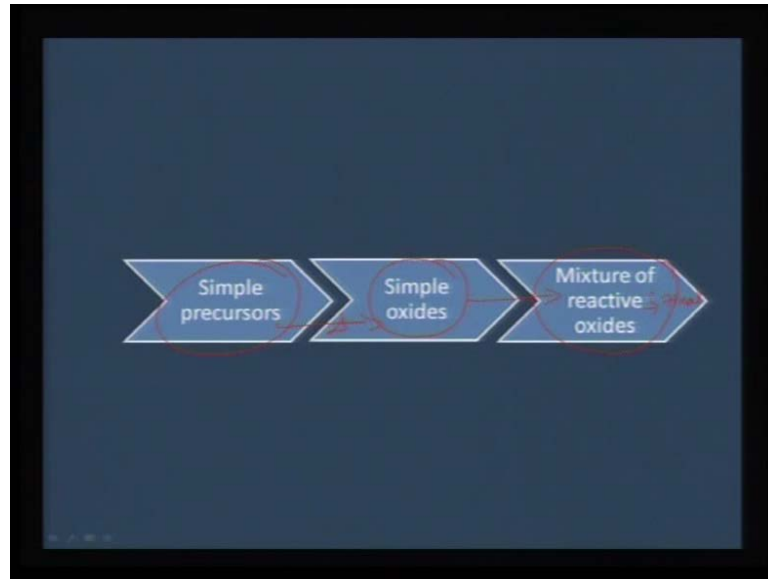
So, in simple precursors when you try to heat it you actually get simple oxides. And this simple oxides can actually be a mixture of reactive oxides it need not be the final oxide. It will be a mixture of reactive oxides which on further heating can give final compound. So, that is the approach of precursor. In the next talk I will tell you about all the simple precursors that can be used for making such final compounds which are oxide materials.

When you talk about solid solution precursors we are actually going to prepare simple oxides or we are going to prepare solid solution oxides. And solid solution precursors

can also be used for making complex oxides and we can explore unusual possibilities. So, solid solution precursor can also give simple oxides like the simple precursors, but along with that it can also give solid solution oxides and complex oxides. And different other possibilities can be worked out that is the advantage of a solid solution precursor. I will start with 1 or 2 classic examples which stands off in the precursor chemistry over 30 40 years now. So, if we can understand the notion of a solid solution precursor then we can look for many applications for functional materials.

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This is one of the finest paper that has been published in a in 1987 by Patil's group from I I S C Bangalore what they attempted was using hydrazine precursors to get corresponding metal oxides. Why hydrazine precursors are useful as you would see in the previous lectures when I talked about combustion we talked about the potential potentiality of hydrazine precursors, because they release enormous energy during decomposition. Let us take a case of monoclinic hydrazinium, metal hydrazine, carboxylate hydrates. It is a simple ligand; the ligand is to be viewed like this N 2 H 3 C O O which is nothing but hydrazine carboxylate we can write this as N H 2 N H C double bond O O H. So, this is a unidentate ligand; this hydrogen can be replaced as a result if you have a metal core this can actually get bonded to this. And there is a covalent bonding between oxygen and this metal.

So, two such molecules hydrazine carboxylate ligands can bind toward divalent metal to form a divalent complex. For example let us take the case of nickel hydrazine carboxylate ligand and cobalt hydrazine carboxylate ligand. If you would look at the x-ray pattern and analyze the x-ray diffraction pattern you can calculate the lattice constants and you would see the lattice constants are nearly the same. So, if these are nearly the same then it gives me advantage for me to dope one with the other nickel and cobalt together. For example, I can make a solid solution like this magnesium 1 by 3 that is 33 percent magnesium and cobalt 2 by 3 that is 66 percent cobalt.

So, as a result I can actually make a precursor which can accommodate both magnesium and cobalt together because they have the same crystal structure. If you actually look at all these mixed metal complexes all the mixed metal complexes have the same lattice constant or comparable one to that of the individual complexes. So, as a result we can say these are solid solution precursors they are precursors for some oxide. But we call them as solid solution precursor, because they can accommodate more than one metals and still maintain the same crystal lattice.

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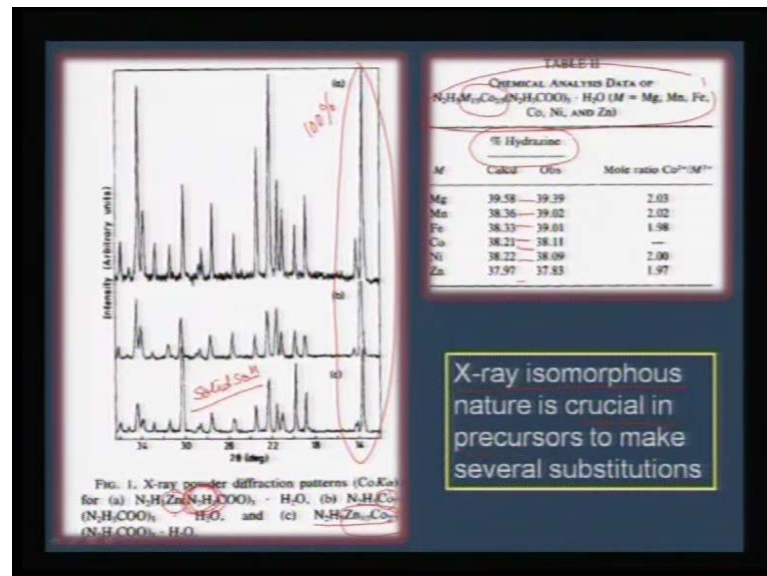
So, we call this as solid solution precursor and typically, if you look at the x-ray mapping. I just want to draw your attention to this first peak which is coming at 14 degree. When you do the powder x-ray diffraction you as you can see here this tall peak which is usually referred to as 100 percent peak is coming at nearly 14 degrees. And

irrespective of what the metal ion is whether it is zinc or it is cobalt. You still see the same crystal structure and because of this crystal structure it is possible for me to make zinc and cobalt together which is nothing but your c. So, when I make comparison between a and b then it gives me possibility to go for the solid solution which is c. So, essentially this solid solution zinc cobalt hydrazine carboxylate resembles that of both cobalt hydrazine carboxylate and zinc hydrazine carboxylate complex.

As a result we can look at the chemical analysis, chemical analysis can give you some idea about the precursor composition. For example, I can try to calculate the hydrazine content here as you can see there is a excellent match between the hydrazine concentration in the complex for I am talking about this N 2 H 3. So, essentially you can make a solid solution by combining stoichiometric amount of any metal and cobalt. So, the buzz word here is their x-ray isomorphous, in other words they are similar in their crystal structure. Therefore, this is crucial in precursors to make several substitution.

