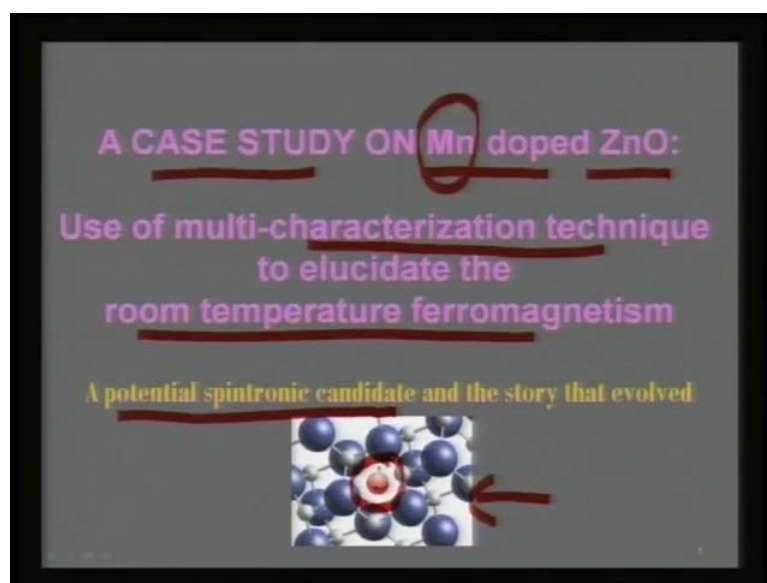


Materials Chemistry
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Module - 4
Lecture - 1
Case Study of ZnO

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In this module, we have been looking at the characterization techniques. And the way we have faced understanding the characterization techniques, and how we can learn from these instruments, may namely diffraction, spectroscopy, microscopy methods. We instead of learning each and every technique, it is better that we look at some case studies and then we will understand, in a comprehensive way. How we can use these techniques, to elucidate structure and to correlate that with the property that we are seeing.

So, in today's lecture we are going to look at a Case Study on zinc oxide, which is doped with manganese. In the last 7 years, this particular study has brought in lot of research focus. Mainly because it addressed one of the very sensitive area called spintronics. In fact, this lecture is aimed to show how simple techniques can be used to understand whether we are really hitting the bull's eye. Because it is possible that we can prepare several compounds, but yet not knowing that we have not achieved the final product.

So, in this connection we will try to see how all the characterization techniques can be combined to get a comprehensive idea of a single system, that is manganese doped zinc oxide. Why it is important, because it shows room temperature ferromagnetism, as a result it finds a potential spintronic application, but what I am going to tell is the story that evolved around this one single system. And how cautious as a chemist or a physicist or as technologists, we need to be and how these characterization techniques can come handy to understand.

This is a simple cartoon, we can try to visualize which is typical of zinc oxide Woodside structure. And if we try to incorporate a magnetic ion, with a spin or it could be any other ion which can induce a ferromagnetism, how this ferromagnetic core can influence zinc oxide. Now, notably manganese is not a ferromagnetic compound, so we are going to look at the origin of magnetic property in zinc oxide, using a doping of a nonmagnetic ion. So, it is a much simpler issue how to elucidate the ferromagnetic component that is present in zinc oxide, because both zinc oxide as well as manganese that is doped there Mn^{2+} both are not magnetic. So, it is much easier for us to evaluate what is really going on there.

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Mn-ZnO

Mn doped ZnO has gained immense interest in past few years.

Mn doping affects the optical properties of ZnO due to the high band gap (4.2eV) of MnO.

Mn being antiferromagnetic metal, should not show a ferromagnetic behavior.

Mn doped ZnO has been observed to show room temperature ferromagnetism.

The origin of RT FM is still an unsolved issue of debate.

The potential advantages of such spintronic devices will be higher speed, greater efficiency, and better stability at a reduced power consumption.

Now, what is the big hype about manganese zinc oxide. Since it is a case study, I want to single out some of the importance of this before we go into a in depth analysis, manganese is a doped zinc oxide has gained more intense research activity in the past

few years as I told you. And because zinc oxide is optically very, very potential candidate for photonic applications, any doping would affect the photonic properties or optical properties, specially if you dope it with a high band gap material that is MnO.

So, if it is manganese which is going as Mn²⁺ plus into zinc site, then you would see a clear shift in the optical property. Manganese also being anti ferromagnetic metal, the doping of MnO we can call this MnO in zinc oxide lattice, should not necessarily show a ferromagnetic property it should not show. So, it makes the case much more interesting for us to understand, where is the magnetism coming from.

But, what is peculiar of this manganese doped zinc oxide is you observe this at room temperature, any compound which gives traces of impurities is supposed to show T_c below room temperature. But manganese doped zinc oxide shows above room temperature that makes it much more interesting to know, where this comes from.

So, the question of origin of room temperature ferromagnetism after 7 years of effort is still not a resolved picture, although plenty of indication is there about what exactly is happening. The potential advantage of such spintronic materials is that you can make a spintronic device, and that will be higher speed greater efficiency and better stability at a reduced power consumption. This is the implication as far as spintronic application is concerned, so with this in perception.

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> Reports have attributed RT FM to:

- Mn²⁺ in Zn²⁺ sites [Nat. Mater. 2 (2003) 673]
- Presence of Mn(III) and Mn(IV) leading to double exchange via oxygen ion [J. Appl. Phys. 101 (2007) 09H103]
- Defect states controlled magnetism [J. Am. Chem. Soc. 127 (2005) 5292]
- Due to metastable Mn_{2-x}Zn_xO_{3-x} phase formation [Nat. Mater. 3 (2004) 709]
- Due to segregated metallic clusters [Phys. Rev. Lett. 92 (2004) 166601]

> The interesting optical and magnetic properties of Mn-ZnO has brought it attention for the magneto-optical applications in the field of spintronics and dilute magnetic semiconductors.

Let us see, where it all started how the story evolved. Report started coming as early as 2003 with a breaking news. In nature materials this is actually a Swedish group, professor k v rao's group which published that, manganese took place when it is substituted in zinc 2 plus sites that is ZnO , it shows room temperature ferromagnetism.

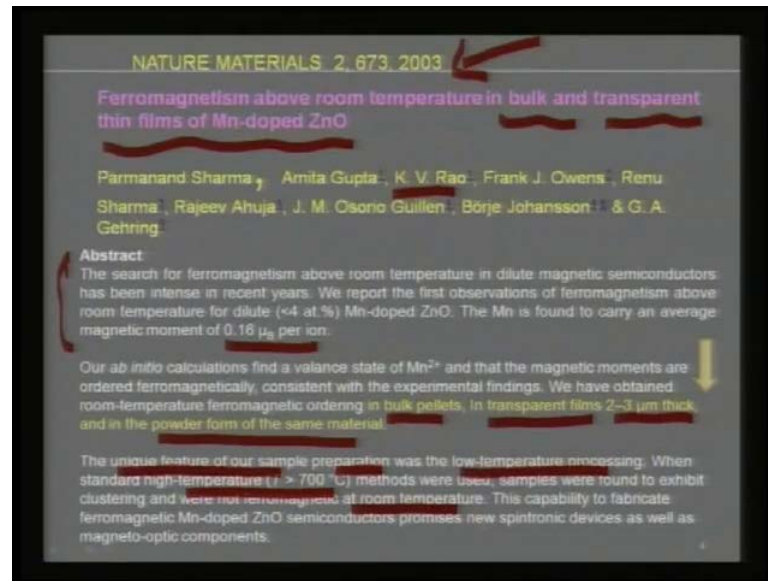
And soon there was a report, saying that the observed magnetism is not coming from manganese substituted in ZnO , but it is due to a metastable phase, such as Mn_2O_3 seemingly substituted with Zn_2O_3 . So, there are several related papers which has come out, which further shows the implication of the impurity phases, which can cause magnetic signal. Due to segregated magnetic clusters this magnetic signature can come, which was published in PRL in 2004.

And someone elucidated that there is presence of Mn^{3+} and Mn^{4+} which leads to a double exchange mediated, ferromagnetism which appeared as late as 2007. And defect structures were also contributing to the magnetic properties, which was told in 2005. So, as you see here historically this is the first paper and the second paper that comes along is this. Now, in the next few slides I will try to show you, what were the contradictions and how the analytical instruments are techniques that were used help us understand what really was going.

This lecture is intended not to put any research group in darker side. But just to highlight based on the published reports, how careful we need to be when we are preparing oxides and when we make assertion that there is a magnetism in a particular compound. So, with this as a disclaimer I would like to show some of the results.

Now, in nature materials 2003 as you know, professor rao's group published this article, saying ferromagnetism is above room temperature both in bulk and transparent films which brought a curiosity among the scientific community. Because, sometimes you can see ferromagnetism in bulk, but it need not actually transpose in the thin film form or sometimes it may be there in thin film, it need not be in bulk.

