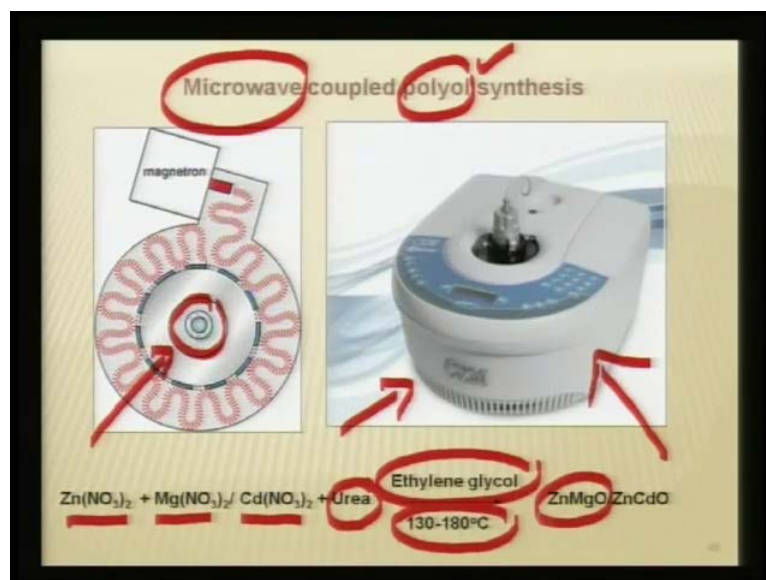


Materials Chemistry
Prof. S. Sundar Manoharan
Department of Chemistry
Indian Institute of Technology, Kanpur

Module - 6
Lecture - 4
Inorganic Phosphors II

In the last lecture, we looked at the quantum size effect, we looked at doping effect and alloying effect, in wide bandgap semiconductors, mainly we looked at two examples on cadmium sulphide. And especially with reference to quantum effects how cadmium sulphide can be doped with different other chalcogenides or cadmium sulphide prepared by different routes. How it affects the quantum, how it pronounces a quantum size effect, and how the emission features can be changed with respect to the particle size of cadmium sulphide. So, this one of the cases that we looked into in the last lecture and also we took specific examples of zinc sulphide which is a prominent phosphor, which is used in display devices mainly it is the core for application in a cathode ray tube devices.

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So, we also saw how zinc sulphide can be tuned and by substituting with different transition metal ions, how you can get desired color purity and as a result we also looked at the specific examples of doping zinc and cadmium and manganese together to get a full width with a half maximum beyond 150 nanometers, thereby trying to harvest white

light. And the last example we saw was on alloying effect of zinc oxide and we took examples of doping it with both cadmium as well as manganese in zinc oxide, one of the main challenges of this zinc oxide alloying is the solubility.

In solid state method, the solubility of magnesium into zinc oxide is just 4 percent, it is not possible to dope more than that because of the structural or crystal symmetry mismatch. Zinc oxide is a hexagonal symmetry whereas cadmium oxide or magnesium oxide is of cubic symmetry, and therefore doping a cubic symmetry related oxide into a hexagonal lattice is very tricky. So, I showed you couple of examples where we can try to push more of magnesium into zinc oxide lattice by adopting different chemical approaches. And today I am going to actually look into another aspect of sophisticated wet chemistry route, which can be used for alloying zinc oxide.

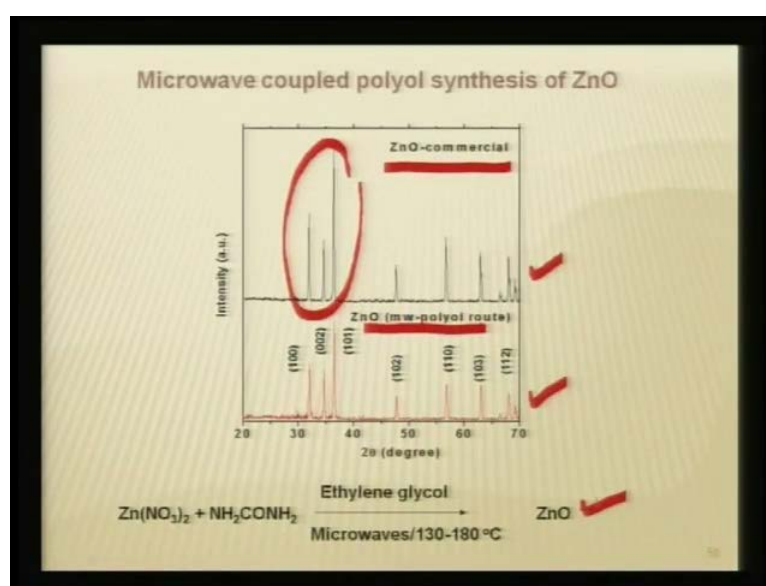
One of the most prominent method is called microwave coupled polyol synthesis, and microwave coupled polyol synthesis is upcoming method which can be used for variety of systems, not only for inorganic oxides microwave coupled synthesis is used predominately in organic synthesis also. But, what we are trying to do is use microwave, and we are also trying to use polyol to hydrolyze the zinc salt in order to get zinc oxide in one pot reaction.

Now, this is the one of the cartoon that shows what this microwave coupled polyol synthesis is; we basically use a magnetron as a source for producing microwave and in a commercial system like see like that sold by CM corporation. You can see that microwaves are focused more to the cavity, so if you have a small vessel then it is possible for you to concentrate to this cavity your microwave radiation, and thereby you can try to effect mechanical reaction.

So, this is a commercial microwave unit, which can actually help us with this sort of synthesis and also we are trying to use polyol, polyol method is nothing but take a metal salt and then you take urea which is a base. And then take ethylene glycol which is a hydrolyzing solvent as well as it is a polyol, which can be used as a solvent, it is a both hydrolyzing agent as well as it is a solvent. Therefore, if you take zinc nitrate and magnesium nitrate and cadmium nitrate in proportions that you want either for alloying with cadmium or magnesium as per the case.

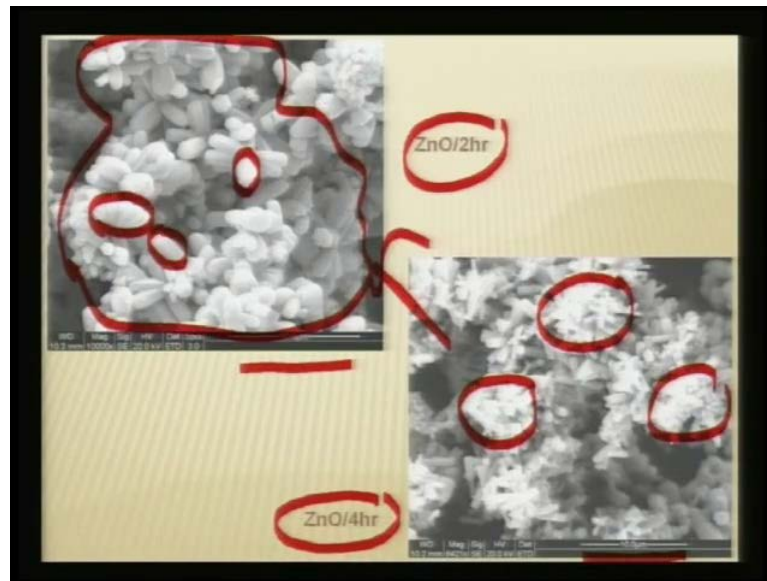
Now, if you try to expose this to one thirty to 180 degree C, you can see at the end of this hydrolysis process, you can straight away get zinc magnesium oxide. This is one of a very clean reaction, because you seldom come with any other side products except of the salts of the metals, which we will go as mineral acid. So, it is a very viable reaction one can resort for, so this way you can alloy with magnesium or you can alloy with cadmium. In this lecture I will specifically try to show you how critical these chemical routes can be in order to hold the photo luminescent properties of this alloy zinc oxide compounds.