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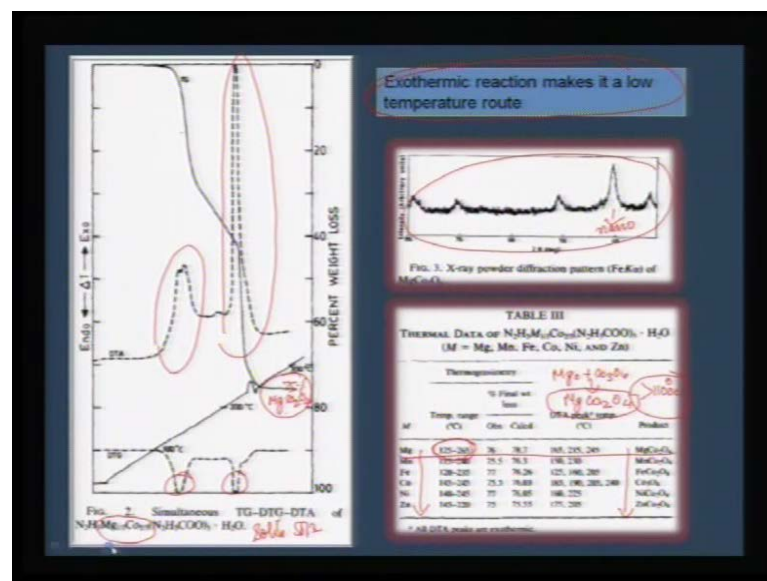
Now, what is the power of this precursor? Can I use this for some application; yes, because if I try to decompose this precursor what I have shown you here any precursor if I take. And if I try to do a thermal analysis thermogravimetry actually is very very refined for example, you take the case of magnesium cobalt solid solution; this is a solid solution. And if you are going to run the t g d t a this is your t g pattern which shows that there is a weight loss up to 75 percent. So, nearly 75 percent weight loss is there and

during this weight loss program there are 2 things happening one there is a peak here. And then there is another peak which is forming here both incidentally are exothermic in nature. So, initially there is a decomposition followed by another decomposition which is clearly seen. And in the d t g you can see there are 2 step decompositions. And the best part of this study is that the decomposition is over below 250 degree c maximum.

So, the final product that I will be getting here is nothing but magnesium cobaltite that is what we see here magnesium cobaltite is formed. And as you would see from the decomposition range between 125 to 265, the compound has totally decomposed into the final product incidentally magnesium cobaltite. If you were to prepare using a solid state method the minimum temperature that is required for M g o plus C O 3 O 4 to give M g c O 2 O 4 is above 1100 degree c. You need this much of thermodynamic requirement for this final phase to form. Whereas, in the precursor route solid solution precursor route you are able to prepare the same compound in a record temperature of 265 or 300 maximum let us say.

So, at 300 degree c if you can prepare such a spinel compound then the compound has to be highly reactive. And that is what we see from this x-ray pattern that the x-ray pattern clearly shows broad peaks indicating that they are nano in size. Because they are nano in size they will be very very reactive x-ray broadening is a very good parameter to understand whether it is a nanocrystalline phase or whether it is a highly crystalline phase not only this composition a variety of solid solution. And the respective cobaltites can be made out of this precursor route. The importance of this solid solution precursor is to do with the exothermic reaction which makes it a low temperature route. Now, we will see some more examples of this solid solution precursor.

Autocatalytic, self propagating combustible decomposition leading to voluminous oxides
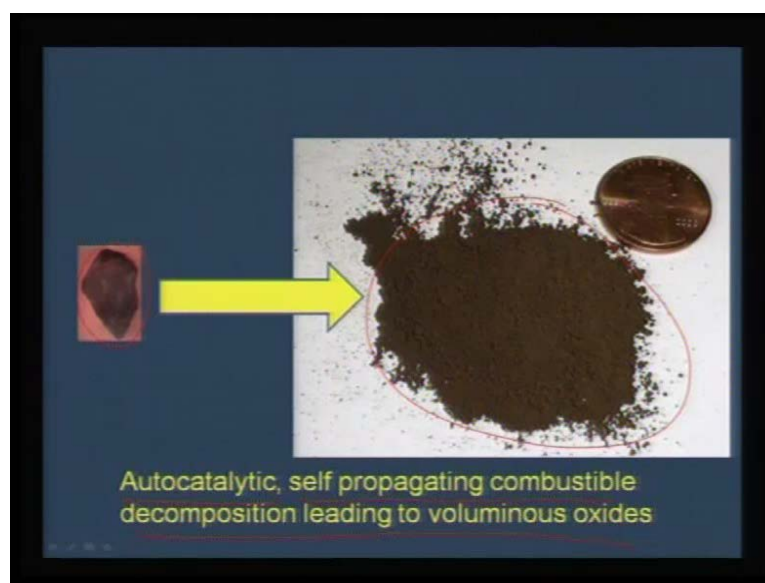
And see, what is the strength? Suppose the crystal of these hydrazine carboxylates are taken to be like this may. In fact, this hydrazine carboxylate if you mix these 2 salts and put the hydrazine carboxylate ligand in 2 3 days time. You would be able to isolate beautiful crystals like this and if I try to heat this crystal in one sense you would get this much of powder. In our regular practice, we know that if you take any compound and you heat it will only reduce in size. But what happens here is there is a autocatalytic and self propagating combustible decomposition which leads to a voluminous oxide that is the beauty of this hydrazine carboxylate precursors. But this may not be the true story when you try to look at simple precursors like nitrates, carbonates or sulphates or acetate precursors they would not actually give you such voluminous compound. So, when you talk about a voluminous compound then you are talking about the increase in surface area. Therefore, it will be highly reactive and it can be used for many applications. So, these properties will be actually reflected in the oxide phase and that is what we have seeing here.

In this table some properties of the cobaltites the x-ray patterns all show that the cobalt cobaltites. Whatever is prepared with magnesium manganese iron cobalt nickel or zinc they are all showing a cubic phase and look at the specific surface area measured using b e t method. You can see here iron tops E t A l which means iron cobaltite is the most reactive cum or the most voluminous in size. And as a result you can look at the average particle size and the crystalline size to be quite distinct from the other oxides. The crystallite size that you see from XRD is a true measure of the particle size close to whatever you learn from T m. So, if you can see here it is roughly of the order of 6.5 nanometer and because this is so small the surface area is very large and we can make several comparisons of that.

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If you can make simple spinels then it is possible for us to make complex spinels also for example, instead of just zinc ferrite I can make nickel zinc ferried, because nickel hydrazine carboxylate, zinc hydrazine carboxylate and hydrazine carboxylate all have the same crystal structure. Therefore, it is possible for make for me to make a carboxylate precursor as unique as this with this formula. And if I am going to heat this irrespective of whatever is the substitution I am going to get the corresponding nickel zinc ferrite.

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And we can actually try to map the composition by studying the element percentage in these precursors. For example we can analyze quantitatively nickel zinc and iron present in the precursor. And we can make sure that we have the right stoichiometry and as you would see here that these precursors are decomposing well below 200 degree c which is never possible through any other method. And because they are highly exothermic in nature you can make the whole series of nickel zinc ferrite. Incidentally nickel zinc ferrite is a very important compound for core applications in a power electronics and also it is used as a memory storage material.