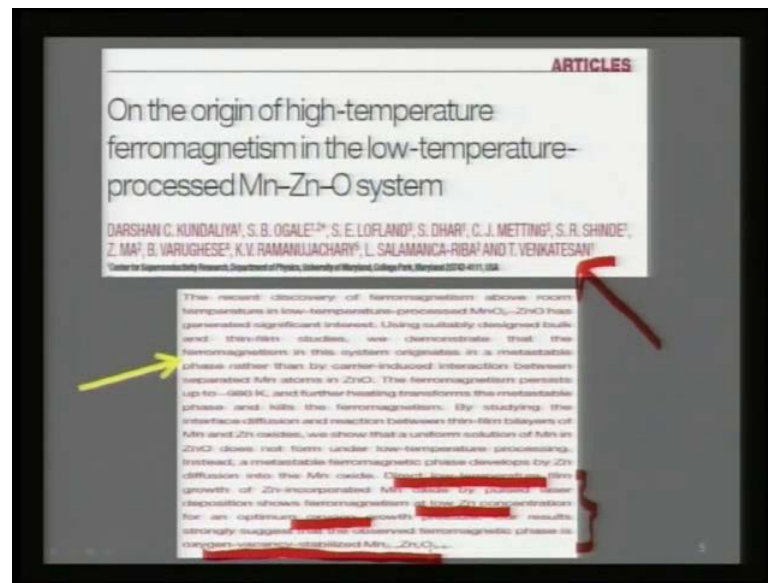
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But, when it goes hand in hand and when we see that the bulk pellets, as well as transparent films of very thin order they show, this sort of ferromagnetism then you are bound to believe that something is really happening. So, what was the abstract the abstract said, the search for ferromagnetism above room temperature in dilute magnetic semiconductors, has been intense activity in recent years. We report the first observations of ferromagnetism, above room temperature for dilute that is less than 4 atom percent manganese doped zinc oxide.

The manganese is found to carry an average magnetic moment of 0.16 μ_B per ion. And what did they say, they also said the unique feature of our sample preparation is that it is a low temperature processing, all the samples were prepared below 700 and they could do this pronouncing that there is a room temperature effect, and they also said that this could be the new spintronic device for magneto optic devices.

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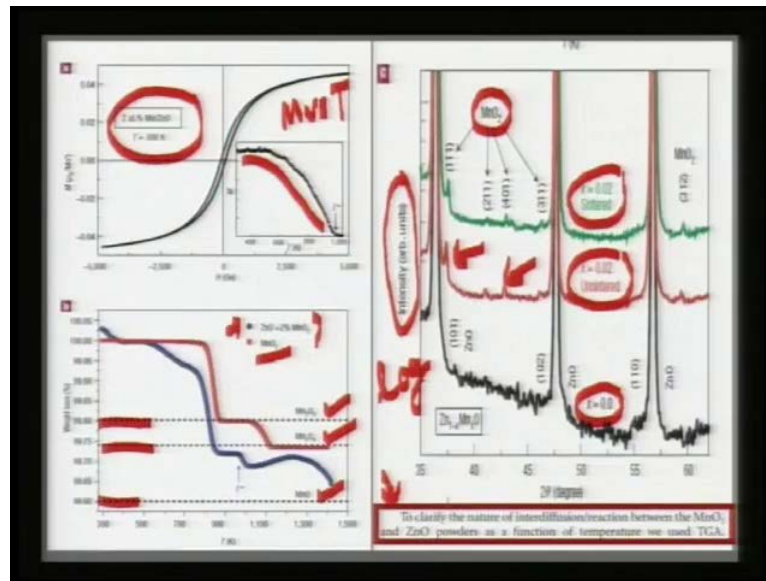


Now, soon after this report there was counter argument from this group, this is professor Venkatesan's group in University of Maryland, at college park. And they came with another paper, in the same magazine that is nature materials, in a span of just 9 months. Where they said, on the origin of high temperature ferromagnetism in the low temperature processed manganese oxide compound. I would not like to read through the whole thing, but all I would like to pinpoint is direct low temperature thin film, deposition shows ferromagnetism at low zinc concentration.

And for an optimum oxygen growth pressure, our results strongly suggest that the absorbed ferromagnetic phase is oxygen vacancy stabilize $Mn_{n-2}Zn_xO_{3-\delta}$. If I have to sum up in the first place, what exactly their finding was this is the abstract that they showed, and we will just see through few slides to see how they progressively elucidated this, which will be a fundamental importance for our understanding about how to use these techniques and how handy it can be.

Now, this is the 2 percent manganese doped zinc oxide, if you measure you will see a clear ferromagnetic loop and that magnetic loop is at 300 k. Now, if you look at this ferromagnetic loop as clear as this, one would blindly say I have a magnetic material and carefully if you try to run m versus T . You see here, there is a ferromagnetic transition down to 1000 Kelvin; that means, T_c is somewhere around 700 above 700 degree centigrade.

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So, because it is showing a t_c above 700 degree centigrade you can be sure that at room temperature it has to be a room temperature ferromagnetic. So, there is nothing wrong with this compound, but we need to understand whether it is clearly a dilute magnetic semiconductor or not.

So, what this group did they took both zinc oxide plus 2 percent MnO_2 that is doped. Then mix it together and try to do a t_g analysis this is what they have to say to clarify the nature of interdiffusion, reactions between MnO_2 and zinc oxide powders as a function of temperature, we used thermo gravimetric analysis. Thermogravimetry is not a very, very astounding or a very costly instrument it is affordable and almost every lab or analytical centers would have it.

But, look at the way that the group has resorted to use a simple technique not much involved, but to elucidate some primary features out of it, what did they do they just took this mixture of 2 percent MnO_2 . And then did the thermo gravimetric analysis, and also they took just MnO_2 which is the starting material and do the thermo gravimetric analysis in air.

So, if you try to heat MnO_2 you can see this red graph which clearly shows two plateau, first there is no change, no loss of oxygen up to nearly 700 k. And beyond 760 k you see a sharp fall and all these horizontal lines that you are seeing here, is the

calculated values for different composition of manganese. Namely Mn_2O_3 or Mn_3O_4 or MnO , these are the components that can come if you take MnO_2 and heat it in air.

So, if Mn_2O_3 is forming then this should be in the first plateau if Mn_3O_4 is forming this should be in this plateau. So, look at this there is some similarity between the 2 percent manganese oxide doped zinc oxide, versus the standard MnO_2 what is happening, you see the same sort of a fall. And the first plateau is actually resembling that of Mn_2O_3 and then there is another plateau, which is similar to Mn_3O_4 . So, you are almost getting a similar feature that of a MnO_2 in zinc oxide.

But, only thing the formation of Mn_3O_4 here is above 1000 Kelvin whereas, that region is actually more favored, even at low temperature as low as say 980. So, there is a considerable shift in the formation of the second plateau that is Mn_3O_4 , similarly you can see the Mn_2O_3 formation seems to be happening, much below the standard.

So, there could be some thing that we can pick up as it is that in the presence of ZnO the formation of both Mn_2O_3 and Mn_3O_4 are favored at much lower temperature, this is the first lesson that we can take. Another thing that the Mn_2O_3 Mn_3O_4 are still present in 2 percent MnO_2 doped zinc oxide therefore, there is a clue that probably manganese is not exactly getting doped, even at 700, 900 k it is still remaining as a phase of m_3O_4 or m_2O_3 .

Now, we can resort to the bulk x-ray pattern. So, these are the bulk x-ray patterns this is for zinc oxide, which shows the hexagonal structure and this is characterized by 3 intense peaks, 1 around 35, 1 around 47 and 1 around 57 you see these three peaks. And suppose, you are going to take 2 percent of MnO_2 and you are going to mix it, with the this ZnO you would see, for the unsintered sample there are some signatures here, which is not present in the pure ZnO .

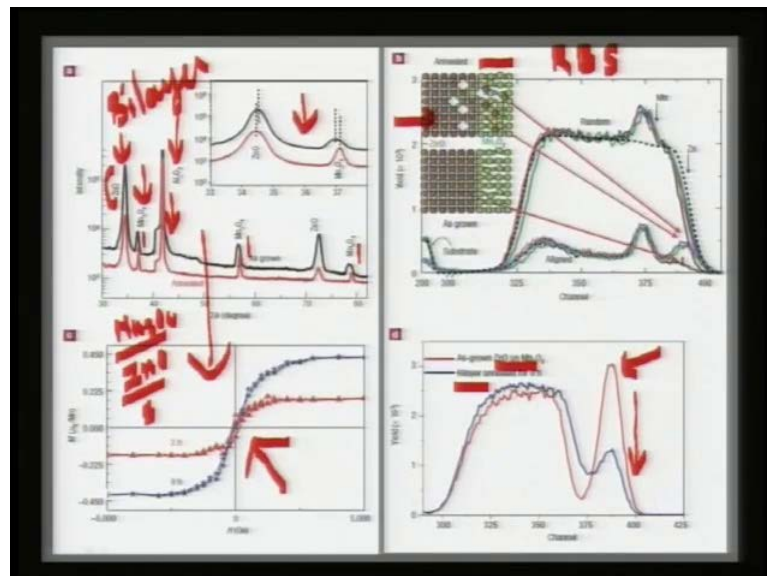
So, for example, this feature and these are some of the features that are coming only few physically mix MnO_2 with ZnO . So, this is the feature number 2, if you start sintering this compound below 700 k, you see still there are reflections of MnO_2 here, there is one reflection of MnO_2 here, there is a reflection of MnO_2 here, there is another one here, there is in other words even at 700 k you do not seem to see this MnO_2 signature vanishing.