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Now, this is a XRD cartoon, which tells us what is the x ray pattern of a commercial zinc oxide, and this commercial zinc oxide shows the hexagonal feature, and typical of this three peak that comes around 30 degrees. Now, if you carefully look at the X ray pattern of a commercial zinc oxide and one produced by microwave polyol route, one would see that almost there is excellent matching between the commercial X ray pattern and the one prepared by polyol route. So, it is a sheer temptation for any synthetic chemist to be satisfied that everything goes well, because you do not see any vivid impurity that is coming out in any other form. Therefore, you would only be glad to use this compound as it is, but if you carefully look at this reaction and look at the sort of products that you are getting.

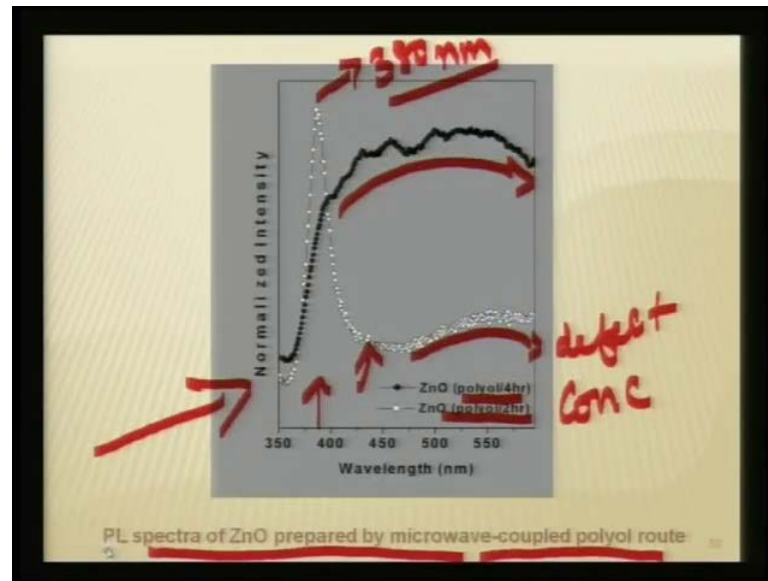
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It is more heartening to see that the zinc oxide that you get by refluxing in microwave chamber, for 2 hours gives this sort of nanopods of zinc oxide material, and you can see that it is produced throughout the SEM picture. Therefore, one can say that these are all tripods or tetrapods of zinc oxide which can be, you can see here these are clustering together, so one can clearly say these are not dispersed nano rods, but they nucleate and keep growing in bunches, nevertheless each of the rods are nearly to the dimension of the others.

So, we can say these are monosize rods, but the same reaction if you extend it for 4 hours, you can see here the morphology of this zinc oxide is changing. And you could also see for the same ten micron scale bar you can see vividly, the size of zinc oxide has changed and also the features are no more similar to what we see in this view graph. Therefore, the refluxing condition and sort of nucleation that is coming out of this process seems to be clearly affecting the morphology of the zinc oxide particles, so what could be the direct consequence.

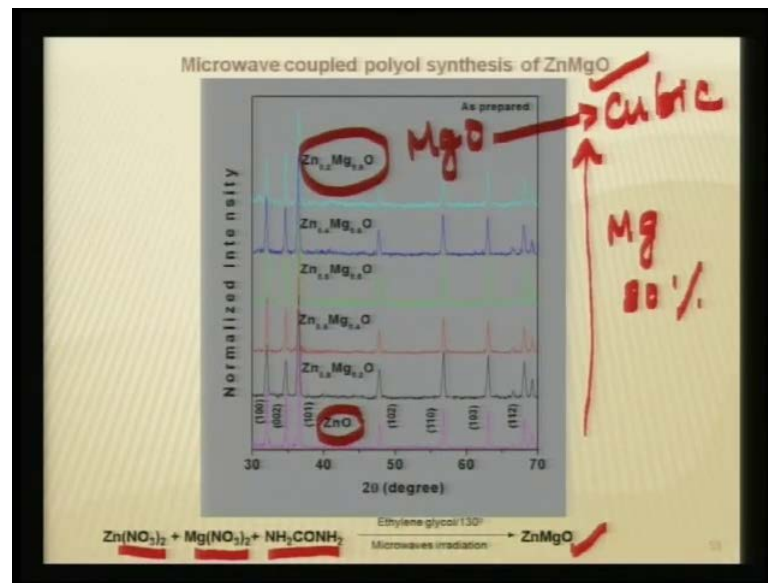
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If you look at the photoluminescence spectra of zinc oxide prepared by this microwave polyol route, one can clearly see that if you try to control this reaction with just 2 hours. You can see that the open circled emission spectra clearly shows that you can get this 380 nanometer emission peak which is critical for zinc oxide. And one should also notice that there is a small hump coming here, and this hump is actually attributed to defect concentration and this is attributed to band to band emission.

So, in two are exposed polyol route, you can clearly say that you are able to get this 380 nanometer emission peak whereas, if you expose this for 4 hours in microwave, you can see that this is the profile that you get. What it means is the band to band emission is totally masked by the defect concentration, so something has to be done and we can also look at what could be the influence.

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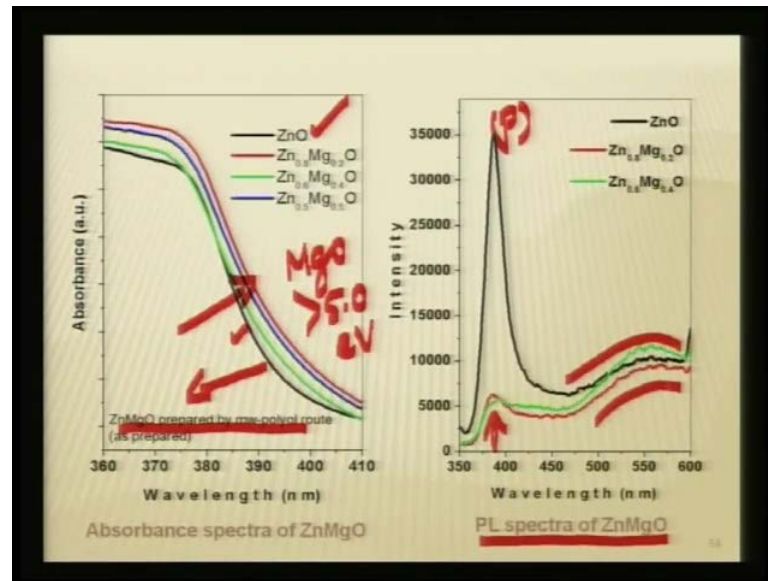


If you are going to dope it with magnesium on the other hand, so this is a microwave coupled polyol synthesis of zinc magnesium oxide, now from zinc oxide with this minimum chemistry, and with this minimum information on the p l, we can try to see what is the effect? When you dope it with magnesium oxide. So, this is zinc magnesium oxide alloy we can call it, and how do you prepare you take zinc nitrate magnesium nitrate you can put urea, urea is actually a base, and then you try to reflux this in ethylene glycol using the voyager instrument, you can get zinc magnesium oxide.