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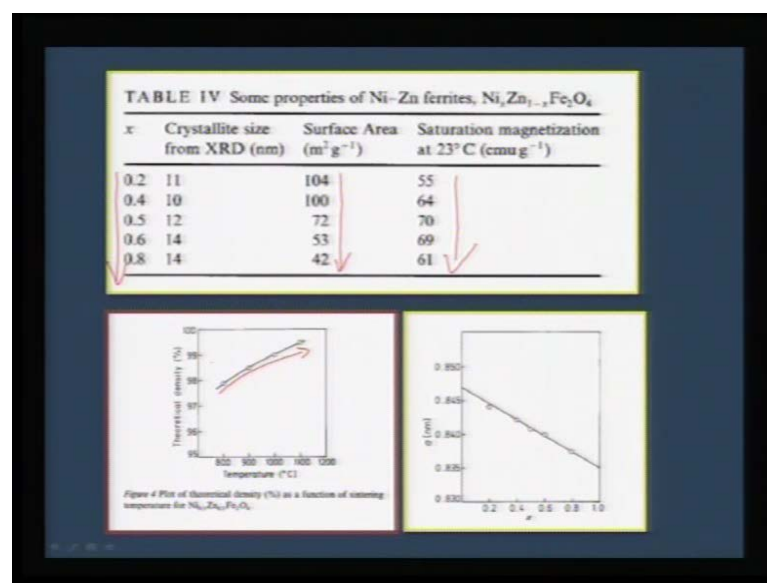
And because of its reactivity you can see with substitution of nickel the surface area keeps decreasing. That means, nickel is affecting the combustion more the combustion less the surface area and the saturation magnetization improves with nickel substitution. And this powders can be densified and the densification profile clearly shows that you can get up to nearly 100 percent sinterability in this compounds because of its fine reactivity.

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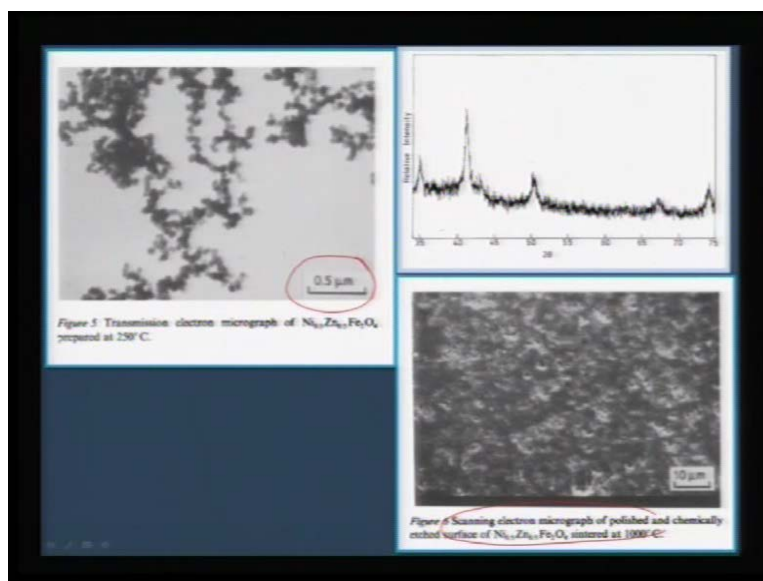
This is the T M micrograph that shows very clearly these are all of the order of 50 nanometers. And they show a very good scanning electron micrograph and the nickel zinc ferrite shows that this is a nanophase powder because of the x-ray broadening as another example I would like to show how.

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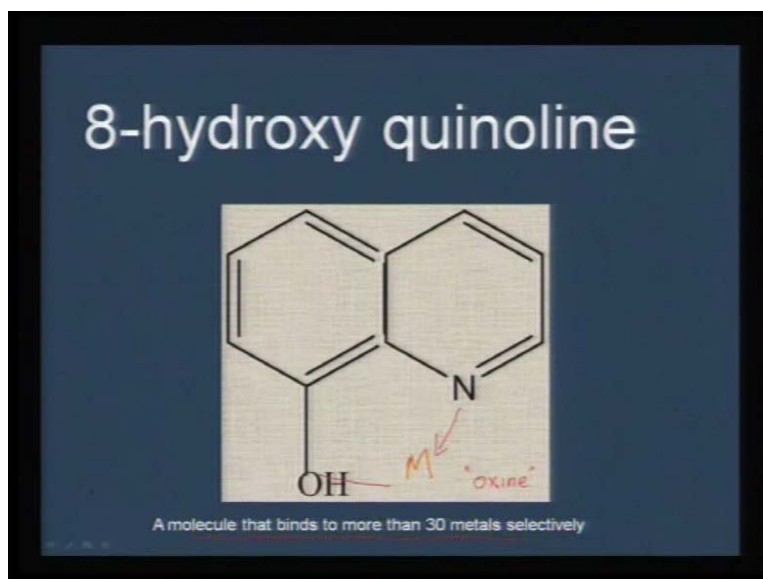
Another well known organic molecule can contribute to material synthesis and it is popularly known as 8 hydroxyl quinoline. This particular ligand has a nitrogen in the phenyl ring and O H moiety. Therefore, this is easily cleavable as a result you can

substitute any metal here. And this metal can be coordinated to both oxygen and nitrogen a assess 5 membered ring because of. So, this is a 5 membered ring which is usually stable. So, as a result this particular 8 hydroxyl quinoline has a very good binding tendency and more than 30 metals in the periodic table have been reported to form complex with 8 hydroxy quinoline.

But the best part is it is very very selective and specific in different P H range it will bind two different metals. And therefore, you can selectively isolate a particular metal even if many metals are available in a given solution. So, it is a analytical reagent and this is also popularly called oxine and there are several papers where the substituted oxines are reported. And also the different metal complexes with oxine derivatives have been reported. I am going to show how this particular molecule can be used for making technologically useful oxides in the next few slides.

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One of the compound that it can form is aluminum tris quinoline complex in other words it is called as A l Q 3 3 quinoline ligands can bind in such a fashion that it forms a octahedral complex. And this octahedral complex is a very unique complex because it was originally meant only to isolate aluminum impurities and served as a detoxicant. So, if there is any aluminum impurity in a food product or. So, or for any other water analysis quinoline was used as a very good precursor to remove those contaminants. But recent past it has been observe that A l Q 3 has a excellent photoemissive property. As a

result this has been used in the organic light emitting displays in the cartoon you see here is a typical light emitting device where you have the anode here and several layers are there.

And the top layer is nothing but your cathode material and in this light actually comes from in between as blue green r red. And this particular layer can be modified by substitution with A l Q 3. And because A l Q 3 is organic molecule it offers several advantages to make large area depositions of L E D displays. Because the conventional inorganic materials cannot be made into a large area displays. What you see here is nothing but the applications of A l Q 3 into variety of electronic displays including T V camera's.