Now, why this was missed out mainly because the earlier group they studied the x-ray with a linear intensity scale. But what we are showing here is the log intensity, when you try to plot the log intensity versus two theta value; you always see all the impurities coming up which are more pronounced. Therefore, as a thumb rule when we tried to work with polycrystalline samples or bulk samples or even with thin film samples, always it is a cardinal rule to look at the log intensity plot of x-ray.

Because, log intensity plot will bring this sort of small features to prominence mainly because a relative to the intense peak of Zn in linear intensity plot you would certainly miss out on these signatures. And this was the first clue, that made the other group to believe that probably manganese is not getting doped in the ZnO lattice. So, this is very crucial the first message that we should take as we go through a set of data's is that never look at the x-ray pattern, without taking a log intensity plot on the y axis.

So, if you get a log intensity plot and then you do not see any impurity feature, you can satisfy yourself saying that there is no secondary phase, which is causing any influence on the physical property that you are studying. So, this is one of the message that we can take.

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Now, this same group went about trying to elucidate if there is any way that they can clearly prove that this is not manganese doping, but any other impurity phase. How did they do this, they resorted now not to bulk compound, but to making thin films and what

sort of thin films you can make, take c axis oriented Al_2O_3 which is also called sapphire. Sapphire is titania or iron doped alumina which can be easily grown as a single crystal material. So, you try to take a single crystal of Al_2O_3 .

And then if you try to put zinc oxide up to 700 angstrom and then over the zinc oxide you can try to put manganese oxide. So, how does it go it is almost like as depicted here you first take the alumina peak that is your sapphire substrate, and then epitaxially grow this much of zinc oxide and after that you try to grow Mn_3O_4 layer, which is marked in the with a green circles. So, this is the film that is grown it is called a bilayer deposition, just to understand what is really happening as you try to anneal the substance.

So, these films are actually grown at a higher temperature meaning below 700 k, below the transition point. So, what is the message that we can take as you see here, you have a intense peak for alumina somewhere here, but along with that you also have the zinc oxide peak here, and one would also observe even for 2 percent doped manganese oxide doped one, you can clearly see in thin sorry the this is not Mn_3O_4 . So, over and above zinc oxide, if you try to put Mn_3O_4 layer.

Then you can see these signals coming here, these are corresponding to Mn_3O_4 and if you try to heat the whole film that is ZnO , MnO_4 , Mn_3O_4 bilayer. Then you can see here, that the annealed one and the unannealed film both are showing, the phases for zinc oxide and Mn_3O_4 . But what do you see here in the inset is there is a slight shift in the peak value for the ZnO peak, and there is a slight shift in the peak value for Mn_3O_4 , which means something has happened at the interface you are still seeing the ZnO phase peak, you are still seeing the Mn_3O_4 phase.

But, on annealing you see a small shift their therefore, something should be happening only at the interface not in the bulk, and what happens at the interface will tell us what sort of evolution is happening with the phase. Now, if you look at the RBS pattern this is RBS spectra nothing but Rutherford backscattering spectrum and this is called a channeling experiment, which will tell us whether in a zinc oxide crystal if there is any impurity is doped, whether that would give a good channel or a disturbed channel.

If the channeling value is good then you say that, there is clear doping if a secondary phase is a forming, then the channeling will be very bad, which means you are not able to a grow a epitaxial layer. So, you can get variety of information from Rutherford back

scattering, so this is the situation for a ZnO layer and then which is capped with the Mn₃O₄ layer. So, this is as grown you have alumina then you put a thick ZnO and then on the top you put Mn₃O₄.

Now, channeling profile will be something like this, the dotted one here is the simulated spectrum for 2 percent manganese oxide doped ZnO. The simulated spectrum has to be something like this, but what you see here for a as grown film, this is the one which is showing that there is a substantial decrease in zinc because you have Mn₃O₄ on the top. But as you anneal the sample you can see here that suddenly there is a camel back that is coming and that camel back is actually due to Mn₃O₄.

So, what really happens between the as grown film and the annealed film, you can see here as it is given in this cartoon the some of the zinc oxide zinc²⁺ ions, are actually diffusing into the Mn₃O₄ layer. And they are getting substituted in the interstitial sites, there are vacancies oxygen's are also lost and zinc is getting incorporated here and there in the Mn₃O₄ matrix. This is the signature that we can get from Rutherford backscattering.

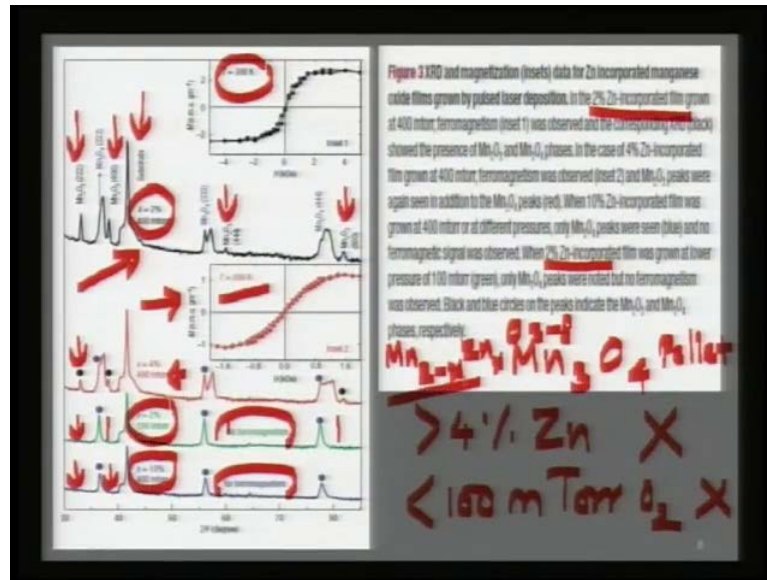
Now, what would happen if you take a such a film and then you heat it this film is nothing but a representation of this configuration. So, you actually have sapphire and then you have the zinc oxide, and then over that you have manganese Mn₃O₄ layer. So, if you try to take VSM loop, you can see here with more and more of annealing temperature the ferromagnetic loop is developing. So, this could actually happen at the interface because of a inter diffusion, across the layers rather than substitution.

So, more and more of zinc seemingly is getting incorporated into the lattice and as a into the Mn₃O₄ lattice, as a result you see the magnetic moment is picking up incidentally this signature is comparable to what is reported. So, instead of a reverse engineering that is zinc manganese getting doped into zinc, we seem to see zinc getting a dispersed into the Mn₃O₄ matrix forming a secondary phase, which is responsible for such a magnetic phase. Now, you can try to reconfirm this by growing zinc oxide on Mn₃O₄ instead of growing Mn₃O₄ layer, like this on ZnO we try to grow ZnO on Mn₃O₄.

Now, if you try to do the channeling studies as you can see here, this is the as grown signature for ZnO on Mn₃O₄, which means there is considerable amount of zinc.

Now, if you try to anneal this compound for 9 hours, you can see considerably the zinc proportion is going down what does it mean, there it is not the reverse transport that is manganese going into zinc oxide, it is the zinc which is diffusing into the manganese oxide layer.

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So, this is a very handy proof and to support this, this group also went about doing another experiment. What did they do here again they took alumina substrate, and over this alumina substrate they just deposited 2 percent zinc oxide incorporated Mn_3O_4 , take Mn_3O_4 and make it as a hard pellet. So, that you can grow films and in this Mn_3O_4 pellet, you try to dope 2 percent zinc.

Now, if you deposit such a film this is what is the x-ray pattern, what does it show you clearly see signature for Mn_2O_3 , you see signature for Mn_2O_3 . Again you see signature for Mn_2O_3 here, along with Mn_2O_3 you also see signature for Mn_3O_4 and you also see signature for Mn_3O_4 . And now, this film clearly shows there is a magnetic signal at 300 k, magnetic signal is clear at room temperature which gives us a clue that zinc can also diffuse into Mn_3O_4 . And it is not the manganese which is diffusing into ZnO .

Now, if you try to monitor what is exactly the mechanism, this is for a x is equal to 2 percent zinc that is doped at 400 millitorr. Suppose, for the same zinc composition if I try to deposit at 100 millitorr, instead of 400 millitorr of oxygen pressure now, you can see

here I am not able to observe any Mn_2O_3 here, there is no Mn_2O_3 , there is no Mn_2O_3 here, there is no Mn_2O_3 here, and there is no Mn_2O_3 here. When I deposit these films at 100 millitorr that is at low partial pressure of oxygen.