Now, what is happening here is you look at the zinc oxide parent compound, and then you try to substitute zinc oxide up to magnesium doping of 80 percent, up to 80 percent of magnesium doping you would see that zinc oxide is clearly showing the hexagonal pattern. What is important for us to note here for this concentration, there is no signature of any MGO coming, and MGO which is also cubic should actually have come out of this phase.

So, you do not see any trace of MGO coming out of the lattice in other words you are able to substitute up to 80 percent of magnesium, this would actually be a very fascinating stuff, if you talk in terms of x ray powder diffraction. So, any synthetic chemist would just walk away with this experience of having doped 80 percent magnesium oxide, but all is not well, in this case if you try to probe more into the properties.

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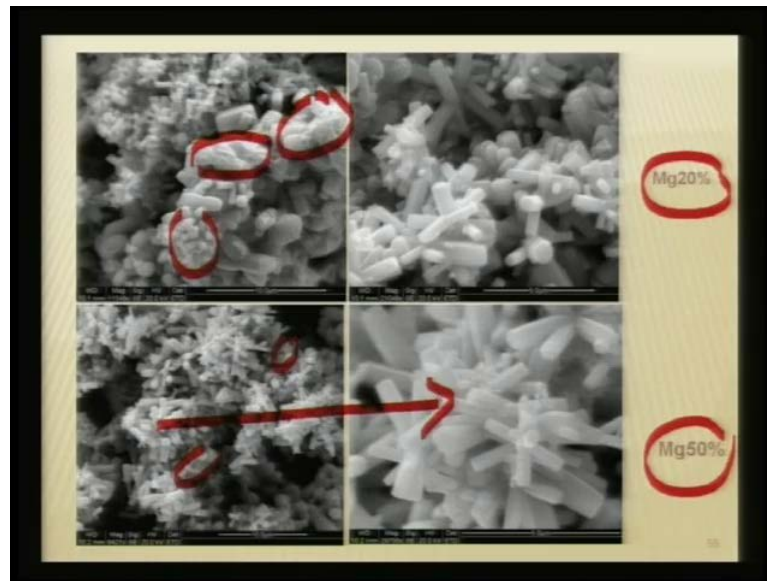


If you look at the absorption spectra absorbance versus wave length for the zinc oxide prepared by microwave polyol route, if you take the as prepared sample here is your zinc oxide, which is the black curve. And the magnesium doped ones are here and you could see here for 40 50 percent instead of the absorption value going down, you see the trend that it is going up. What does it mean, because your MGO has a bandgap which is more than 5 e V, one would expect with more and more of magnesium doping, you should see the band shift towards blue region.

Whereas, you see the negative trend here, but what did we see here in the previous slide, that you do not see any sort of signature for magnesium oxide in the x ray pattern. So, one would be positively looking for a downward trend instead of a upward trend, and this goes further to say what could have happened, if you look at the p l spectra of zinc magnesium oxide.

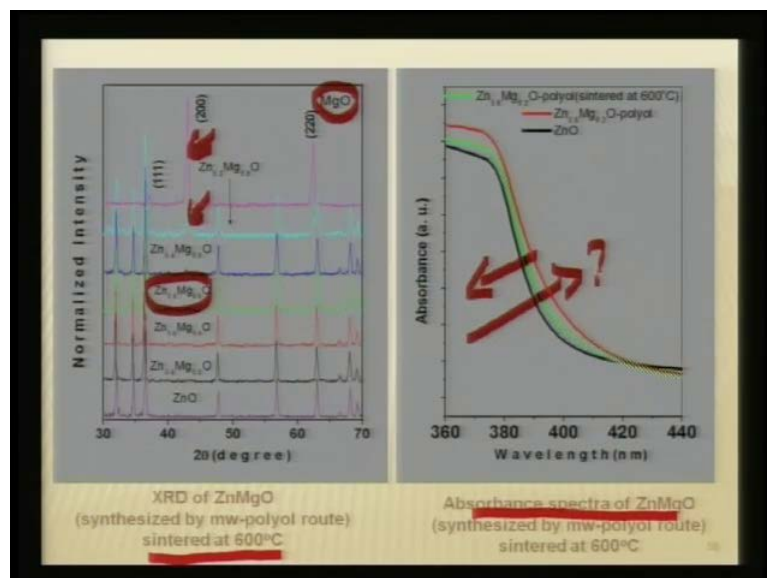
As, you see here this is the parent compound and parent compound clearly shows the 380 nanometer peak with little bit of a defect concentration whereas, magnesium totally seems to kill the band to band emission, so the and also we see the defect induced emission seems to be predominating in this case. So, something has happened either magnesium has quenched the p l or something else is happening because even with 40 percent loading, you are not able to really see what is the influence of magnesium doping or alloying.

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Now, you can see here vividly that there are some clues, as you see from the 20 percent and 50 percent doping, in all this there is some sort of a strange feature in all this particles. You can see these are quite different compared to the rod shaped particles, this is the enlarged version of the zinc oxides rods, but nevertheless you see some other features sticking on to this rods, so you really do not know what is the segregating feature of this zinc oxide nano rods.

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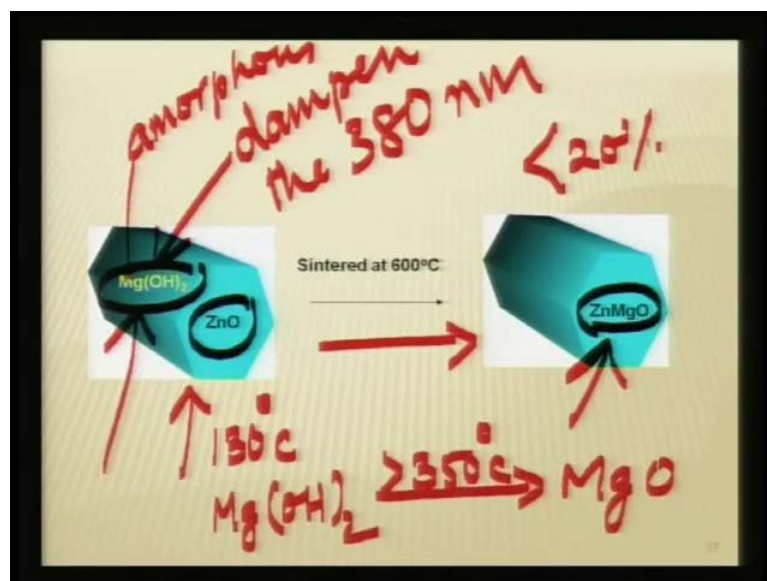


So, if you go further to see what could be the reason, now let us see if we can get any clue by heating those as prepared powders at 600 degree C, so let us take the x r d of zinc magnesium oxide which is synthesized by polyol. Now, whatever we have seen in the earlier XRD spectra is that of the as prepared one, I am going to take those powders and heat it at 600 degree. You would see that magnesium oxide pattern is this, and as you heat it beyond 50 percent of zinc doping, you can see that this signature is propping out which is purely coming from magnesium oxide.