And many other display devices where both small and large area can be attempted using this. Another advantage of organic L E D as I would discuss in the in one of the modules subsequent to preparation I will highlight on the nature of applications of this A l Q 3 molecule in OLED devices. So, it is also called as Kodak molecule because Kodak Company was the first one to use a organic molecule like A l Q 3 in their camera display. Therefore, this is patented by Kodak and this is the AUIPAC name for that tris 8 hydroxy quinolinato aluminum 3.

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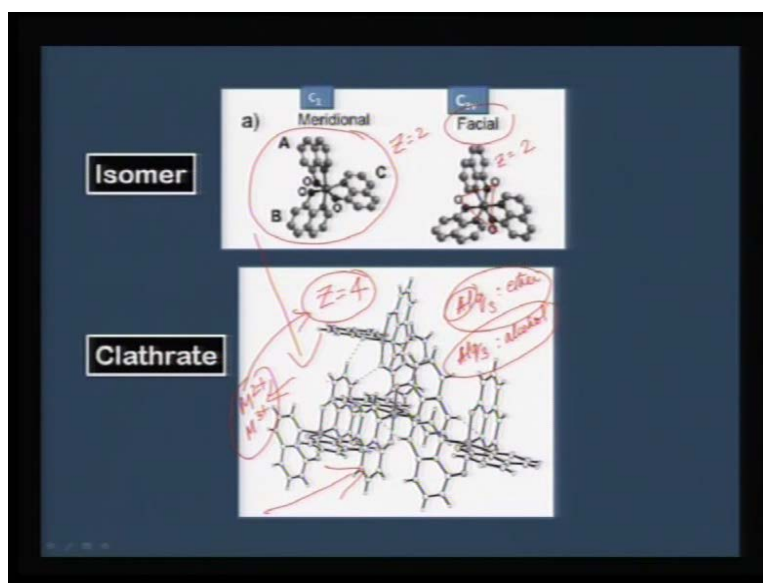
Now, what we do with this ligand if you closely look at the crystal structure of A l Q 3 A l Q 3 is not a simple structure. Because it can actually form a isomer called mer isomer in

the mer isomer the oxygen positions can be placed like this in the octahedral coordination. Therefore, you can see the mapping of the relative three quinoline molecules are there and the relative oxygen positions are varying. If it is a facial isomer with c 3 v symmetry then you would see the oxygen is placed in a trigonal fashion. So, depending on whether it is meridional or facial you can try to study its application. And therefore, this gives you flexibility to play around with either of these isomers for a specific application another isomer which is not that well studied.

But also, it has been documented is the clathrate; clathrate is nothing but a bigger molecule. If you look at the crystal structure, the three dimensional display of this lattice in this case it is mostly z is equal to 2 which means there are 2 molecules in a unit cell both a meridional and facial. Whereas, when you look at clathrate; clathrate is nothing but A l Q 3 with some adduct such as organic molecule. For example, if I am going to do a reaction of A l Q 3 in ether then it will form a ether clathrate. Suppose I am going to do this reaction in organic solvent like alcohol in alcohol for example, then I would get a alcohol clathrate. Now, what is a strange about this clathrate is because it is a bigger molecule compared to the mer or facial isomer the unit cell becomes larger. And as a result four unit cell 4 molecules are there in a unit cell when the crystal lattice is bigger.

There is always a flexibility for you to disturb this crystal lattice in a very unique way you can either go into the structure and come out without causing any damage to the crystal structure. Therefore the notion here is can be tried to put any other metal ion whether it is m 2 plus or m n m 3 plus different valent metal ions. But of a comparable ionic size into the lattice where A l Q 3 is forming therefore, A l Q 3 can be systematically replaced by any other metal ions. Then it will give us the notion of a solid solution, but only thing that we need to understand here is when I am trying to put this substituent's I should not disturb the clathrate x-ray structure. So, as long as the clathrate structure is retained I can go for n number of combinations and that is the basis for the solid solution precursor in A l Q 3.
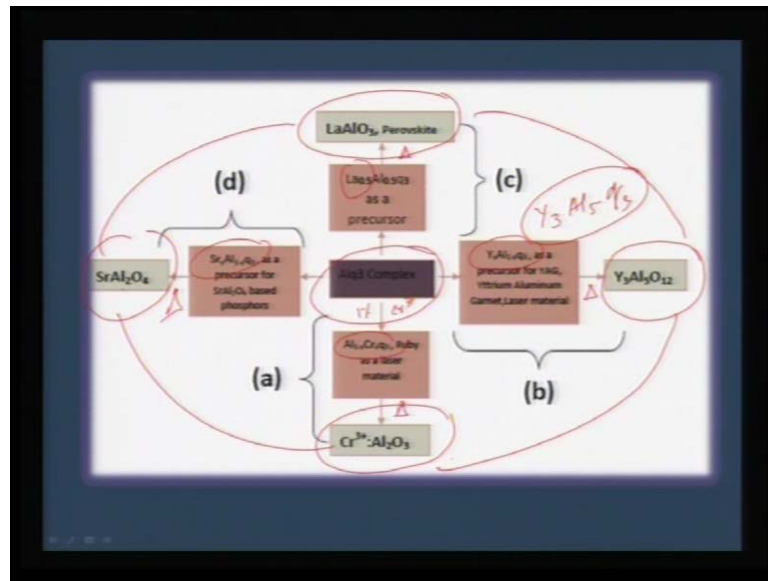
So, let me take A l Q 3 complex and suppose I am going to put 50 percent of lanthanum in the aluminum site. Then I would expect a precursor like l a 0.5 a l 0.5 q 3 suppose I am going to put little amount of chromium 3 plus let us say 1 percent. Then I can get a solid solution like this a a l 1 minus x c r x q 3 or if I am going to put yttrium there in a composition y 3 a l 5 q 3. Then I can expect a yttrium aluminum quinoline complex or I can get a strontium aluminum quinoline complex. What is the objective if I prepare this complex and if they are solid solution? Then I would like to see, what is the end product? My anticipated end product in this case is actually a corresponding oxide which on calcination at low temperature or high temperature that is immaterial. But what I need is these are difficult compounds to prepare And I would like to get this oxides made using this aluminum A l Q 3 solid solutions.
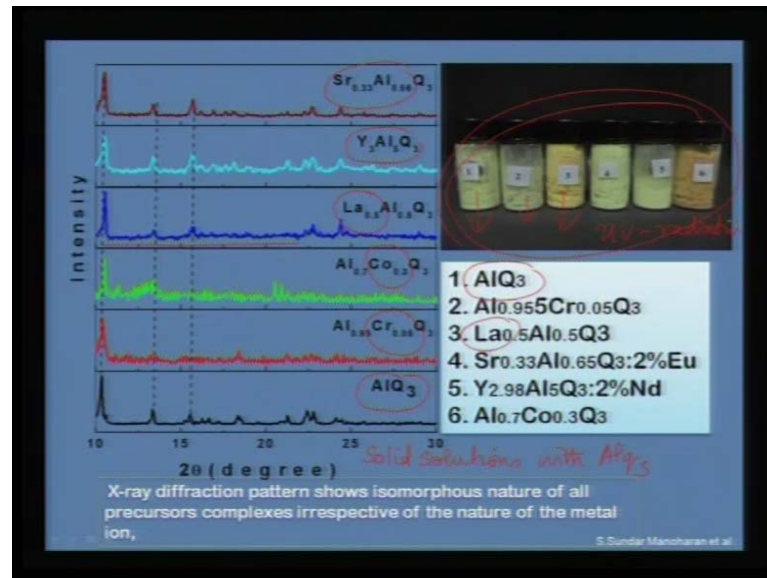
So, let us see what happens when we substitute the metals as you could see here A l Q 3 has a typical x-ray mapping like this where you have a very strong peak somewhere around 10 degree c. And if I am going to put only less than one percent of chromium in this A l Q 3 you can see that the crystal structure absolutely remains the same. Now I can again go to another situation where I am going to put 30 percent of cobalt there. And you would see the still the A l Q 3 structure is retained. Or if I am going to put 50 percent of lanthanum still this crystal structure is retained. Or you can go for any other complex variation in all these cases you would see that A l Q 3 x-ray structure is retained.

