

Materials Chemistry
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Module - 7
Lecture - 3
Perceptions and Projections

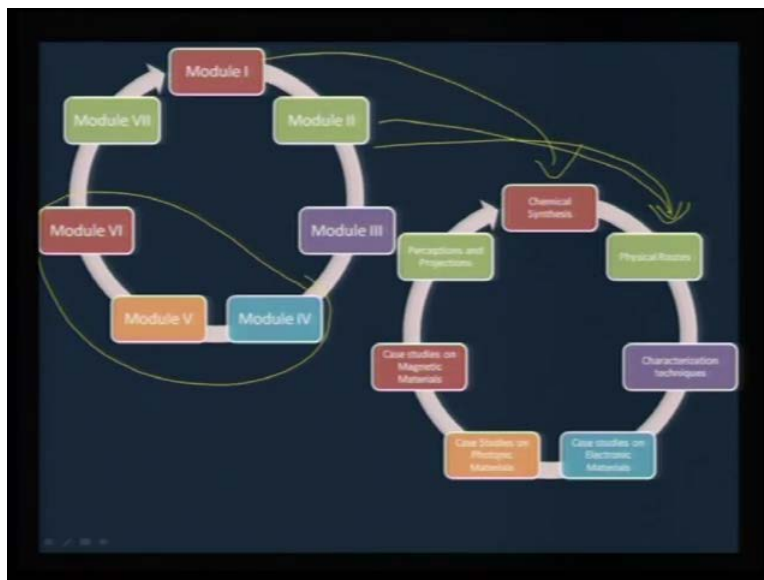
This is the last lecture in the materials chemistry course, which I have titled as Perceptions and Projections. So far, we have looked at various aspects of materials, and the course has been divided mainly into two parts. One to do deal with different approaches to make materials, and how to characterize them, and the other major part has been to study in terms of it applications in photonics, electronics, and in magnetism. In the first few modules, we have stressed on the need for chemistry routes, and how chemical principles can be applied to make materials, and specially nano materials in bulk form and in thin film forms. And also as a single crystals, how materials can be made using soft and unconventional wet chemical routes.

In the second part of this course, we have mainly looked at topical studies, basically on magnetism and on electronic properties and on photonic properties. I would like to quickly recap in this lecture on some of the essential things that we touched upon, as a projections in the very first lecture I had mentioned, what we would be studying in this course. I just want to recap on all those items or issues that we have seen so far. And also in between I will try to project some of the crucial research, evidences that are needed in materials chemistry, which will deeply affect the applications. So, let me quickly run through some of the slides, which will give us a quick recap of what we have seen in the last 30 odd lectures. And then we will see how we can look forward to extending some of these materials which has shown potential applications.

To start with we listed several modules that would comprise this course, module 1 to 7 and each of this module was particularly designed to drive home theme. And module 1 was mainly highlighted in order to bring about the issues related to chemical synthesis, and we have seen over half a dozen of chemical routes. And we will also quickly touch upon some of the chemical principles that we have learnt in this course. And in module 2 we have seen some of the characterization techniques, which are inevitable to elucidate this structure of new and known materials that we prepare. Chapter 3 is about the

characterization techniques, and chapter 2 we have looked at the physical routes that is thin film routes. And in 4 to 6, we have looked at the several case studies on different materials.

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As I told you that materials chemistry, and the need for studying materials chemistry as a course; mainly because, it is integrating almost all the branches of chemistry, physical, organic, inorganic and polymer chemistry, all this together put together gives a very good flair for understanding materials world. Therefore, materials chemistry almost acts

like a hub to bring several researches to a common platform. Therefore, there is no more demarcation between physical organic or inorganic that is one of the very, very important influence of materials chemistry.