So, if the doping is actually there, then what should happen when you are trying to sinter this compound magnesium oxide peak should not come, that is a clear signature for magnesium doping. But, what we really see is if you heat it even up to a ambient temperature say, yellow temperature we can say at 600 degree you can clearly see that magnesium is coming out. And what is the influence on the p l or absorption spectra of zinc magnesium oxide, clearly shows that there is still upward trend in the bandage instead of a downward trend this is expected, but this is what is happening.

So, what we can clearly understand is that although, there is a clean phase that we can see in the case of X ray within the detectable limit there is something else that is happening other than a clear alloying effect that is going on. Therefore, X ray can actually mislead, when you carefully look at this seems to a phase aggregation that is happening what could be the reason.

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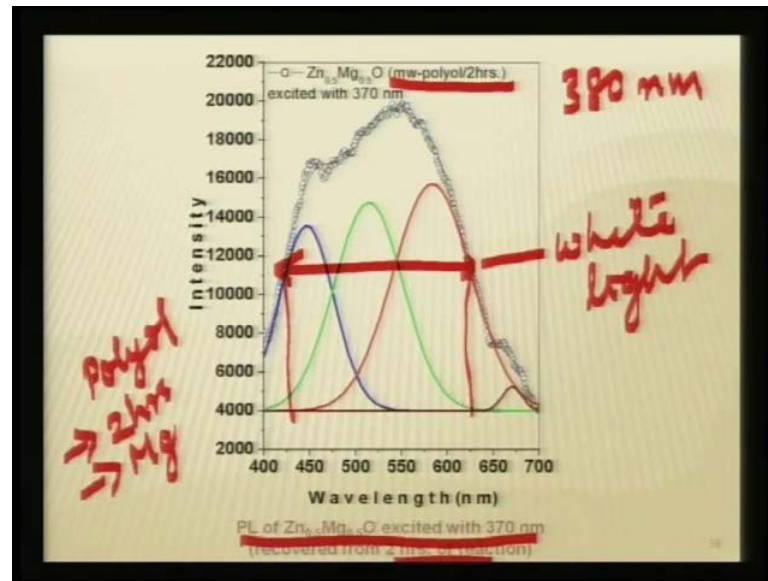
Now, this is a cartoon which gives sort of an idea what must have happened, when zinc oxide is actually getting formed and when it is sintered at 600 degree, the true doping may be happening at this stage. In other words here, you would see zinc magnesium oxide alloy may be forming for the first time, but the as prepared compound may have zinc oxide rods predominately coated by magnesium hydroxide.

Why, because the processing route to prepare this zinc oxide rod is only at 130 degree C which gives you this zinc oxide rods, but if you look at the decomposition temperature of magnesium hydroxide. Magnesium hydroxide decomposes only above 350 degree C whereas, if you take cadmium hydroxide which will come at a later stage cadmium hydroxide will decompose at less than 150 degree C.

So, magnesium hydroxide because it decomposes only above 350 degree C, when you do the polyol synthesis when magnesium nitrate is getting converted to magnesium hydroxide, and that gets just surface coated on zinc oxide. So, it is not exactly doping therefore, the magnesium hydroxide seems to dampen, the 380 nanometer peak that is why you see a sharp decreases in the 380 nanometer band to band h peak, and not only that magnesium hydroxide is not able to suppress the defect free, defect induced emission in zinc oxide rods. So, it is very deceptive why magnesium hydroxide does not show in X ray because this is amorphous phase.

So, in X ray you would see a clear zinc oxide pattern that is coming out whereas, magnesium still remains as a hydroxide and it is not really got substituted, so what we can say is may be less than 20 percent of magnesium doping. Probably, this is zinc magnesium oxide is getting doped whereas, above anything above 20 30 percent you are seeing the magnesium oxide clearly crystallizing out as a MGO phase. So, this is very important clue for us to know, whether we can we can play around with such soft chemistry routes, which are convincingly giving X ray pattern, but in essence we will see that there are lot more chemistry that is going on in this zinc oxides rods.

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Now, as a case if we suppose take that this is achievable zinc magnesium 50 50 alloy as I told you two are polyol synthesized zinc oxide powders are showing very less defect free concentration, and also you get the 380 nanometer emission peak much more. So, we have optimized to hold this reaction only for 2 hours, and if you if you excite this powder, then one can see that the p l of this powder recovered after 2 hours of reaction shows a broad emission.

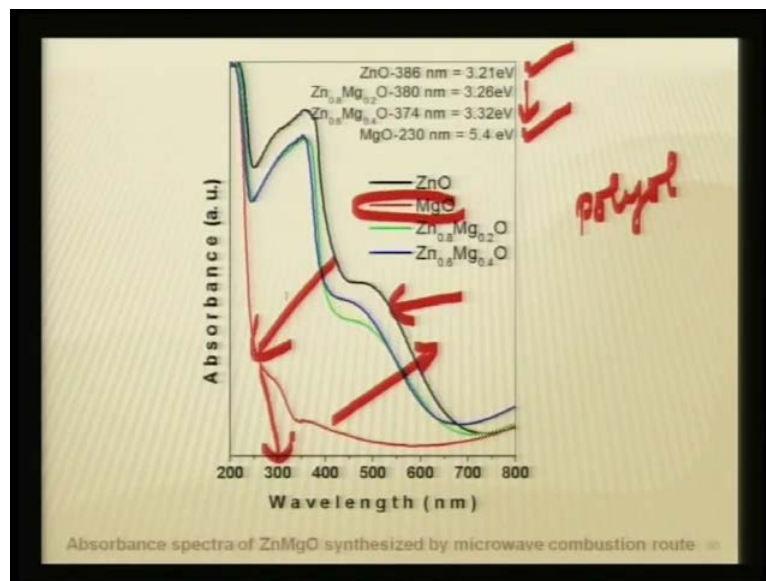
And this broad emission is beyond 150 nanometer, you can see here, so this is roughly from 400 to 600, so for this alloy powder you can see a white light or a broad emission, that is coming. This is not due to defect induced emission you can see the component of the 380 nanometer peak also here, and the broadening that is coming due to true alloying effect.