Therefore I can call all this as solid solutions with A l Q 3 and I can list those compositions A l Q 3 or a l 0.95 chromium 0.05 and so on. And as you would see here very clearly that they are different compounds from the color that they show in a UV light; you can clearly see that the compositionally they are different. And their photoluminescence property is also different what you see here one is nothing but your A l Q 3 as you would see it gives around a greenish yellow light which is used for OLED applications. If you are going to put chromium slightly the color comes down if you are going to put lanthanum you can see yellow or yellowish orange color that is coming out. So, this is under UV radiation and this consolidates that such precursors have been made and they are solid solutions in nature.

So, what do we do with this? If I am going to now anneal these compounds I am expecting is the corresponding metal oxide. And if it is a solid solution I should not see mixture of oxides, but only one particular phase of oxides. So, the corresponding oxides that I am anticipating here with different heat treatment process either 900 or 1000 or 1300 which we can vary because these are all the ranges where these oxides are reported to form. So, I can just try to heat it to see whether I am getting a single phase compound. So, if I am going to heat for example, A l Q 3 doped with chromium. Then I am anticipating a ruby powder to come which is less than 5 percent though chromium doped A l 2 O 3 or if I am going to decompose this Y 3 A l 5 Q 3. Then I am going to look at yag which is nothing but a lazing material.

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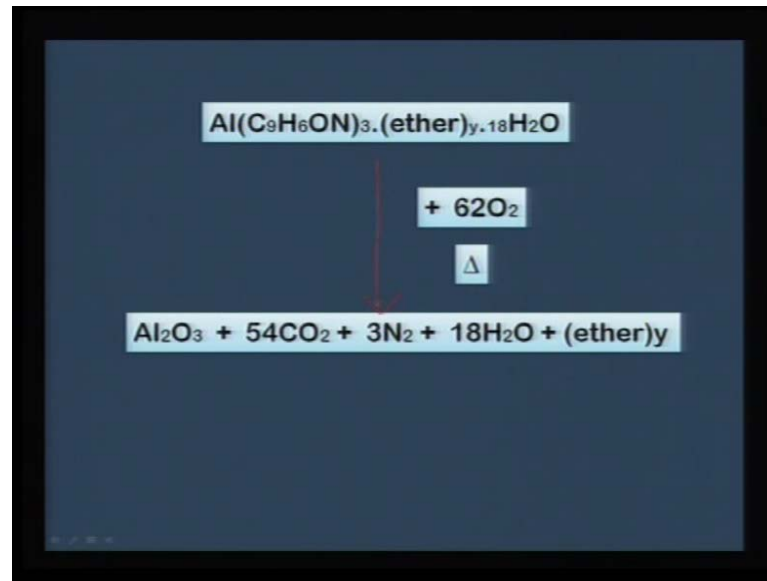
Now, you can see here this is the protocol that we can follow take the precursive solution. And then you try to heat it in air what you would expect is aluminum oxide and for other ones.

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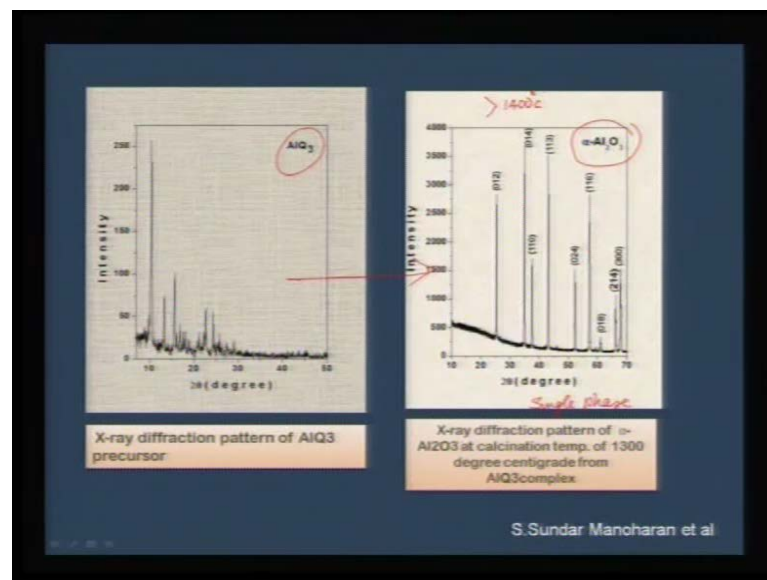
The corresponding metal oxides indeed in this x-ray pattern we see the same thing A l Q 3 as you see is the precursor and on decomposing this I get a very a very highly crystalline single phase A l 2 O 3. And what is the beauty here is I am not getting any other phases of alumina other than alpha phase which is a high temperature phase. And