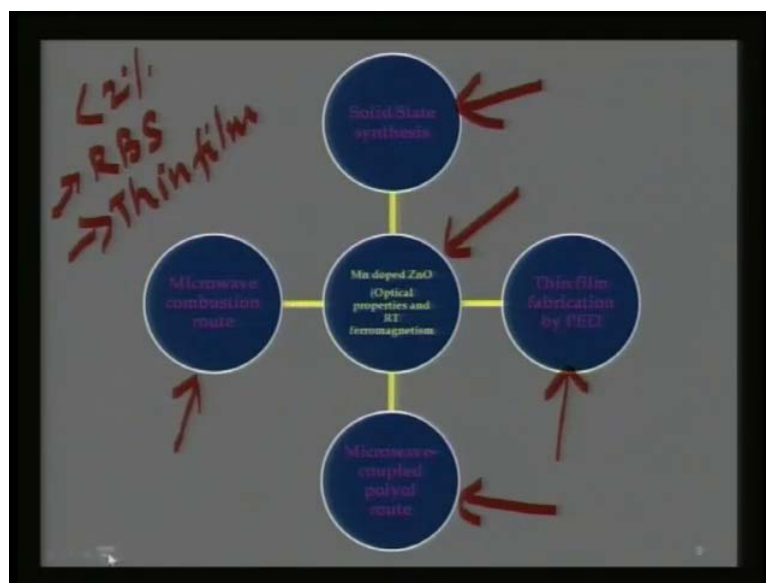
Now, I can twist this again instead keeping same 400 millitorr I can try to substitute now 4 percent of zinc. Now, if I try to increase zinc concentration at 400 millitorr again I am seeing a nice magnetic loop, this is a room temperature signal, so 2 percent or 4 percent zinc at 400 millitorr of oxygen partial pressure, I am getting a film which is ferromagnetic. Now, the same 4 percent if I try to do at 2 percent I am losing the ferromagnetic signal.

Now, keep the 400 millitorr constant and then try to substitute with 10 percent of zinc, again you would see Mn_2O_3 is not there, when Mn_2O_3 is not there then you can clearly see that there is no ferromagnetism. Now, when you do it at low partial pressure you again see there is no ferromagnetism, so two things are happening, higher than 4 percent Zn there is no ferromagnetism, and less than 100 millitorr of oxygen again there is no ferromagnetism.

So, two things are clearly proving that there is something happening between the zinc that is getting diffused into the manganese Mn_3O_4 layer rather than Mn getting diffused into ZnO . So, this clearly proves that it is the 2 percent zinc oxide that is getting into Mn_3O_4 phase, as a result it is the $Mn_{2-x}Zn_xO_{3-\delta}$ which is responsible for ferromagnetism. So, whenever there is lack of Mn_2O_3 then there is no ferromagnetism, Mn_3O_4 is not effected, Mn_2O_3 seems to be the clue and when Mn_2O_3 is always present you see, there is a clear ferromagnetic loop coming.

So, this group went about to propose that it is not zinc that is doped into sorry this is not manganese that is doped into ZnO . Rather it is defect induced concentration in $Mn_{2-x}Zn_xO_{3-\delta}$, which is actually stabilizing a ferromagnetic signal above room temperature.

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Now, this is a very classic example to show that the characterization techniques that we employ can be both useful and it can be risky. Because, blindly when you look at a magnetic signature, if anything that is coming that cannot substantiate that it is a true property of a material. Specially, when you are trying to dope impurities of the order of 2 percent or 4 percent, one has to be extremely careful to see what is the exact mechanism that underlies the magnetic property.

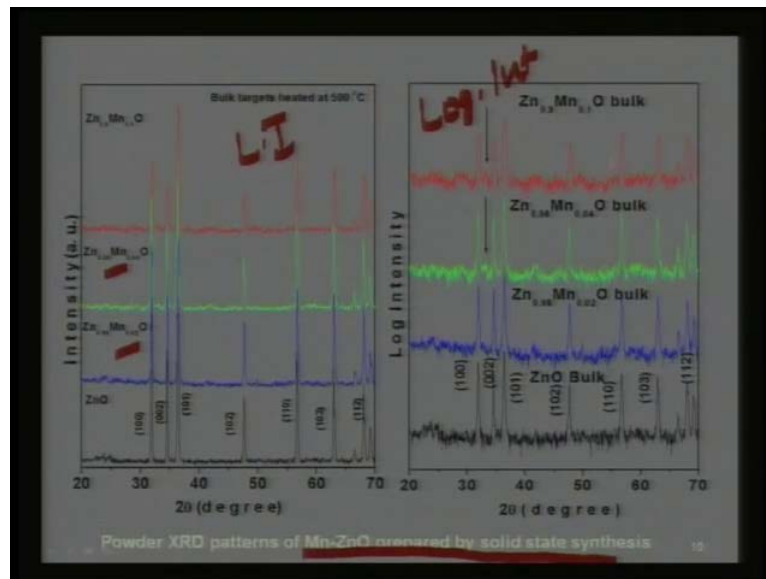
Now, the sort of characterization tools like RBS or thin film whatever thin film based studies these are all very costly, it is not possible always for all the groups to afford. Such exclusive techniques to elucidate, whether the physical properties are going with a structure, but at the same time I have told I have shown you in the previous slides, how simple techniques like thermogravimetry can also be very handy to substantiate this view point. So, in the next few slides I am going to show to you from a chemistry point of view we can try to understand, how the whole thing can be understood.

In fact, the understanding of magnetism now is clear, but from the chemist point of view I would like to throw, different routes by which we can prepare and yet we can draw very conclusive evidence whether manganese is really getting doped or not in bulk or in thin film form. So, for this reason I have chosen four techniques that one can employ to study one single property, that is manganese doped ZnO, ZnO and we can employ

the simple solid state synthesis for comparison. Already I have shown you some of the results from the other group.

We can try to, make a thin film out of pulsed electron deposition or we can use microwave coupled polyol route which I would be also discussing this example in module 6, when we talk about optical properties in solids. And I will also show you another example of microwave combustion route, all this the physical picture or the mechanistic understanding about these preparation routes, I have already discussed in the first module. But never the less I will use this four techniques to show how this can be understood from a chemist point of view.

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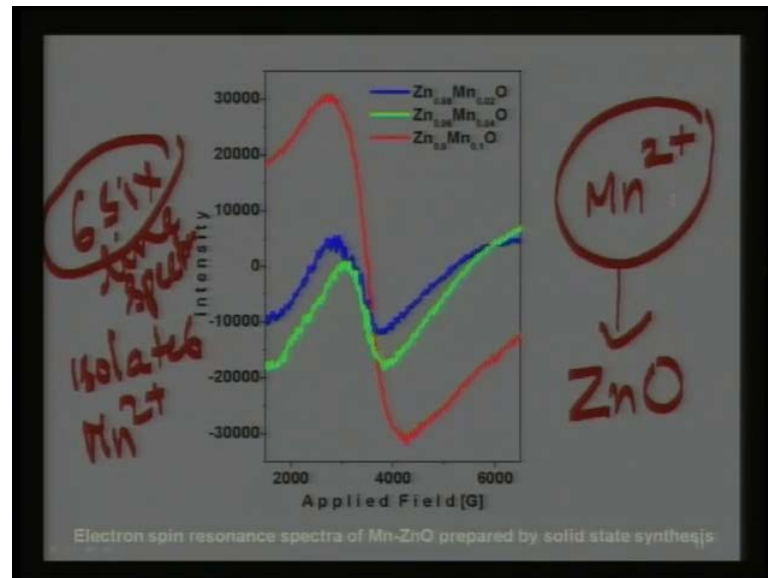


Let us, take the case of manganese doped zinc oxide prepared by a solid state synthesis. And here, if you look at the x-ray pattern you can clearly see that all the x-ray patterns are looking very clean, whether you dope with 2 percent or 4 percent it gives a convincingly clear x-ray pattern. Now, as we already saw that log intensity plots are very, very important than seeing the linear intensity plot, as you would see this is a linear intensity plot, and this is a log intensity plot of the same pattern. And you can see although this looks noisy this will give you clear evidence whether any impurities are hiding here.

So, it is always careful for people working on bulk to probe the log intensity plot of x-ray. Than to simply be gratified by a linear intensity plot, and all these plots what you are

see here on left side and right side is the same plot, but plotted in different scale. So, you can clearly see there is no evidence of any secondary phase coming here, but what can we say.

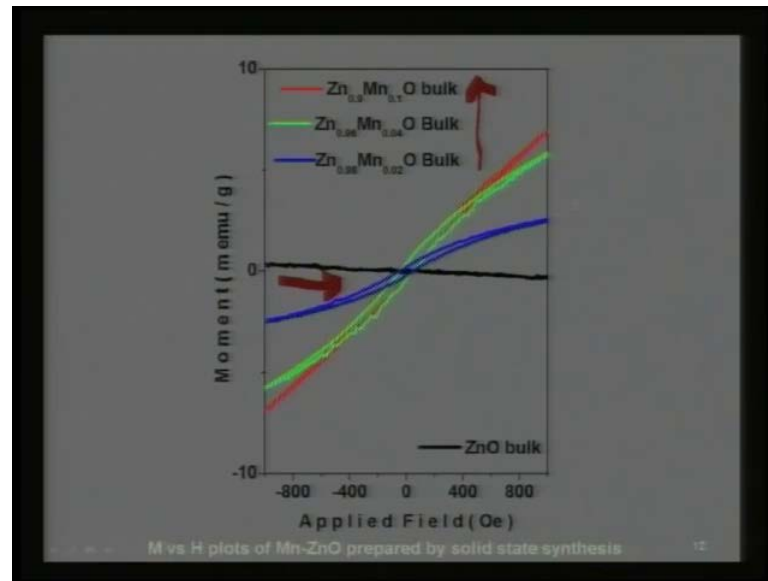
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Now, if you try to look at ESR spectra, ESR spectra clearly gives you clue about whether it is Mn^{2+} or not. In fact, Mn^{2+} is possible doping Mn^{2+} in solid state method is possible, but the ESR spectra does not give a clue that these are isolated Mn^{2+} core, which is sitting in ZnO matrix. Why because if it is a isolated Mn^{2+} then the ESR signal has to be a 6 line, it should be a 6 line spectra. But what we see here is a gross broad ESR spectra showing that there is a cumulative effect or there is manganese interaction in the ZnO .