So, this is very critical for us to understand if I am using polyol synthesis, then what are the governing conditions one anything above 2 hours seems to induce oxygen deficiency in the zinc oxide rods. And also we see that magnesium oxide cannot be doped in into zinc oxide matrix, because it goes through a pathway where magnesium hydroxide seems to remain as a amorphous form coating on zinc oxides nano rods.

magnesium hydroxide, as we discussed in the earlier case, there is a clear substitution may be up to 30 40 percent of magnesium. And this is very important because as I told in the beginning of the previous lecture, doping zinc oxide with magnesium by ceramic route you cannot achieve more than 4 percent of magnesium, but this is a exothermic reaction, where you can try to stabilize metastable phases.

Therefore, even though you are doping 30 40 percent of magnesium you can successfully dope that much amount of magnesium into the zinc oxide lattice, but there is a limiting effect to that you cannot rely on the same method to dope more than 50 percent. So, this is one of the catchy information that we can get out of this combustion approach, but one should see what is the influence? If truly magnesium oxide is doped then you would see the absorbance feature, UV visible spectra and the p l spectra being affected.

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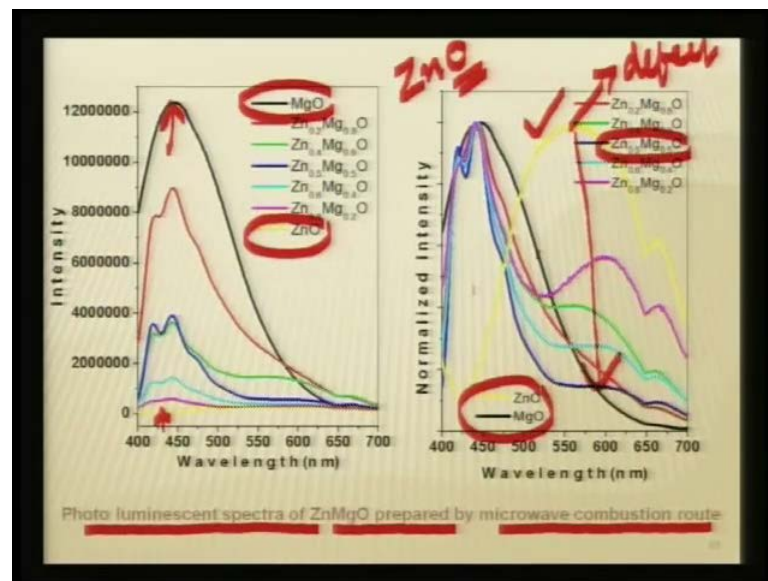
So, what could be the consequence if you look at the absorbance spectra of zinc oxide synthesized by microwave combustion route, you can see here that zinc oxide is here, which is a wide bandgap semiconductor. And magnesium oxide which is narrow bandgap semiconductor is pushed down, and this is a expected trend compared to the microwave polyol route, you can clearly see the absorption edge is pushed to the UV range.

So, what we can clearly say is magnesium is getting doped, because there is a trend which is as expected and I want to again emphasize this point that in polyol route, it is

the approach is this way the bandgap the band edge is shifting towards the red. And therefore, we concluded that there is no proper substitution of magnesium whereas, in microwave combustion case, we see because of the exothermicity of this reaction and also, because this is a instant combustion reaction, and also because it is a fast quenching reaction.

You are able to principally stabilize a metastable phase, and we also seen we have seen in the previous cartoon that the x ray is as convincing, as the polyol route, but you can see the absorbance feature completely different from the other case. So, you can see on a the zinc oxide which has bandgap of 3.2 magnesium oxide having bandgap 5.2 exactly matching, and then when you dope magnesium oxide, you can see that there is progressive shift in the bandage, although this is not a very convincing trend. So, this may not be a very pure or a very convincing doping, but nevertheless you we can be convince up to 20 30 percent we are able to push magnesium into the zinc oxide lattice.

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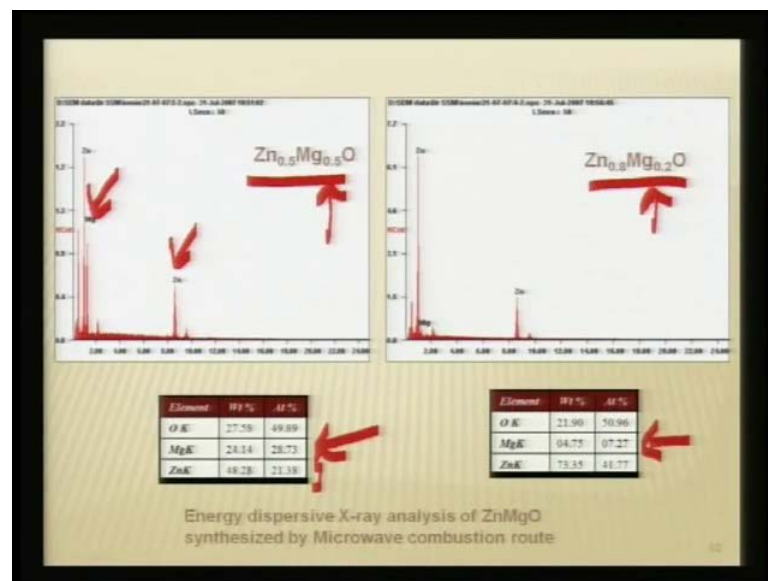


Now, this is the consequence of on the p l the photo luminescence spectra of zinc oxide prepared by microwave combustion route clearly shows the following trend, what is the situation. If you take magnesium oxide as expected magnesium oxide is showing the p l feature here, but once you start doping zinc in this case, zinc oxide losses completely the band to band emission, neither it shows the defect free concentration.

Whereas, if you take the p l spectra of the reverse doping effect for example, if you take the magnesium oxide here, and then if you take zinc oxide, you can clearly see zinc oxide is totally dominated by the 550 nanometer emission, which is the defect induced emission, this is due to defect. So, in microwave we are able to achieve a larger doping of magnesium into the zinc oxide lattice, but we are completely missing out on the oxygen concentration, and this defect when we say is mainly coming from the oxygen defect.

So, more and more of oxygen defect induced emission is actually dominating zinc oxide case, but nevertheless one can see, when you try to dope it with magnesium using combustion reaction you can see clearly that this defect induced concentration is nearly vanishing. For example, if you take the case of a 50 percent of magnesium, almost you do not see any defect induced concentration that is pronounced, and the peak is actually shifting more towards 380 nanometers, clearly showing that magnesium can be alloyed with zinc oxide using microwave combustion route.