this high temperature phase oxides cannot be formed through other routes without heating it to 1400 degree c. As you would see from the thermogravimetry that these compounds can be prepared as early as 600 degree c there is no need for you to even go up to 1400 c. So, these are very potential precursors which can be used to translate into corresponding oxides.
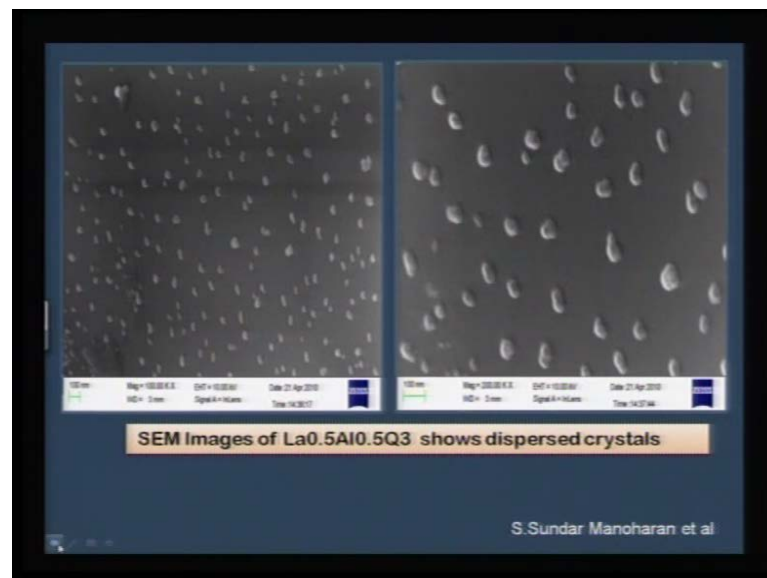
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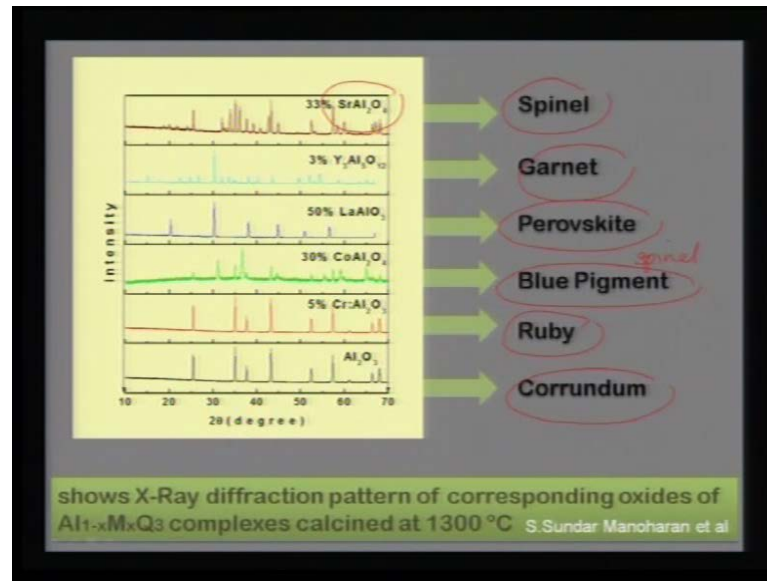
And here is the cartoon which gives you a clear indication for example, strontium aluminate this is a spinel form yttrium aluminum. Garnet is a garnet type A l l A l O 3 is a perovskite then you have cobalt a aluminate which is a spinel and it is also used as a blue pigment. Then you have ruby powder which can be made by just doping with chromium and this is the basic compound.

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SEM Images of AlQ3
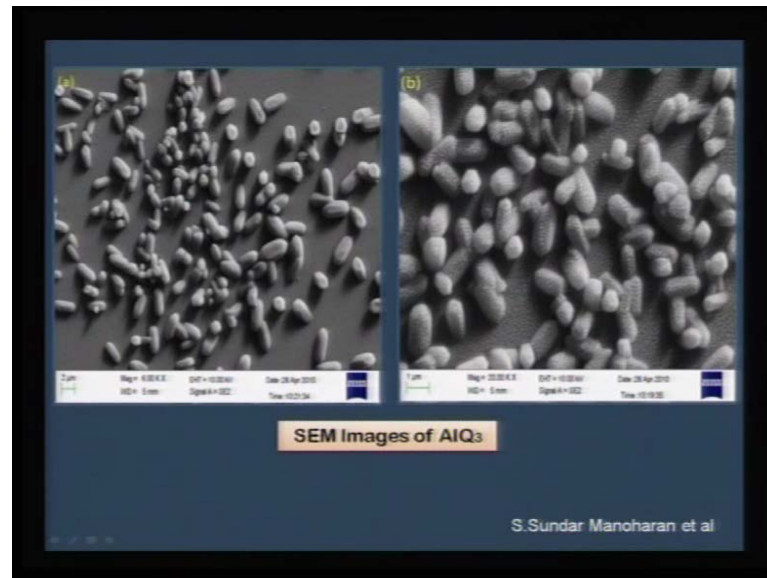
And the structural evolution is really remarkable you can see the way the precursors form. For example if you take the A l Q 3 then these shapes are quite unique.

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SEM Images of La0.5Al0.5Q3 shows dispersed crystals

When you compare with l a A l Q 3 because in l a A l Q 3 you see a dispersed crystals which is quite different in their morphology compared to A l Q 3 and if you.

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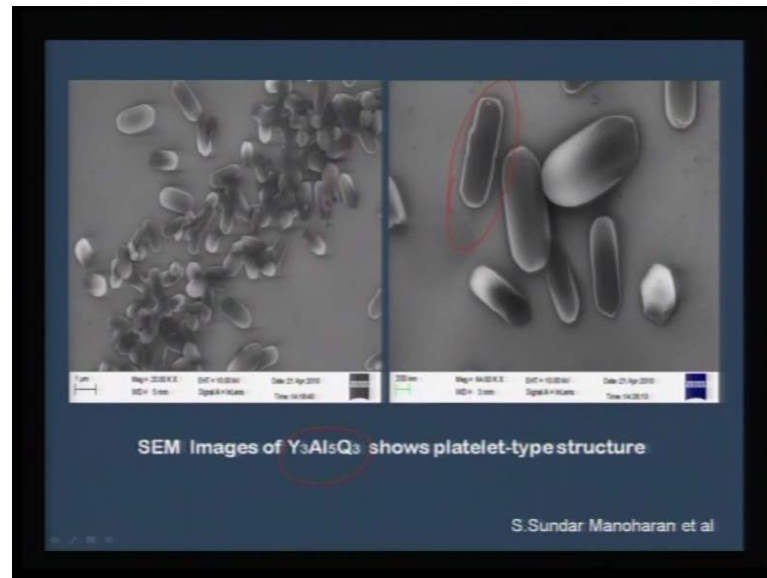
If you go to other composition for example, the precursors for yag you can see the crystals are of a very different shape and size. And this ensures that any amount of doping is possible, but they result in different specific stoichiometries for example, I can also.