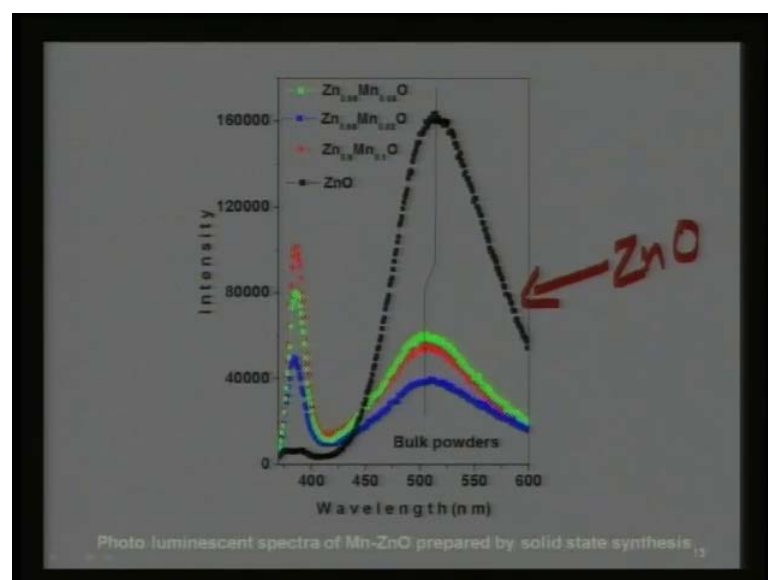
It may be substituted, but these manganese are not isolated, as a result you do not get the splitting 6 lines spectra rather you are getting a broad spectra. So, there is a limitation in the solid state feature that you are effectively able to grow or substitute manganese, yet the compound suffers from manganese manganese interaction. Therefore, the magnetic property is limited by this Mn^{2+} interaction.

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That is what you exactly see because you clearly see that your ZnO bulk is nonmagnetic and it does not show any loop. But with increase in concentration of manganese from 2 percent to 4 to 10 percent you clearly see, that the moment is increasing. So, this magnetic property is actually coming from Mn, Mn interaction rather than coming from a pure doped situation. We will see other examples in the next few slides.

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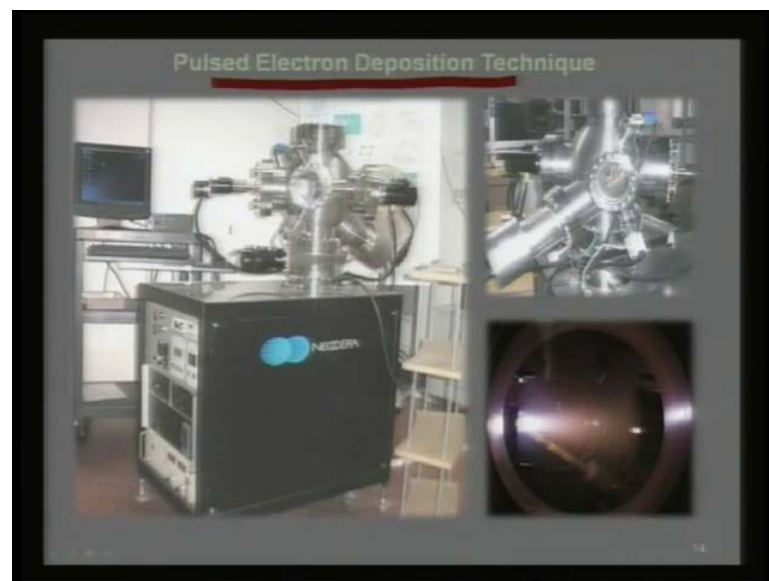


In the same sample, we can also get clue whether manganese is really getting doped. If you take the photoluminescence spectra of manganese doped in zinc oxide, you can

clearly see that this is the peak for undoped ZnO powder, which is synthesized by solid state. All we can see here, is a defect induced PL emission that is characteristic of this 550 broad peak, if it is really band to band edge as I have discussed earlier in the other lectures, the band to band edge should actually come here at 380.

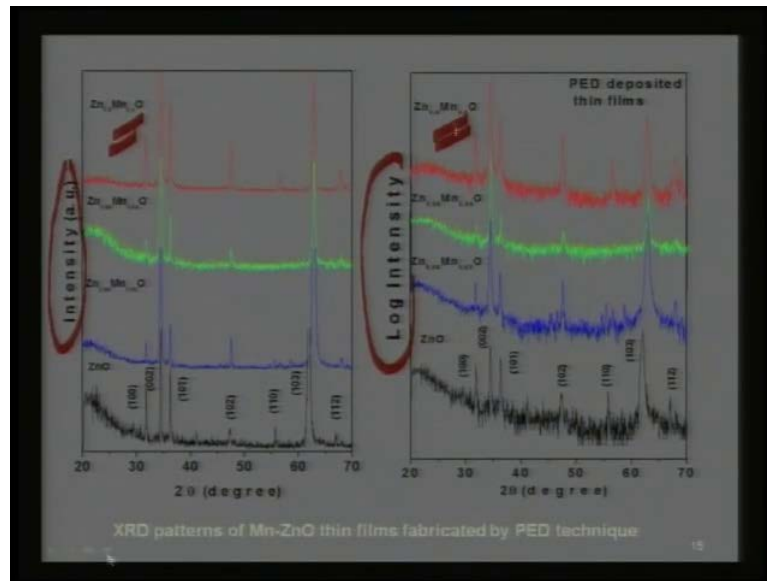
But, one thing we can be clear that when manganese is getting doped you can clearly see, that this surface or defect induced emission is suppressed and the band to band edge emission is getting favored. Although still there is considerable defects, one can say that manganese is getting substituted in some form, but not necessarily to affect the magnetic property. But there is a corporate effect and manganese seems to be suppressing the oxygen deficiency because manganese is able to bring in oxygen while zinc is actually losing oxygen in the lattice. So, this is one of the viewpoint from the solid state prepared sample.

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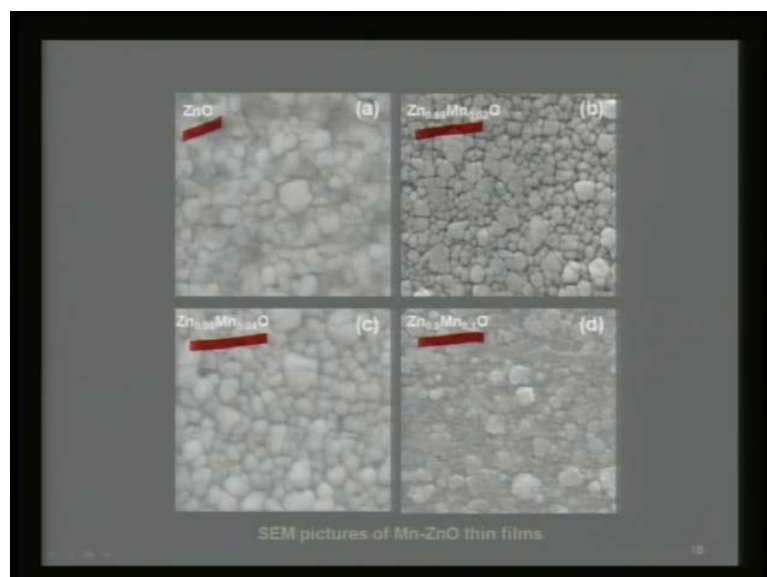
Now, let us go to same manganese 2 percent or 4 percent doped zinc oxide system, but this time instead of solid state, we will use pulsed electron deposition. Because, pulsed electron deposition is also complementary to PLD as I have already discussed in module 2. So, this is a simple a set up of PED which we can use for making such a samples.