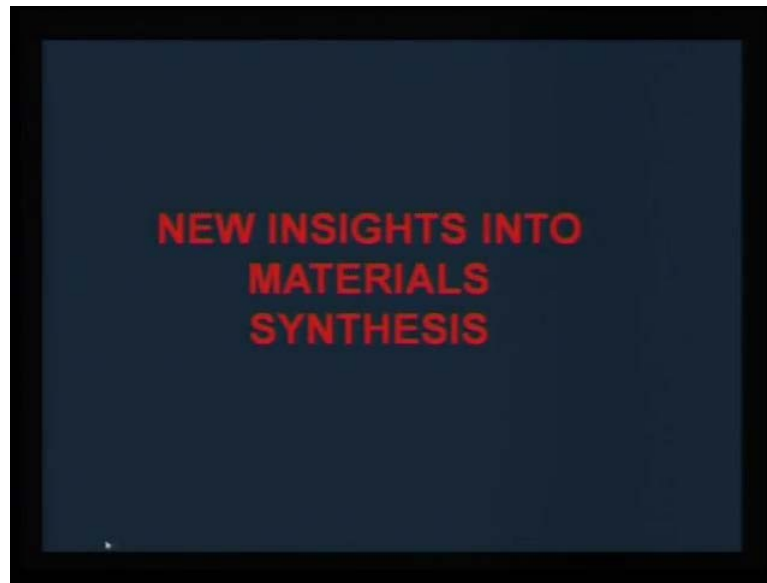
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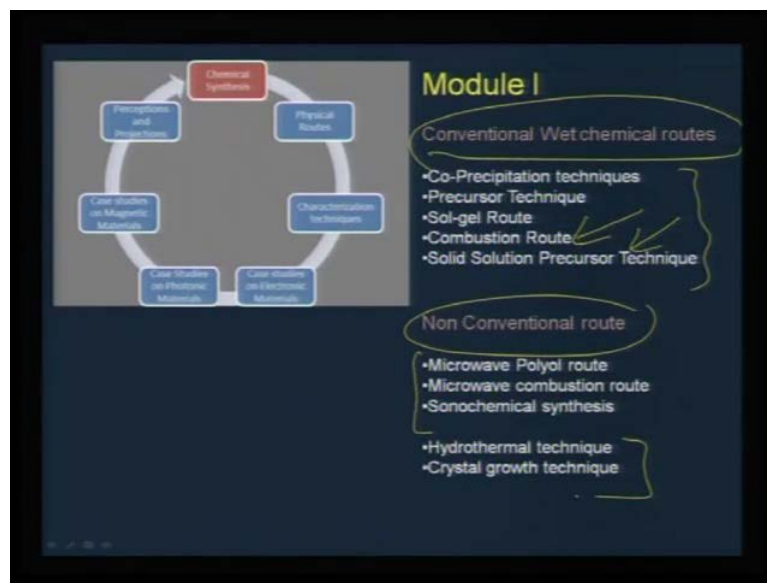
And not only within the branch of chemistry, but around the sphere of chemistry, we have seen technology, material science, biology and physics all merging together with materials chemistry, principles or activities. And therefore, it has lead to a very a crucial role for materials chemistry to bring many branches of science and engineering together. Therefore, it has been a interesting journey for us to see, how so many groups can merge to attack new materials which are useful for functional applications. One of the few in sites that we have derived from materials synthesis that is in module 1 is to understand new material principles.

Specially those which are not known to a common chemist, and in that we have actually looked at conventional wet chemical routes, and non-conventional wet chemical routes. And the conventional one most of us are, obviously exposed to, but here also I have brought in number of discussions or number of examples on combustion route, which is not well known, but still it is one of the most popular emerging tool in a wet chemistry routes.

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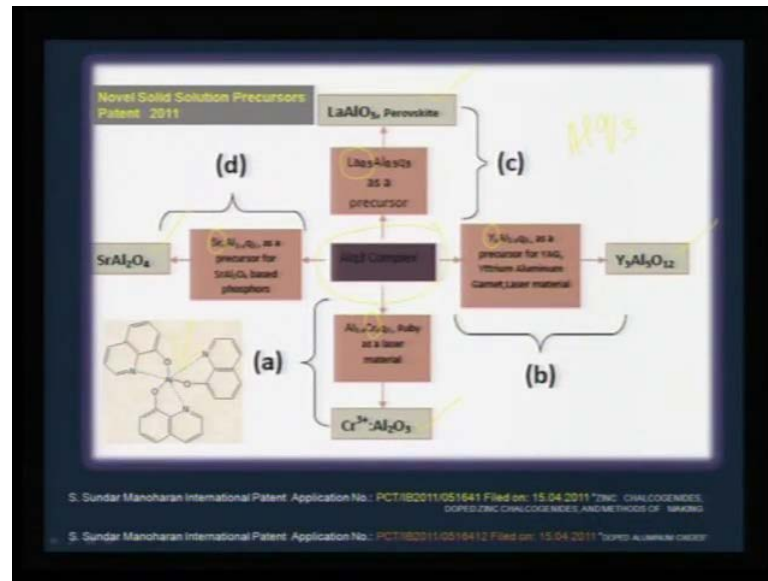


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And also I have discussed with you about solids solution precursor technique, which is one of the very useful approaches to make materials in a very quantitative way. And I will also show some of our recent results to impress upon the solid solution precursor technique, why it is going to govern the materials chemistry field for a longer time period. In non conventional route we have emphasized on microwave based research, and using sonochemistry which is a secondary effect on making materials, it is not a direct interaction, but we use the secondary effect to make nano materials.