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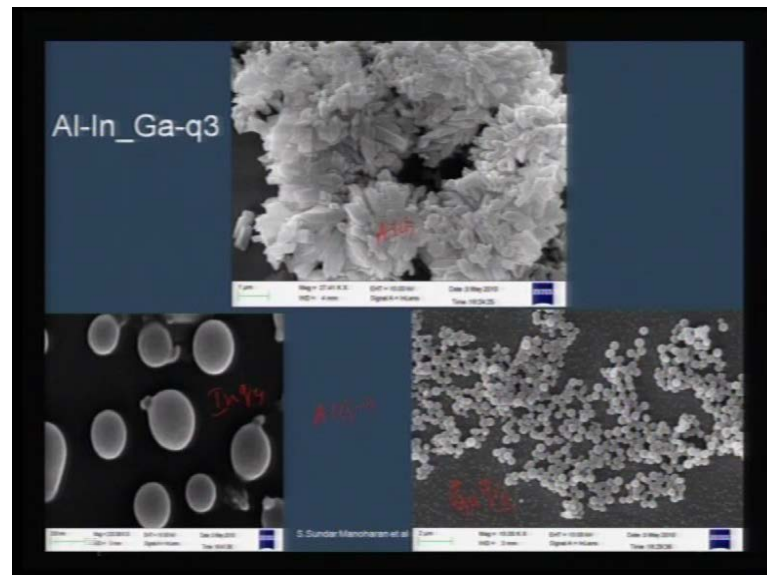
Try to make AIG which is nothing but aluminum indium gallium oxide and if I want to make that AIG compound. Then I can start with aluminum doped with the indium and gallium precisely. This is the cartoon for indium Q 3; this is the cartoon for gallium Q 3.

And this is the picture of all 3 compounds together aluminum, indium and gallium together as you can see here depending on the composition the morphology changes drastically.

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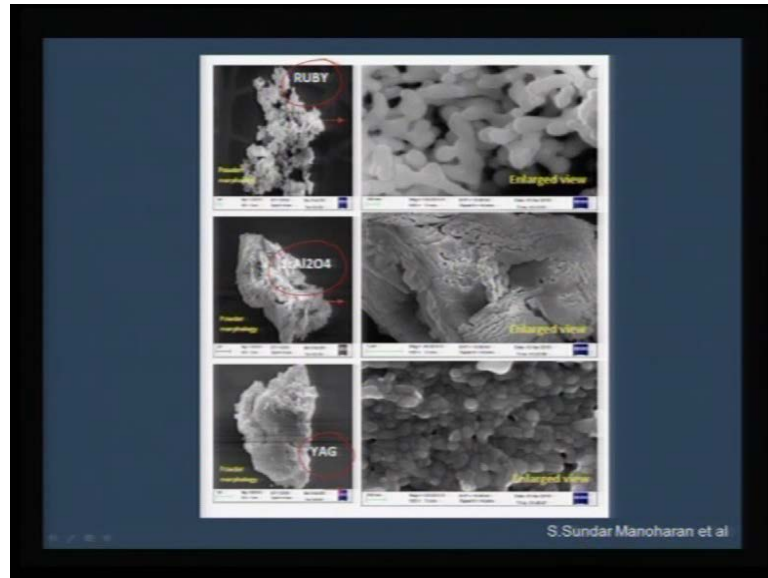
And when you correspondingly decompose those quinoline complexes you can get the ruby powder you can get strontium aluminate which is phosphor yag. And all the oxides also have a very specific morphology and which is which is also influenced by the morphology of the parent precursors.

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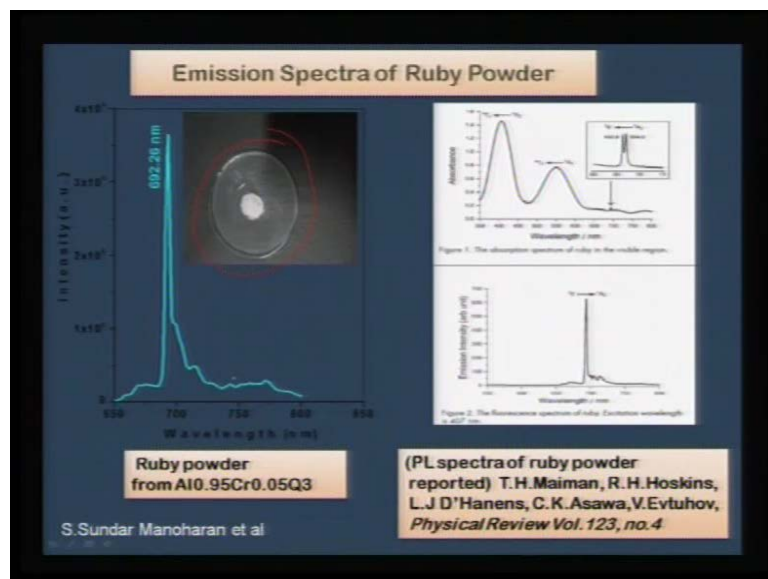
And to ensure that we indeed make ruby powders this is the emission spectra, which clearly shows that ruby powder can be made using this sort of approach which is a Very versatile one.

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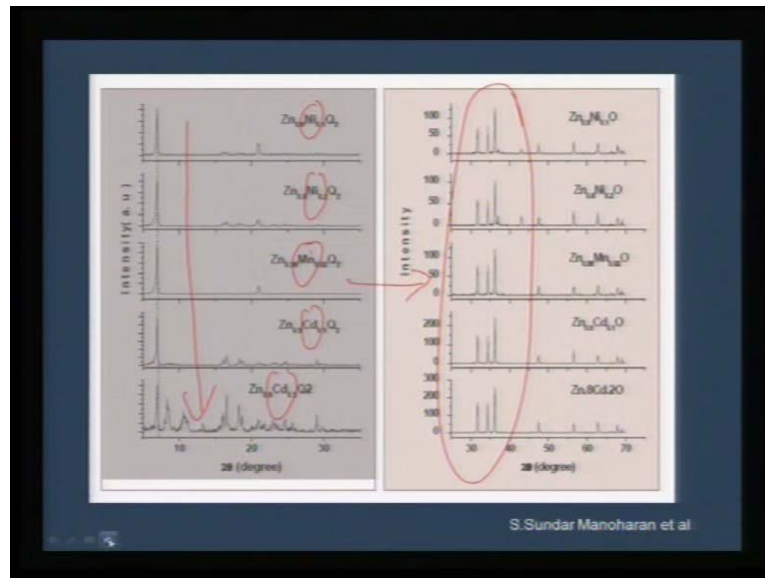
Not only we can do this for aluminum, but we can also play around with such precursors for zinc based compounds. For example, if you take zinc quinoline and substitute with any other metal ion nickel or manganese or cadmium you can get the precursors which are as you see from here. They are all isomorphous they have the same structural pattern therefore, I can make a solid solution. And correspondingly when I heat it I am able to get hexagonal zinc oxide outside face very clearly formed over.