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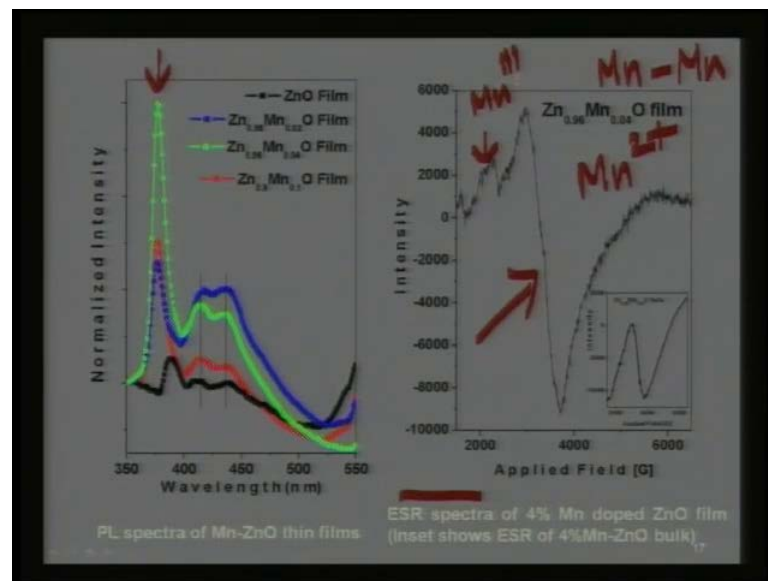
And look at the x-ray pattern of this manganese doped zinc oxide films, these are the zinc oxide films which is plotted in log intensity. And the same films which are deposited on quartz plate in this case, if you grow this zinc oxide you can clearly see they show very clean feature. And you would not expect any sort of manganese impurity in these ZnO films therefore, one can clearly walk out, walk away with the understanding that manganese is getting doped. And in this case you can also see that you can dope even 10 percent of manganese without any trace impurity for manganese here.

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So, having said that look at the micro structure this is how the ZnO films, are when you deposit using PED. Now, this is for the 2 percent manganese, this is for 4 percent manganese and when you go to 10 percent you do not see the same sort of a feature, there is something else happening therefore, compositionally it may be 10 percent doped sample, but there could be some thing else happening. So, it need not necessarily be a doped zinc oxide film.

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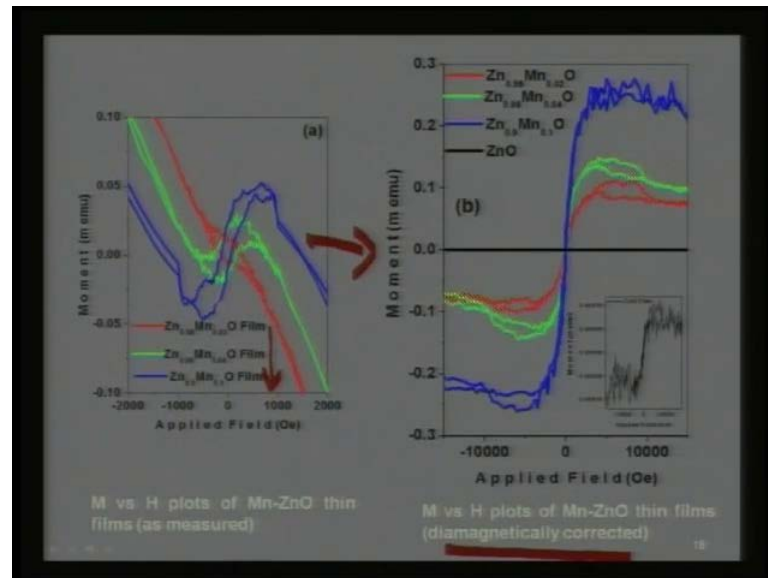


So, let us look at the PL spectra and the ESR spectra, as you would see here compared to the solid state grown films, you still see a very nice 380 nanometer peak for manganese doped ones. And here again the same story as that of solid state, where you see the zinc oxide shows a very low 380 nanometer peak mainly because it is losing much on the defect induced concentration. Whereas, manganese doped ones are suppressing the 550 nanometer peak, but it is showing the 380 nanometer peak.

And when you go to the ESR spectra for 2 percent or 4 percent peak, and the this is what the cartoon says that there is no signature of isolated Mn²⁺ signal. Rather see a very broad signal and this broad signal is suggesting that Mn²⁺ are having some sort of clustering. If it is Mn-Mn interaction then you would expect some thing like this and there is also another signature here, which is typical for Mn₃O₄ phase, which although you do not see in the bulk form.

But, yet you see there is a clear signal for something other than $M \propto x^2$, there is a signal it could actually come from $M \propto x^3$ or $M \propto x^4$ concentration. So, this is the situation if you try to look at the PED grown thin films.

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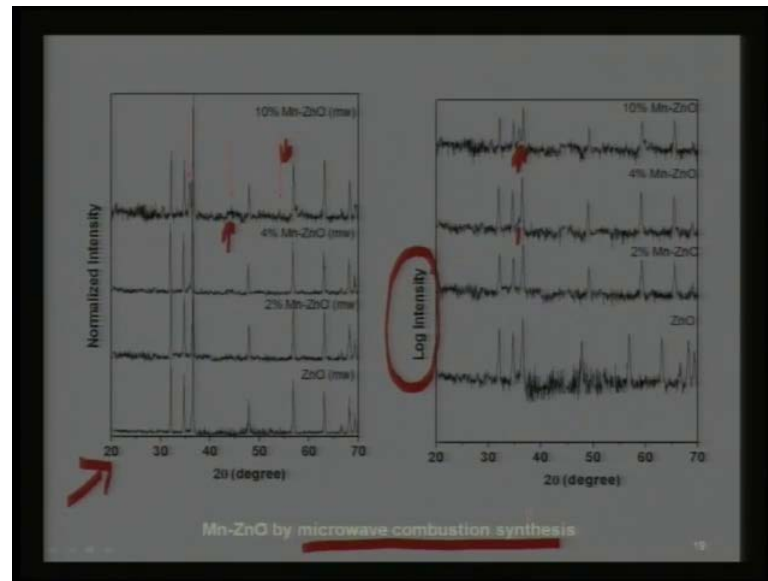


Now, what is more convincing when you look at it is the magnetic property unless you, see a unlike the other case where you see a faint magnetic signature. If you grow PED grown films then you can see, for 2 to 10 percent you can clearly see the signal changing, for 2 percent you see a negative slope this is coming mainly because you are using a quartz plate and therefore, the diamagnetic contribution is more. So, you can actually do a diamagnetically corrected compound, and in that case a clear loop is found this is at room temperature.

Now, if you increase the concentration you see the green curve and then the blue curve, which on diamagnetic correction shows a clear loop. So, if you do not probe into ESR and just look at the x-ray, and then the magnetic property you can clearly say that I have doped manganese. Because, there is a monotonic increase in the magnetic moment with respect to substitution therefore, you would clearly convince your self that it is a manganese doped zinc oxide film.

But, this need not be mainly because we see that these are not isolated manganese in these ZnO matrix. So, ESR in this situation comes out very handy.

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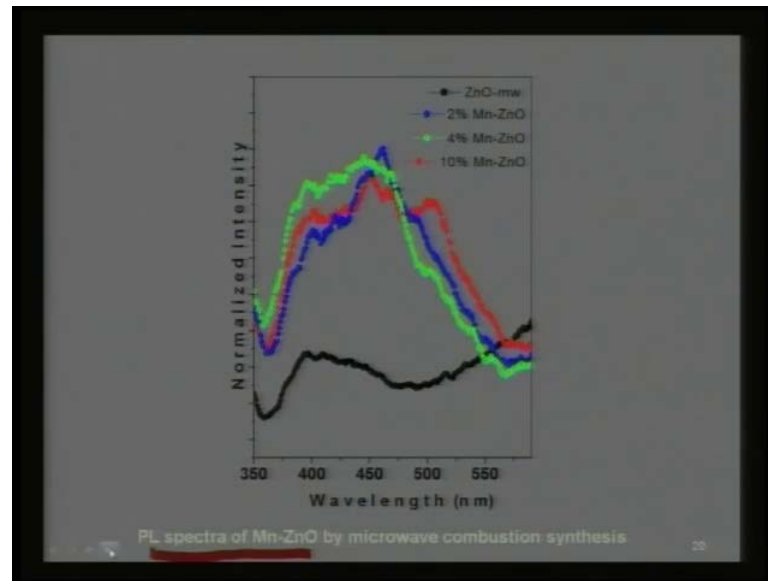


Now, let us go to microwave combustion synthesis microwave combustion synthesis is like a brute force method because you are providing enough of flame temperature. In this reaction for the reaction to occur therefore, you can quickly dope manganese into ZnO lattice, not only that it is a fast quenching reaction as I discussed already in the first module. So, you are actually using a rapid synthesis and a fast quenching method therefore, you can stabilize metastable phase.

For example, if manganese can clearly be doped at high temperature, then you can suddenly cool it and stabilize the metastable phase. And look at the x-ray pattern, you can clearly see the ZnO peak and the microwave combustion stuff, but what is interesting here to find is that at 10 percent, you can clearly see another feature that is coming close to the ZnO peak. And if you plot the whole thing, in log intensity plot you can see this impurity much more pronounced, even at 4 percent you can see the signature there.