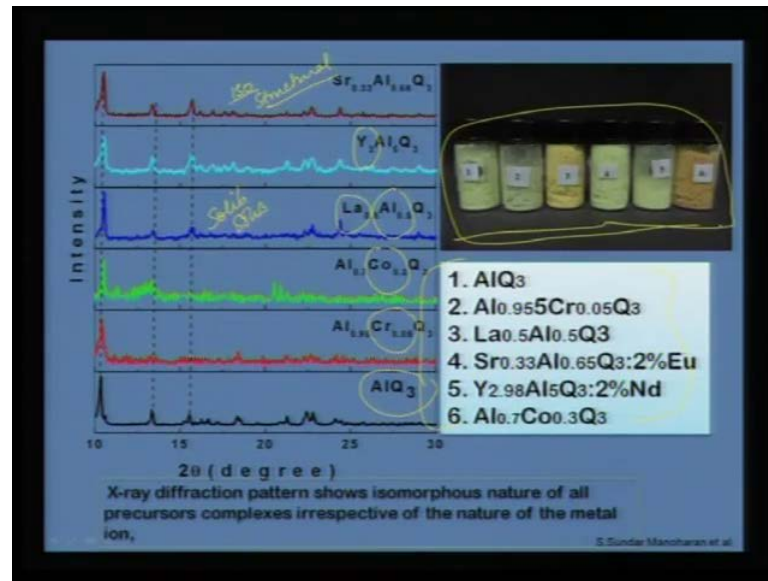
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And we also, I have looked, so far into other non conventional routes that is hydro thermal, and crystal growth techniques. We will look at one of the example that I showed in the precursor route, in the early part of this course that is on solid solution precursors. And this was one of the view graph that I showed to highlight, how using a single molecule we can diversify our area of interest. For example, start with a aluminum q 3 complex which is a well known organic semi conductor compound, which has a very high mobility, very high photo luminescence.

But, using this compound as a base material, merely doping some amount of lanthanum or some amount of chromium or strontium or yttrium; you can actually get into diverse areas of application where you can prepare LaAlO_3 , which is a very good template or single crystal that is used in thin film industry. We can use the same approach to prepare YAG, which is a laser material, ruby which is a laser material and strontium aluminate which has a phosphor material. So, just start with a organic molecule, but you end up with several inorganic photonic materials that is the power of the solid solution precursor route, and we have shown using aluminum q3.

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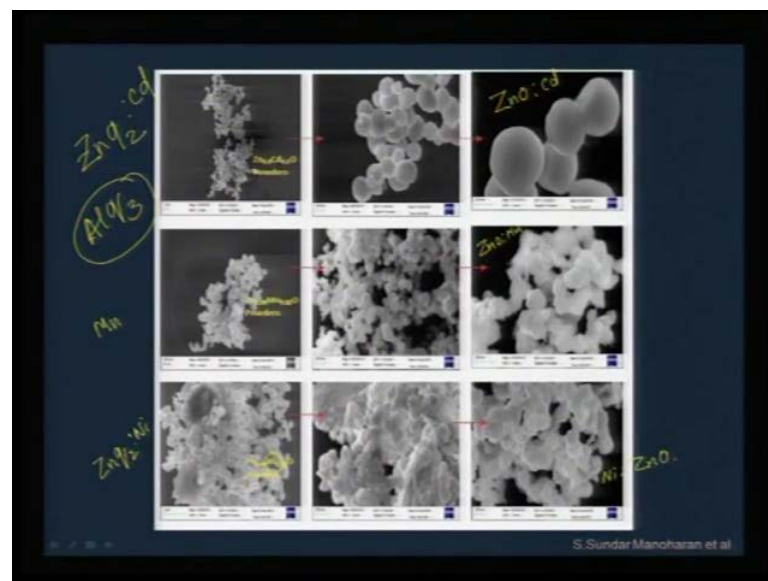
Also we have emphasized in this novel solid solution precursor, what is fundamental to this approach, we have shown in AlQ₃ or chromium doped, cobalt doped, aluminum, lanthanum doped or yttrium doped. Once the main emphasis there is the solid solution, and the solid solution is nothing but, those which show same X-ray crystallography or same crystal morphology. In other words, we talk about a isostructural situation, so if all the components are showing isocrystal structural nature.

Then it is possible for you to put any amount of different metals, as long as you can preserve the same crystal symmetry, and we have shown how all this can act as precursors to get a range of compounds. And as you see all this precursors before they are calcined to the respective oxides, they are all photo luminescent and such precursors have been reported for the first time. And we also have shown in the previous example, how this sort of technologically important oxides can be prepared out of this.