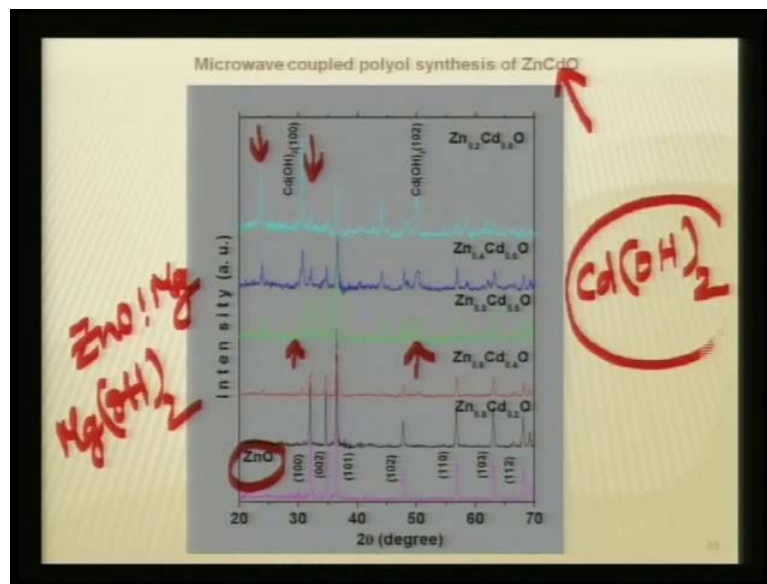
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We can try to evaluate, if this is true and if you take the case of 50 50 alloy or 80 20 magnesium zinc oxide alloy, you can clearly see that there is a good match between zinc and magnesium. Whereas, if you look at the peaks are there, but if you try to quantify in a semi quantitative way, you can see the proportion of magnesium and zinc are not the same as you expect from the combustion reaction.

Therefore, there is some limitation to the doping effect, in case if you are thinking of a 20 percent doping you can see only 8 percent is doped, if you go for 50 percent doping you see roughly 30 percent of magnesium is doped. So, there is still a inconclusive issue revolving the relative stoichiometry, but nevertheless we see this is the maximum that we would go may be up to 30 percent of magnesium can be just doped outright, because of this exothermic process.

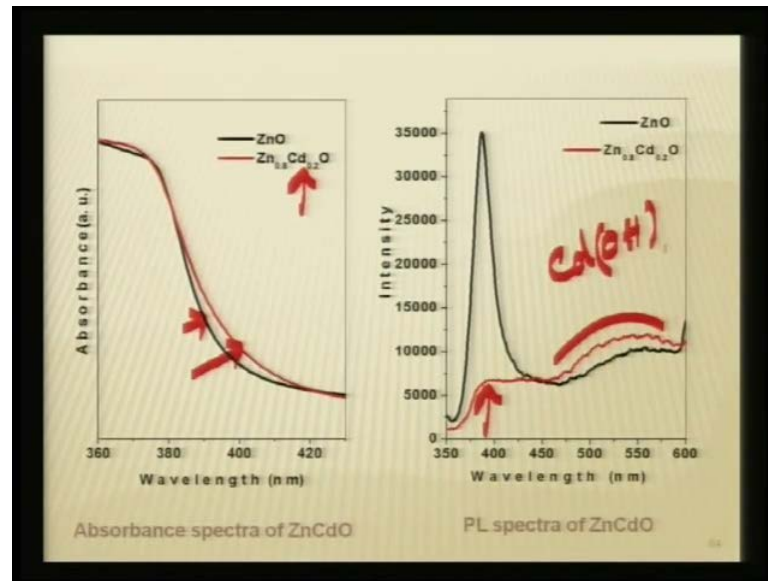
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Now, another case that I would like to press forward is microwave coupled polyol synthesis of zinc cadmium oxide, now in this case we are actually looking at cadmium instead of magnesium doping. And what we see here again a clear phase for zinc oxide and as we continue to dope zinc cadmium, there you can see some peaks are coming here, and there is another peak which is starting to come here, right from say 40 percent of cadmium. What does this amount to this particular feature that is you see here, this is due to cadmium hydroxide.

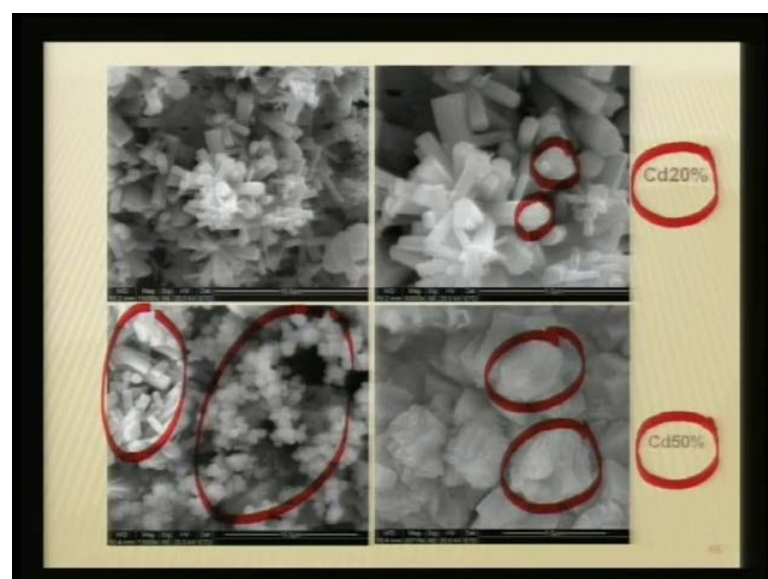
So, just as in the case of zinc oxide magnesium doped with magnesium, we encountered the issue of magnesium hydroxide, which is as a amorphous phase just remains as a amorphous coating on zinc oxide. We also see the same situation for a polyol synthesis of zinc cadmium oxide, so here again the issue of hydroxide seems to be a limiting factor, but if you look at the u v visible spectra this is your zinc oxide.

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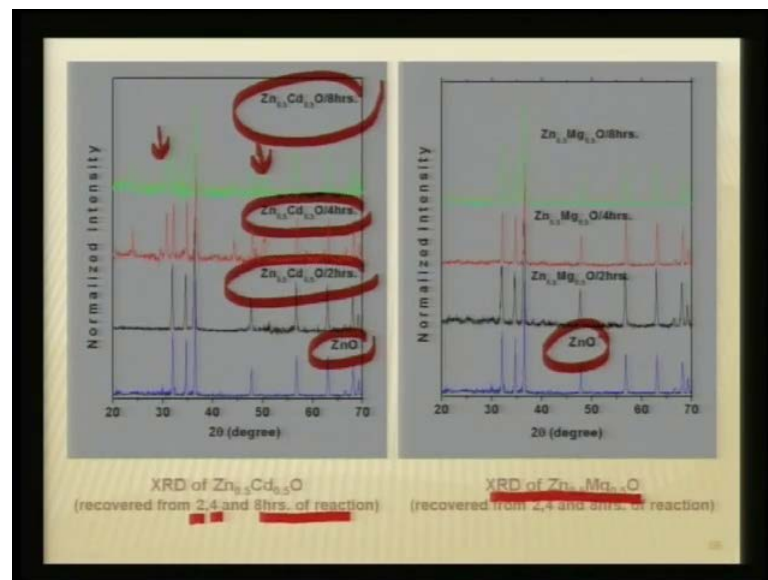
And the cadmiums doped one slightly shows a change, but this is as expected because cadmium is a low bandgap semiconductor therefore, when you try to alloy this compound, you should see a red shifted bandage. And that seems to happening nevertheless this is not more this is not pronounced, because even with 20 percent you are not able to push it significantly. And the p l of this cadmium alloy powder seems to have the same effect like that of magnesium oxide where your band to band emission is almost killed, and surface defect induced emission seems to predominate this would actually happen mainly, because of the cadmium hydroxide coating that may be present.