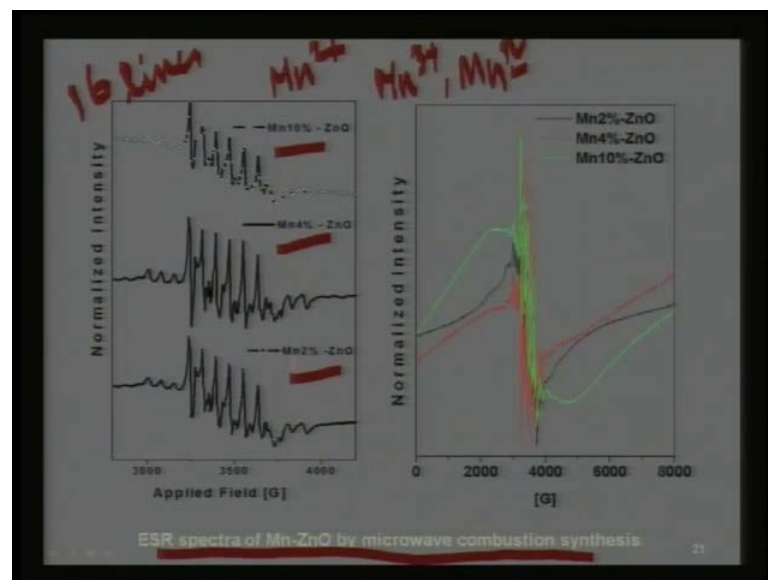
Therefore, it is very, very important for us to carefully look at the signature that is coming out. Note for example, these are all the signatures for MnO which is coming out of the zinc oxide lattice. So, microwave combustion seemingly is able to dope manganese, but there is also a residual impurity that is seen.

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And the PL spectra, is completely plagued with a defect concentration. Therefore, you do not see any band to band emission edge emission, but you see a defect induced or oxygen deficient PL behavior.

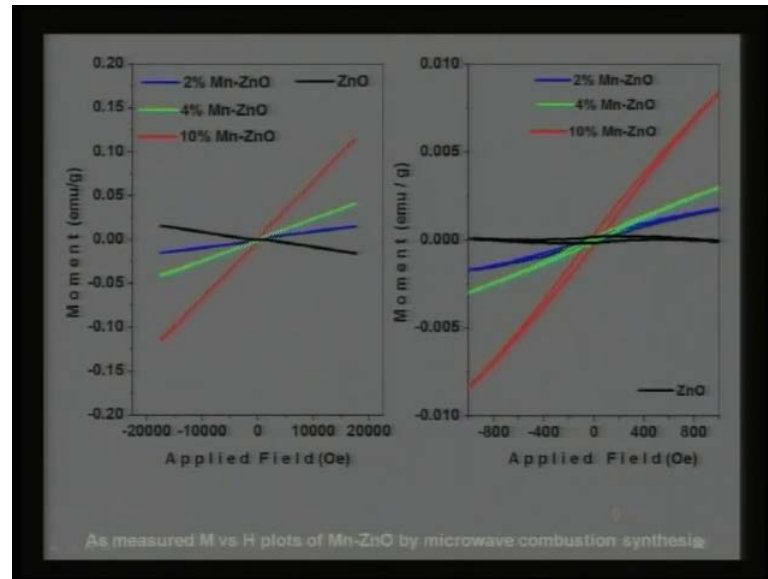
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Now, if you take the ESR spectra of this manganese doped compounds, prepared by microwave combustion route. You see that, you do not exactly see a 6 line spectra, but you are seeing a 16 line spectra, and this 16 line spectra suggest that this is not exactly Mn^{2+} , but these are signatures for both Mn^{3+} and Mn^{4+} concentration.

It is for 2 percent, it is for 4 percent, it is for 10 percent therefore, one can clearly say that in microwave combustion, what is happening is the Mn^{2+} is also getting converted to higher oxidation states, which are Mn^{3+} and Mn^{4+} . And therefore, it is very, very important that we try to look at the ESR spectra, when you are specially studying the manganese system.

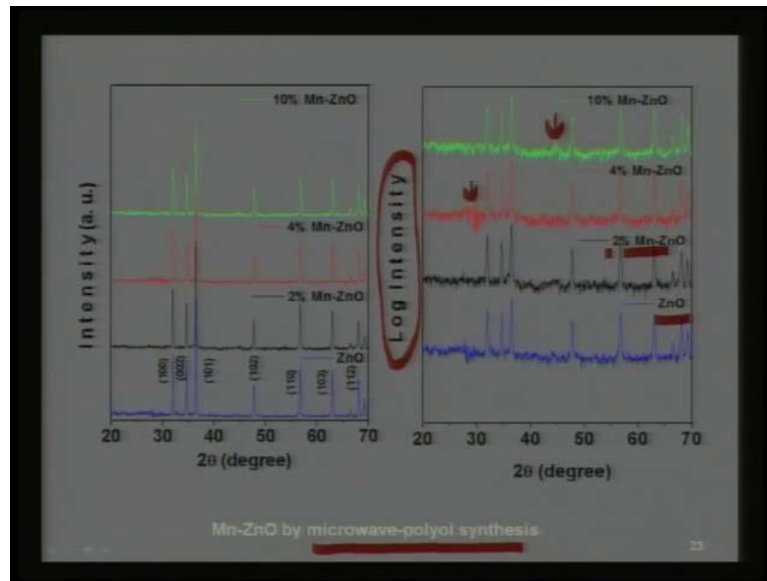
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Look at the magnetic signatures as seen here, ZnO is clearly giving a negative slope. So, there is no problem the moment you put 2 percent it is turning positive and then for 4 percent, and then for 10 percent, you can clearly see a loop therefore it gives a very convincing signature that it is indeed a doped situation. But actually what we see here is it is not just manganese doping it is something more than that, you seem to end up with different oxidation states of manganese. So, a rapid combustion route clearly gives evidence for something, other than manganese $2+$ which is present in the ZnO lattice.

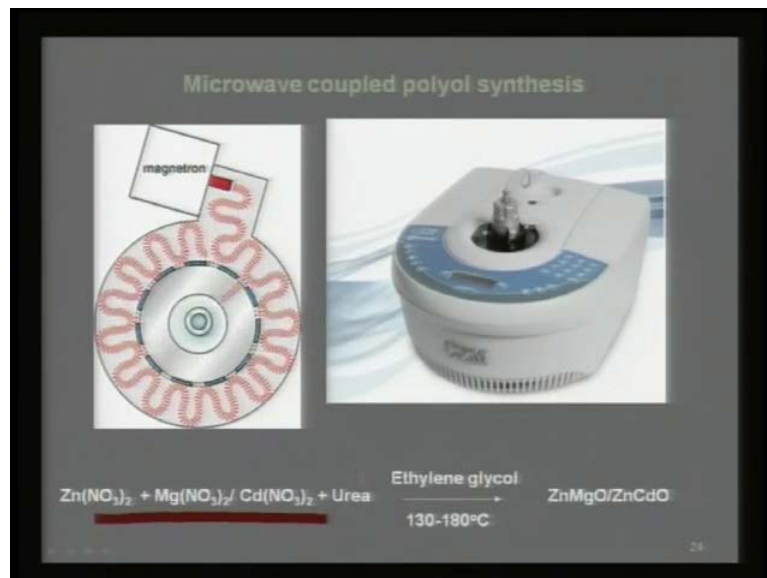
Now, let us go to another soft route this is not a rapid route, like thin film or the microwave combustion route. This is a kinetically controlled one, which I have already discussed in the first module again, on microwave polyol synthesis. Now, look at the x-ray pattern here again, it is very clear that you have a clean phase, there is nothing there, but you can see it is bit noisy there are some small peaks which are emerging here, when you do this plot in log intensity.

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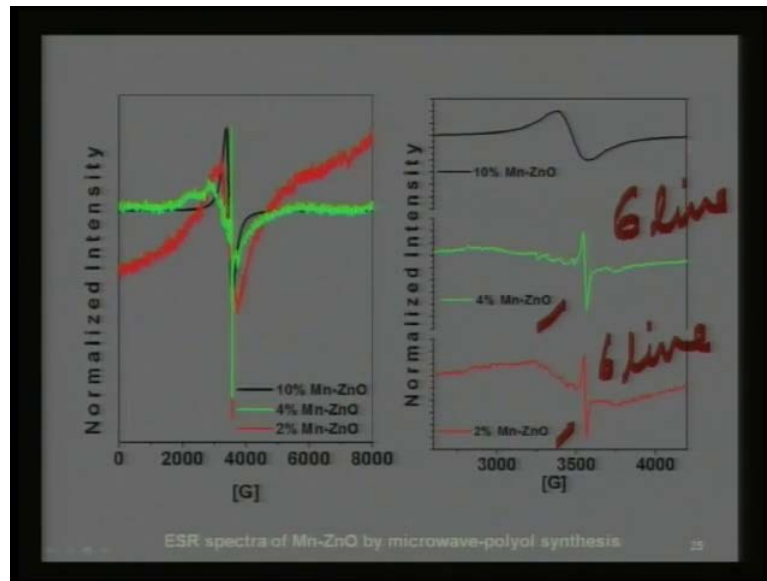
So, in log intensity plot you see there are some disturbing or mild impurity features propping up for 4 percent and 10 percent peak, but seemingly the undoped ones are very clear.