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Solid solution	Corresponding oxide (calcined at high temperature)
AlQ_3	$\alpha\text{-Al}_2\text{O}_3$ (900)
$\text{Al}_{0.95}\text{Cr}_{0.05}\text{Q}_3$	5% Cr: Al_2O_3 (1000)
$\text{Al}_{0.7}\text{Co}_{0.3}\text{Q}_3$	30% Co: Al_2O_3 (1000)
$\text{La}_{0.5}\text{Al}_{0.5}\text{Q}_3$	50% La: Al_2O_3 (1300)
$\text{Y}_3\text{Al}_5\text{Q}_3$	3% $\text{Y}_3\text{Al}_5\text{O}_{12}$ (1300)
$\text{Sr}_{0.33}\text{Al}_{0.66}\text{Q}_3$	33% Sr: Al_2O_3 (1300)

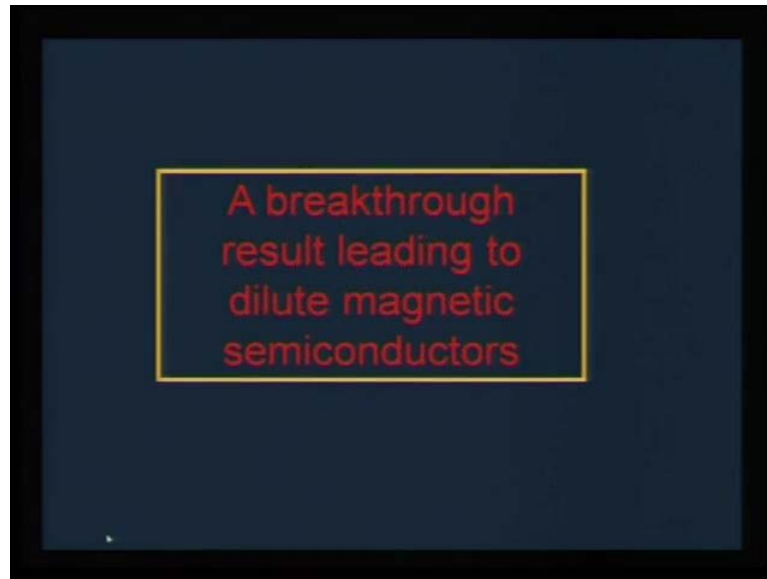
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We have also shown in one of the earlier lectures, how zinc q 2 can also be used, this is something similar to AlQ_3 , what we have seen in the previous two slides. Zinc q 2 is a potential precursor, again using the concept of solid solution, we can dope cadmium in Znq_2 , because cadmium q2 and Znq_2 are isostructural. So, if you put one in another you do not see any phase aggregation, and this can act as a very good precursor for cadmium doped zinc oxide.

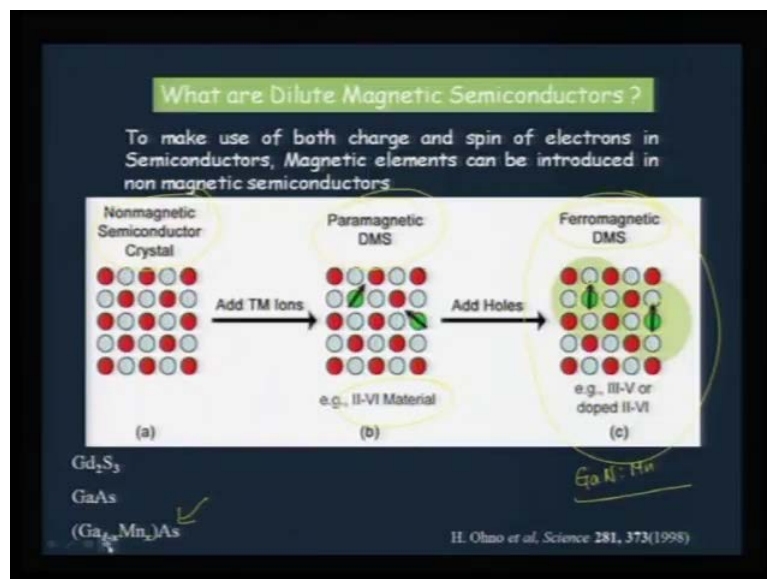
And similarly, we can start with zinc q 2 and dope with manganese and we can get zinc oxide doped with manganese. I will come in next few slides to show you some of our own recent result, and emphasize why this solid solution precursor route is going to go a long way. And similarly, we can prepare Znq2 with nickel doping and you can get nickel doped zinc oxide, which is also ferromagnetic in nature.

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A break through result leading to dilute magnetic semi conductors, we can derive from this solid solution approach.