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White substitutional roll and you can also see with just doping little amount of manganese or cadmium. The morphology of the zinc Q 2 crystal changes abruptly with the doping system as you can see this cauliflower sort of bundles coming out of cadmium substitution platelet type coming out of manganese.
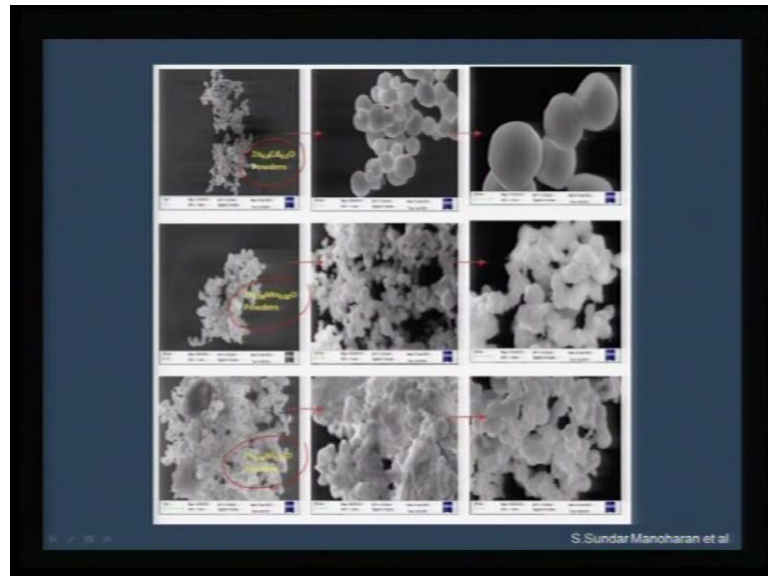
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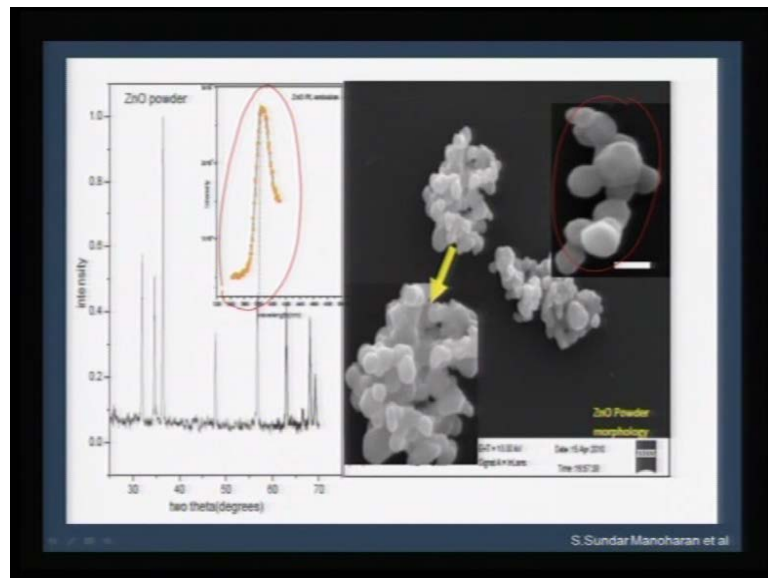
Nevertheless they do affect the surface morphology of the corresponding oxide for example, zinc q 2 u 5 decomposed. I get this sort of nearly spherical platelets of zinc

oxide and the beautiful emission characteristics of band to band emission is also seen here.

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And we can also prepare similarly, cadmium based compounds or manganese based compounds or nickel based compounds. As you would see here even with less than ten percent of doping the crystal's morphology or the surface morphology of these oxides change in a variety of way.

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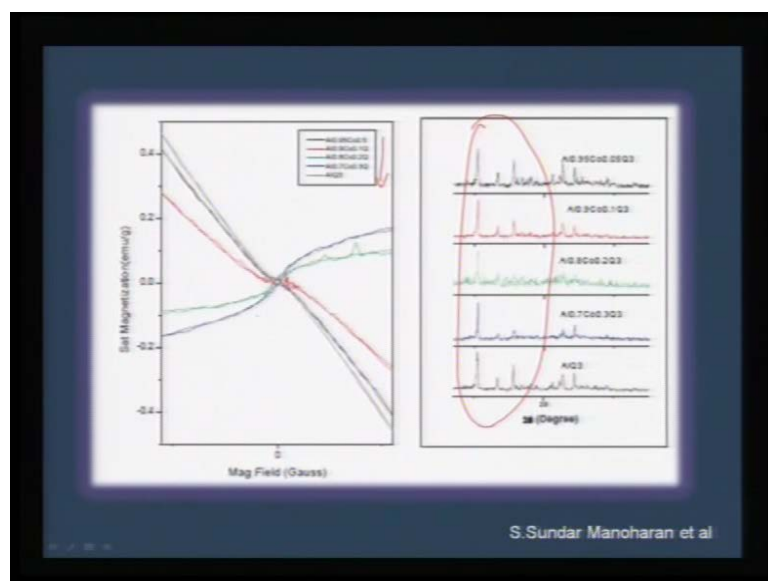
Last 2 slides I would like to sum up that we can also try to tune the magnetism by using the same solid solution precursor notion by substituting very little amount of cobalt from zero percent up to 30 percent. And as you would see here very clearly the precursors are showing the same morphology even up to 30 percent of cobalt doping. But the precursors clearly show a very different trend as far as the magnetic behavior is concerned. So, the undoped one shows almost no magnetism diamagnetic nature. But it reverses and shows a very good hysteresis loop conforming that it is a magnetic compound.

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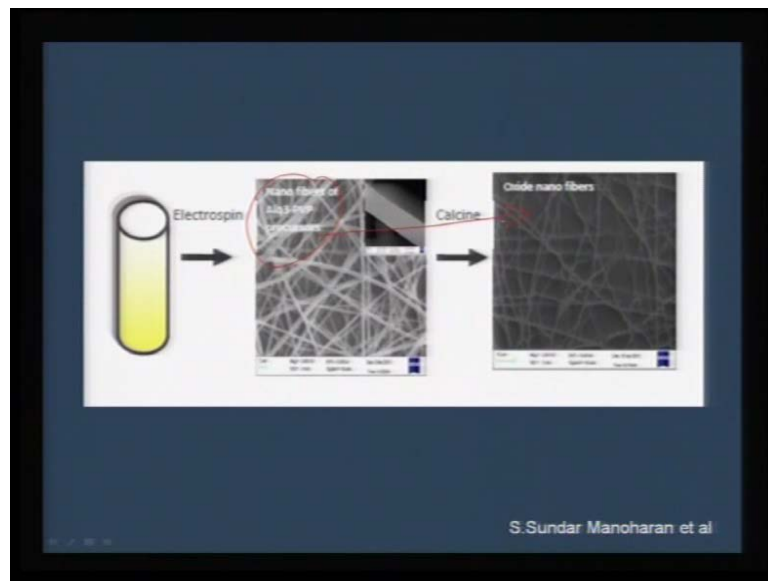
Not only that we can try to extend this sort of precursors to make even nano fibers of the precursors. And correspondingly we can translate into nano oxide fibers making use of the same precursor. So, several possibilities do exist by maintaining the notion of solid solution. So, in general solid solutions are a very powerful technique, because unlike the simple precursors you can fine tune on a range of metal composition. And you can also affect the corresponding property of the oxide. So, it; this solid solution precursors do guarantee that there are many ways by which we can make new structural materials. So, the underlying phenomena, here is the compatibility of the ionic size understanding of the crystal structure. Then there is a tremendous possibility to expand this area to make new materials. We will see in the next slide or in the next lecture, how simple precursors can be used for making complex oxides.