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Now, if you look at the SEM feature of the 20 percent cadmium doped and 50 percent cadmium doped compounds, you can clearly see the effect of cadmium doping, when you go to 20 percent. You see a minimal effect and all these are hexagonal rods of zinc oxide which is propping up, but when you go to 50 percent you see this rod like feature is somewhere here, and you see this sort of features predominating. So, if you just try to maximize or enlarge this portion, then you can see this sort of features coming which seems to be predominately either segregated cadmium oxide or cadmium hydroxide which is actually precipitating out. So, what do we understand, that the cadmium hydroxide, sorry cadmium oxide seems to be there, but it is silently killing the p l effect of this zinc oxide nano rods, so alloying in this case is not really happening.

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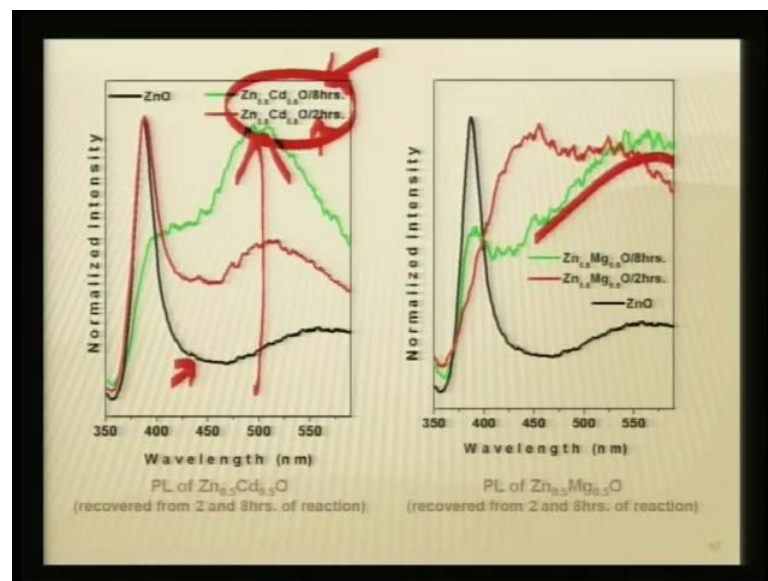


Now, what would happen if you try to take this powders from polyol chamber, if you try to recover this at 2 4 and 8 hours, you can see here this is zinc oxide, now if you try to expose this to microwave polyol route at 2 hours you clearly see a clean feature that of zinc oxide. Whereas, when you keep going to 4 hours and 8 hours you see this hydroxide feature which is propping up, this hydroxide features are coming out. What does; that means, this seems to a kinematic growth and with more and more of nucleation, your cadmium is not actually getting doped into zinc oxide. Whereas, the cadmium hydroxide first starts nucleating and then it starts building up into a crystalline matrix and therefore, along with zinc oxide what is actually growing is the cadmium hydroxide particles, which are actually coming out as a nucleated features.

So, more and more of cadmium hydroxide gets nucleated then they crystallize as a crystalline phase, now these are the XRD features of magnesium doped ones, you would see here 2 4 and 8 hours. If you try to take the powders out and compare with the X ray pattern of zinc oxides, you do not see any feature of hydroxide coming, so in one case magnesium hydroxide just remains as a amorphous phase just coating the zinc oxide rods and killing the p l effect.

Whereas, in the case of cadmium hydroxide same exposure to polyol you see cadmium hydroxide coming out as a secondary phase, which is having it is own nucleation process, so these are both kinematically controlled as well as they are thermodynamically controlled. So, this can clearly give us clue as to how the whole process evolves and how the substitution takes place, so X ray and p l and absorbance spectra can prove as a very critical governing feature, for understanding how this alloying effects can happened.

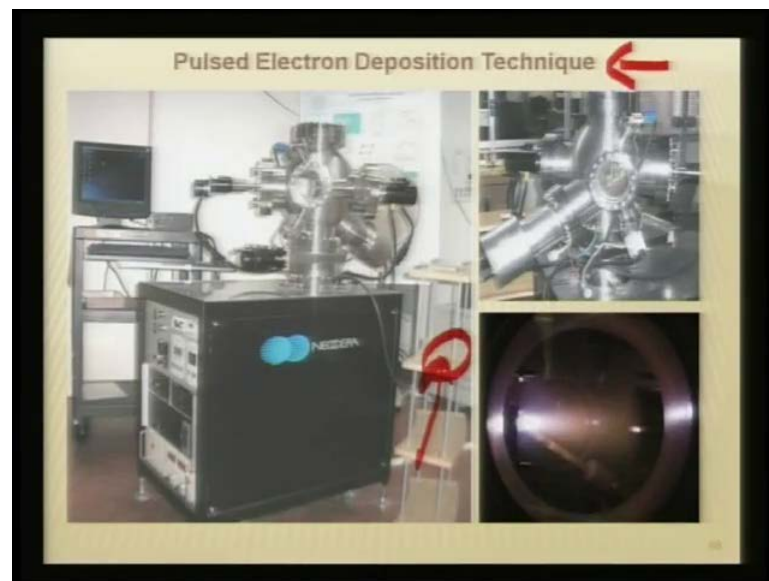
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Just I will close with few more graphs if you take the 2 hour and 8 hour synthesized one which; obviously, this one shows no cadmium hydroxide impurity whereas, in this case it shows hydroxide impurity. You can clearly see this is your zinc oxide and with more and more of exposure to polyol, the defect induced emission is dominating compared to the band to bandage emission.

So, this clearly proves that the surface of your zinc oxide rods are very, very critical and same is true for magnesium doped once, the two are synthesized one shows more features around 380 nanometer, but then it is dominating. Whereas, in the case of 8 hour you see the defect induced concentration is dominating much more, so clearly proves the point that a kinematic approach is very critical or the way they zinc oxide grow in this polyol synthesis is very critical.

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Just with two more slides I would finish suppose you try to completely use a physical vapor deposition technique, as I have already discussed about this technique in module 3, this is a very viable route. If you take zinc oxide commercial powder or any other powders synthesized by the wet chemical routes, and you can try to make films of zinc oxide using this technique, here you are actually trying to house your zinc oxide palate and you are trying to oblate this palate with a pulse electron beam.