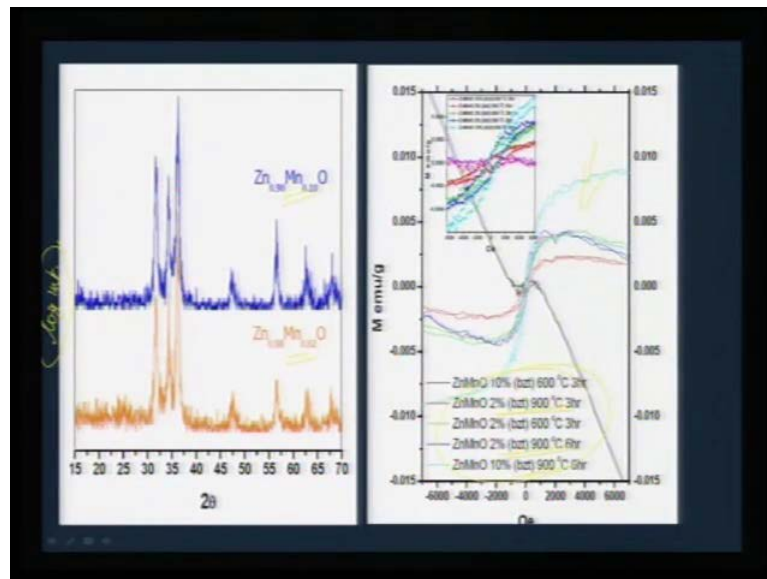
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And as you would see in the next few slides that this is the dilute magnetic semiconductor that we are talking about, this is an ordinary semiconductor. And when you put paramagnetic ions, then they show a paramagnetism of this order which is usually seen in 2, 6 semiconductors. But, once you add holes to it, then you can ferromagnetically order these spins, and as a result you can actually get a ferromagnetic signal in gallium nitrate doped with manganese.

So, this is a fast emerging one, and another suitable example is manganese doped gallium arsenide, these are turning out to be dilute magnetic semiconductors at room temperature. Now, we have also taken the same challenge, but we want to incorporate these magnetic impurities exactly in the zinc site in ZnO.

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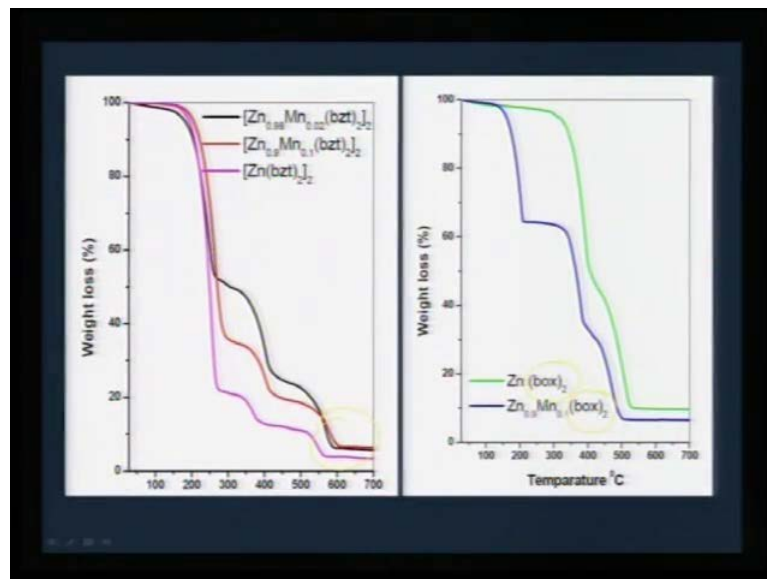
And using the solid solution precursor as you would see here, we can try to get a very highly stoichiometric compound in the form of Zn, manganese oxide, which is 2 percent manganese or 10 percent manganese. And one important thing is this is a log intensity plot that is why you see too noisy, when you plot it in log intensity even smaller impurities can be highlighted. And you can see very well here that there is no extra peak even in log intensity, which means even at 10 percent you do not see any phase segregation of manganese.

And this is very important, because this is the first time ever we are able to see such a trend in manganese doped zinc oxides, reported either by chemical routes or in thin film

form. Now, the most important feature that I want to draw your attention to is this magnetization versus field plot. And for the first time we are seeing any sample that is heated above 600 degrees, or say at 900 degree C is showing a very strong ferromagnetic signal. It has never been reported in any of the earlier literature reports, where magnesium doped zinc oxide shows magnetic behavior at room temperature for any compound that is heated beyond 700 degree C.

Why because, it is a impurity which gets transformed beyond 700 and therefore, only that impurity induced phase is active below 700 degree C. So, for the first time we are showing that, if you take a precursor route it is possible to carefully dope manganese in the zinc site without any phase aggregation, as a result we can stabilize a dilute magnetic semi conducting phase. And this is one of the very novel result that would take this wet chemistry route to a long way.