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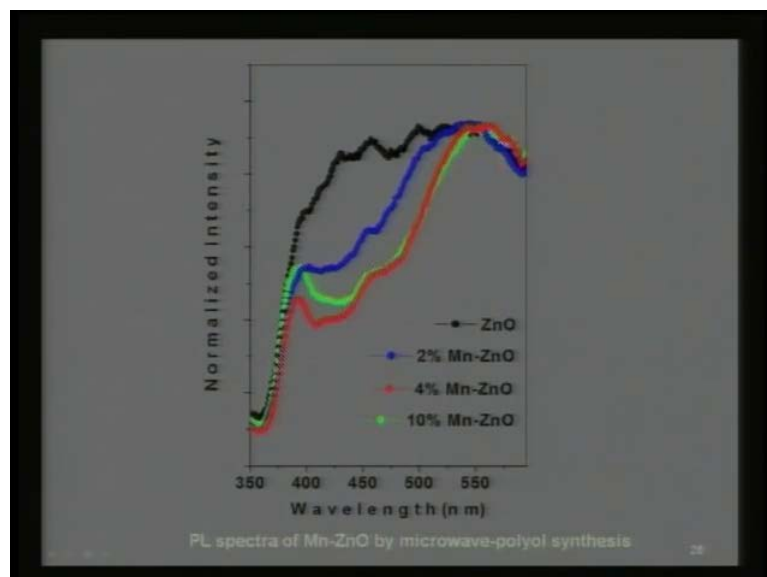
So, with this in view we can try to see what is exactly happening as I have told you earlier, that you can do this using microwave polyol which is the chamber that is used here.

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And if you take the ESR spectra of this manganese oxide powders, you can see that there are interesting features coming up. For 2 percent and 4 percent doped manganese oxide, you clearly see a 6 line spectra, if you amplify this you clearly see that this is a 6 line spectra and this is another 6 line spectra, for your manganese core. But the moment you go to higher percentage you see a very broad peak what does this mean.

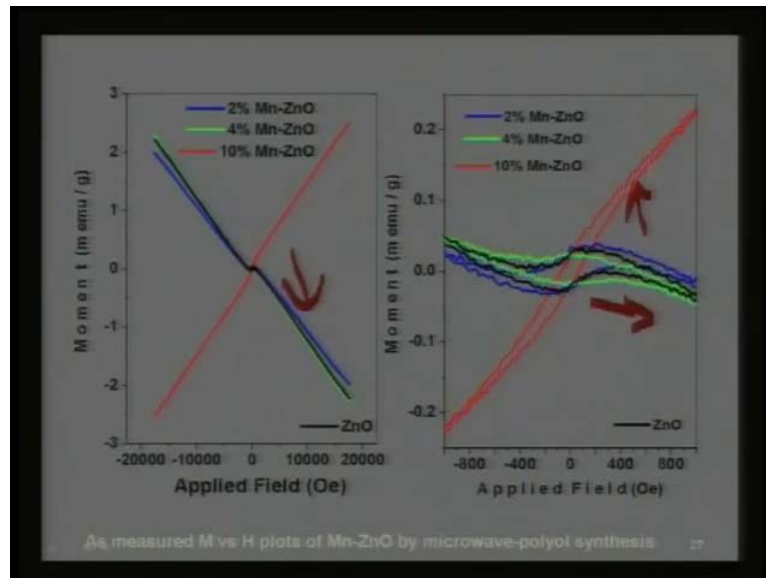
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In a soft route, soft chemical route which is kinetically controlled not thermodynamically controlled, you can essential dope manganese in a better way. There is a definite way

that you can dope manganese into zinc oxide, it is not impossible and that is seen from a 6 line spectra. Now, having said that look at the PL, PL seems to be also again a defect induced PL emission.

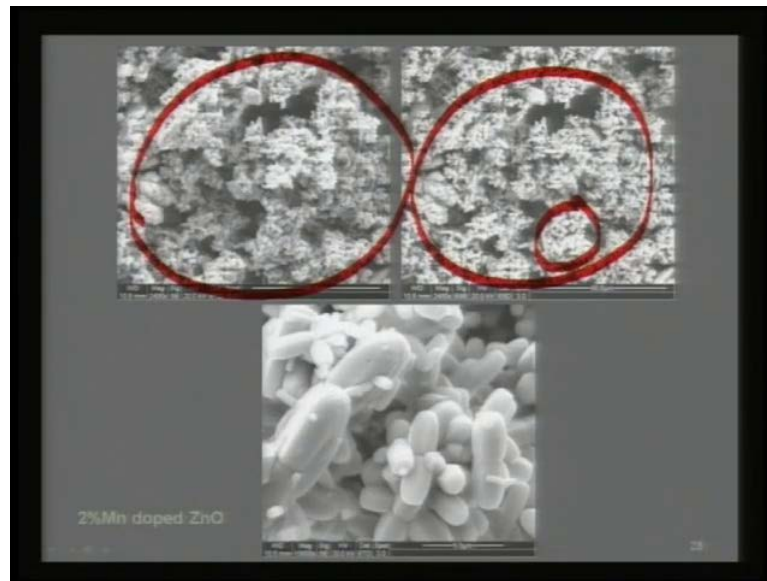
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So, with this in background if you look at the magnetic property, you see again there is a clear evidence for substitution for zinc oxide. There is a clear loop coming whereas, the loops are showing a hysteresis, but then it is not as clear like the way the PED films are made or the microwave combustion route prepared samples. So, if you look at the magnetic property you can clearly say that, even though I have a clear evidence for manganese substitution in zinc oxide.

But, the magnetic property is not convincing because when there is manganese, manganese interaction and a broad zinc oxide spectra, the magnetic feature is nearly in comparison. But when you have a 6 line spectra in all those cases, you still see a diamagnetic contribution more pronounced therefore, we need to be very cautious to say whether manganese is clearly doped or not. If it is clearly doped, we do not see a strong magnetic feature as we have seen in other cases, but when there is a manganese, manganese interaction then you again see something as what is reported.

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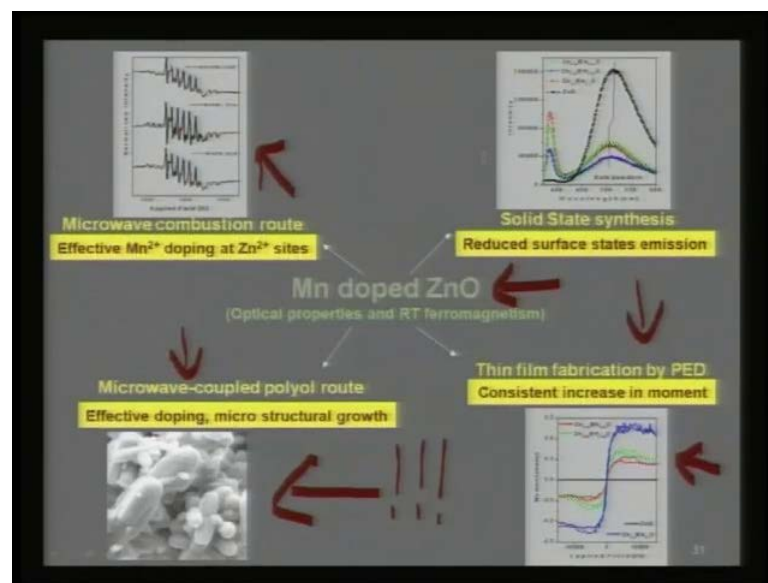
Now, if you look at the SEM features also you can clearly see, that 2 percent and 4 percent manganese are clearly substituted in zinc oxide. For example, you take a microscopic view of this 50 micron region, you can take this is another view graph of 50 micron region. If you try to blow up any sort of regions, you can see these are all nano parts of zinc oxide you do not see any secondary phase, whether in backscattered or secondary electron image, you do not see any secondary phase in this compound. So, we can clearly say that manganese is doped.

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Whereas, if you take 4 percent you see almost the same feature and you do not seem to see any secondary phase that is prominently seen. So, you can have a variety of viewgraphs for that, now go to 10 percent doped one, you can see there are regions which are significantly different from these regions. That means, when you go to higher percentage of manganese, there can be chances for two different things to happen, you know you can have both manganese doped one. As well as manganese segregated one and this is what we see from the x-ray also that some impurity peaks keep propping up above 10 percent.

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So, what do we take lesson from here of all the techniques that we have adopted to prepare this manganese doped zinc oxide. The most favored one, where we can be clearly sure that 2 percent or 4 percent is exactly getting substituted, we can go for the polyol route. Polyol route is the best, for low doping concentration, but what happens the magnetic property is not convincing whereas, in the other cases where we have seen clear evidence for other phases of manganese, you get very arastic magnetic signature.

For example, in the case of microwave combustion route, we get signature for valences other than Mn²⁺. And in solid state synthesis I have shown you, that the magnetic property is very convincing, but then we see this as a case where MnO phase, other phases are segregating. And same way in PED films, you can clearly dope manganese,

but the mechanism of manganese doping does not seem to be clear, although the magnetic features are same.

So, I have shown you one is a milder approach, one one is a brute force approach, one is a thin film approach, one is the conventional solid state approach, we need to be extremely careful. Because, each of these preparatory features seemingly throws a variety of magnetic information. So, this is a very candid study by which we can try to incorporate as many characterization techniques as possible, to understand the physical properties.

Therefore, it is important for every chemist or physicist or any one in this field, who is trying to look at the physical property, to look more carefully into the structural property. So, structural property correlation is very important and we will see in the next slides, other case studies where we can use multicharacterization techniques to elucidate the structure and correlate with the properties.