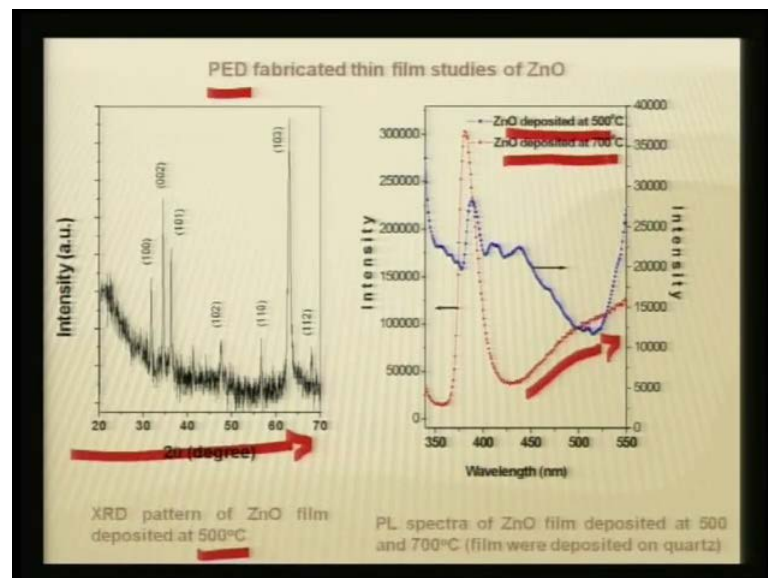
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Maximum Discharge Capacity	20kV
Electrical efficiency	30%
Stored Energy	3J
Gas Pressure	~30mTorr
Discharge Time	~80 – 100 ns
Repetition rate	1 – 10Hz
Electron energy in the beam	≤15keV
Electron Current	1.5kA
Electron beam diameter at the target	~ 2-3 mm
Beam Current density	≤ 10 ⁵ A/cm ²
Power in the Beam	≤ 15 MW
Power density in the beam	≤ 500 MW/cm ²
Maximum Range of electrons	0.4μm

Typical Pulsed Electron Beam Parameter

Now, you can try to make zinc oxide films, and these are the typical PED parameters that one can look for.

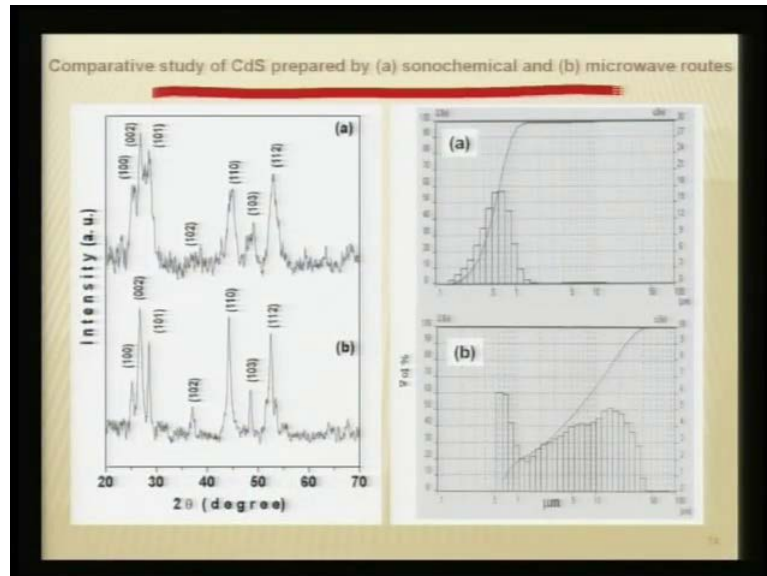
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And what would happen, this is the X ray pattern that you get out of a zinc oxide film that it is deposited at 500 degree C, now you can clearly see that the zinc oxide prepared at 500 C using a PED chamber shows a very sharp emission intense 380 nanometer peak. Although, the surface defect induced emission seems to be still propping up, if you go to 700 degree C deposited one you can clearly see that this emission peak is totally killed.

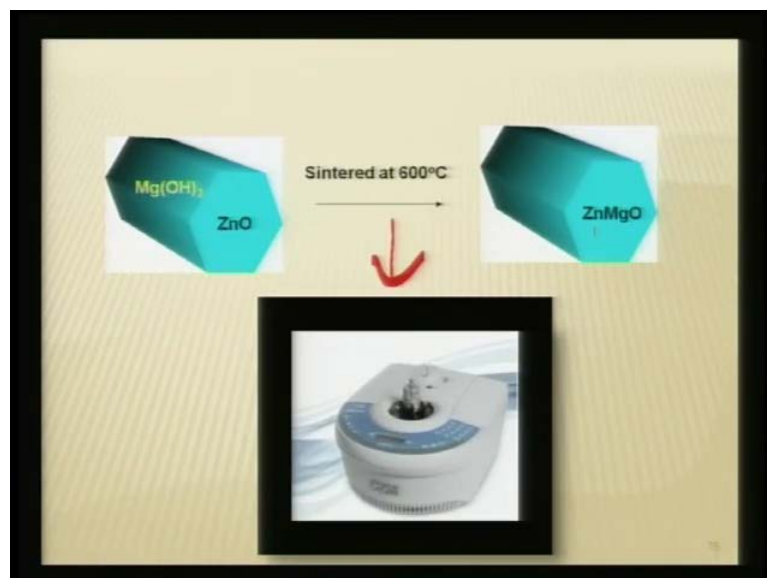
Therefore, the physical vapor deposition technique also has a controlling feature it does not really promote only the band to bandgap, but there is a destroying feature.

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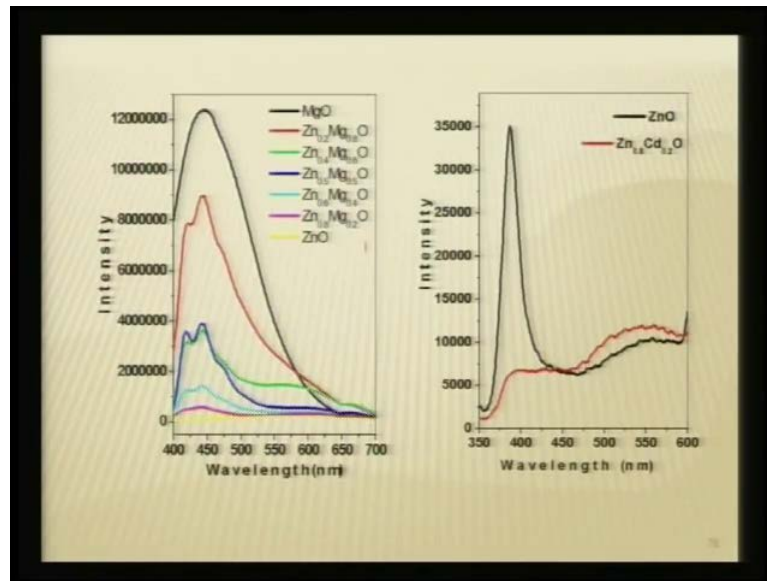
So, with the last slide that I want to show you I have shown in the last two lectures, how quantum effects can be governed by different chemical routes.

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And I have also shown in today's lecture, how microwave polyol route can be used to understand the alloying effect and its influence on p l.

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And also I showed how combustion route can help in preparing this compounds, so the wet chemistry route seems to have a lot of consequence on the photo luminescent properties of this wide band gap semiconductors.