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What is the beauty and why we are able to stabilize such a magnetic phase, even though you heat it up to high temperature is the simple analogy that you can get out of a thermo gravimetric analysis. As you would see here, all this bzt is a benzothiazole based compound, so if you are actually doping this and you are thermally decomposing, you can clearly see that the decomposition is extended up to 600 degree C, were the manganese oxygen bond seems to be much stronger than zinc oxide bond. As a result as

long as manganese oxygen bond is there, it is not going to allow any other secondary phase to form.

So, this simple thermo gravimetric analysis clearly gives an account for why a delayed formation of impurity phase is affected, and this is a simple procedure by which we can effectively dope magnetic impurities into a semi conductor. As you would see here ((Refer Time: 15:10)), we can even try with other substitutions or other ligands, a similar trend is noted therefore, this is for the first time we are documenting that a solid solution precursor can be used to unravel this mystery. And we also have introduced several other wet chemical routes, and non wet chemical routes or non conventional routes. One of the thing that we have highlighted is the use of sonochemical synthesis, and we have already discussed it is cavitation process which gives a hot spot, and this hot spot is able to stabilize nano materials.

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Module I

Chemical Synthesis

Physical Routes

Characterization techniques

Growth of Electronic Materials

Growth of Photonic Materials

Growth of Magnetic Materials

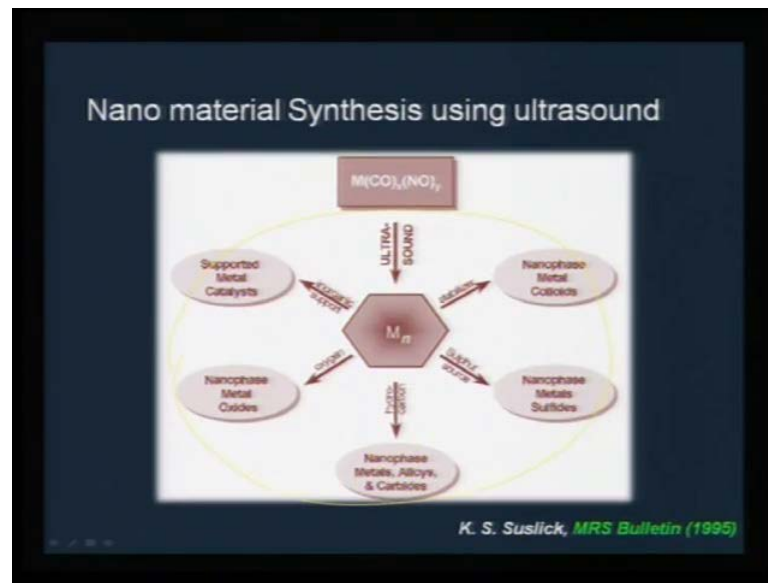
Conventional Wet chemical routes

- Co-Precipitation techniques
- Precursor Technique
- Sol-gel Route
- Combustion Route
- Solid Solution Precursor Technique

Non Conventional route

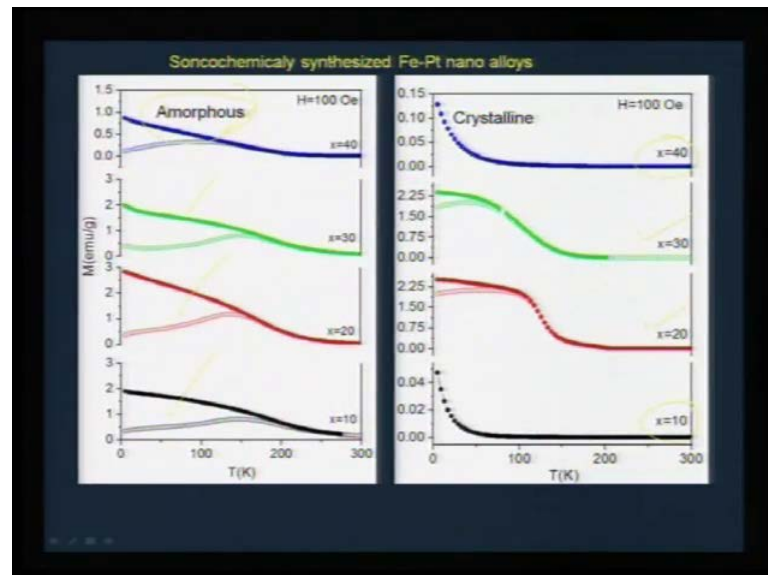
- Microwave Polyol route
- Microwave combustion route
- Sonochemical synthesis
- Hydrothermal technique
- Crystal growth technique

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And through this ultra sound effect, we can make a host of nano materials which can be rendered in different form, either as a sulphide or as a oxide or as a support on a catalyst surface. We can realize this is in many forms provided, we start with the right combination and conditions.

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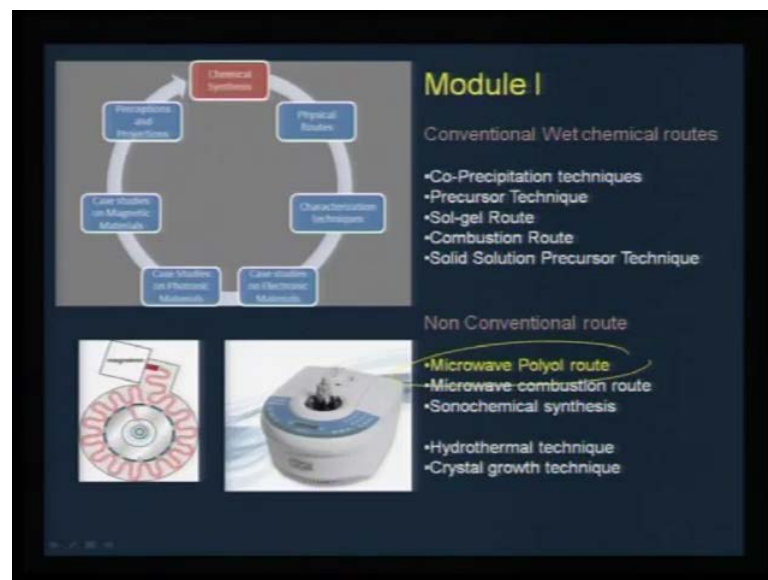


One highlight of this sonochemical process is that, you can prepare everything in amorphous form which means, you can go down to 1 to 2 nanometer in size and because of the strength of able to prepare nano materials in such a small dimension. What we

have seen is, what is observed as a magnetic phase in crystalline situation, were 20 and 30 percent of platinum doped alloys, are supposed to be ferromagnetic whereas, this is supposed to be non magnetic in crystalline phase.

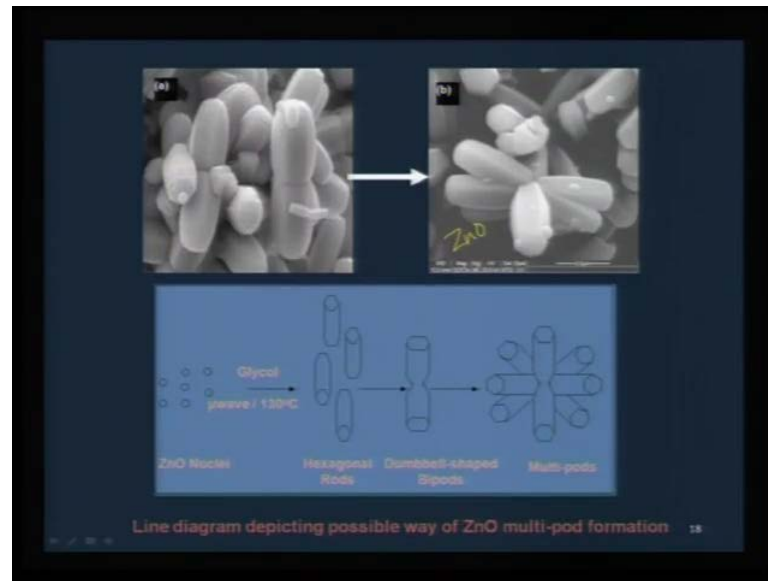
But, in amorphous we are able to see that in all cases, it is turning out to be a ferromagnetic, so this is completely confusing the predictions rendered by crystalline phases, or by equilibrium phase diagram. So, the sonochemical approach seems to hold lot of potential to prepare materials which cannot be ferromagnetically ordered at room temperature. And this is mainly because of a unusual interaction of the sound waves with matter.

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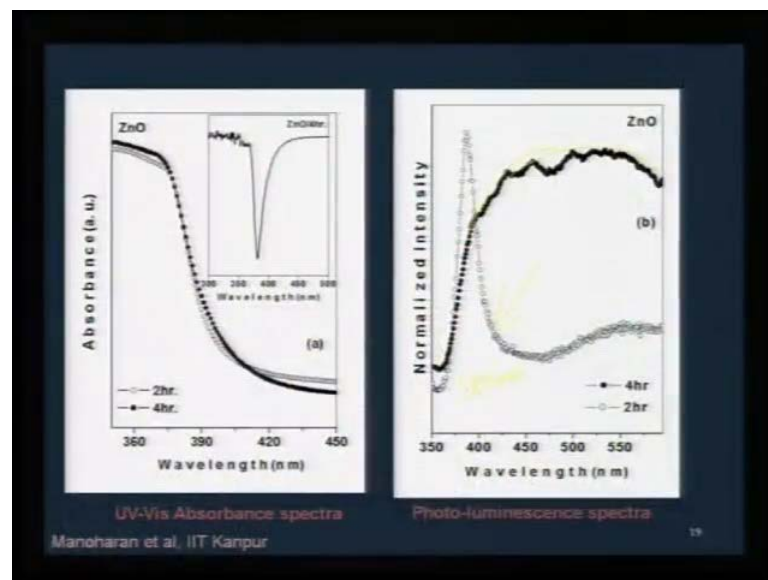
Therefore, we foresee that lot more excitements are in store using sonochemical process; we have also highlighted the use of microwave. How microwaves can be used for a controlled reaction, a chemical reaction, it could require a thermo dynamic condition or a Kinetic condition, in either way microwave synthesis seems to take care of the kinematically controlled, and thermo dynamically controlled processes. And this is one of the view graph that we have shown earlier, to show how such processes can be used lot of conventional commercial instruments are now available for material synthesis.

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This is one such view graph to highlight how zinc oxide can be made, and how this are made as nano parts, and how exposure of microwave can influence the photo luminescence studies.

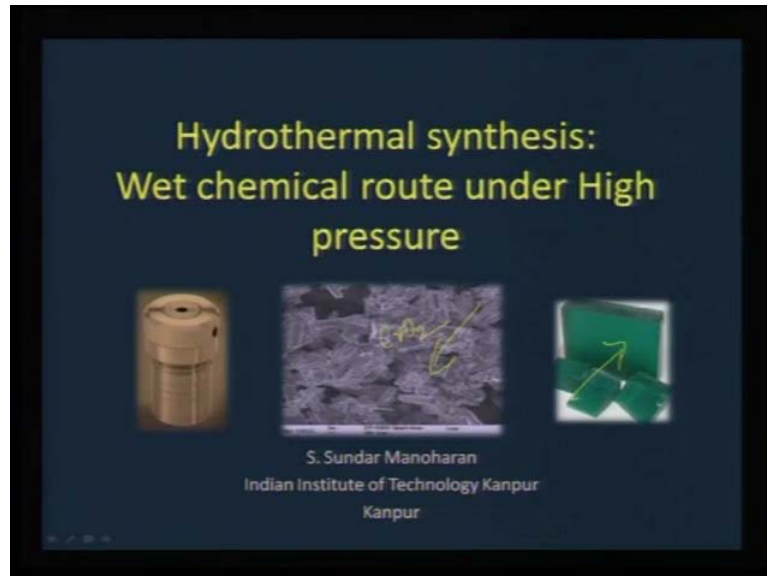
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For example, we have shown that, if you just expose the zinc oxide for 2 hours in microwave you get this characteristic 380 nanometer peak. Whereas, if you are going to expose the microwave for a longer time, at 4 hours you totally kill this 380 nanometer emission, and what you see is a defect induced emission that is coming. So, this gives a

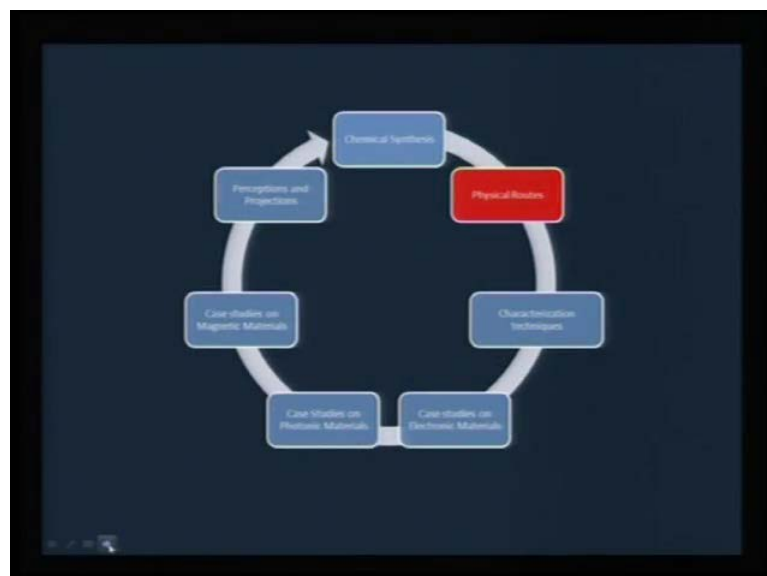
clear idea how the chemical synthesis has to be fine tuned and controlled, and how they can be very selective and specific in making materials of different composition.

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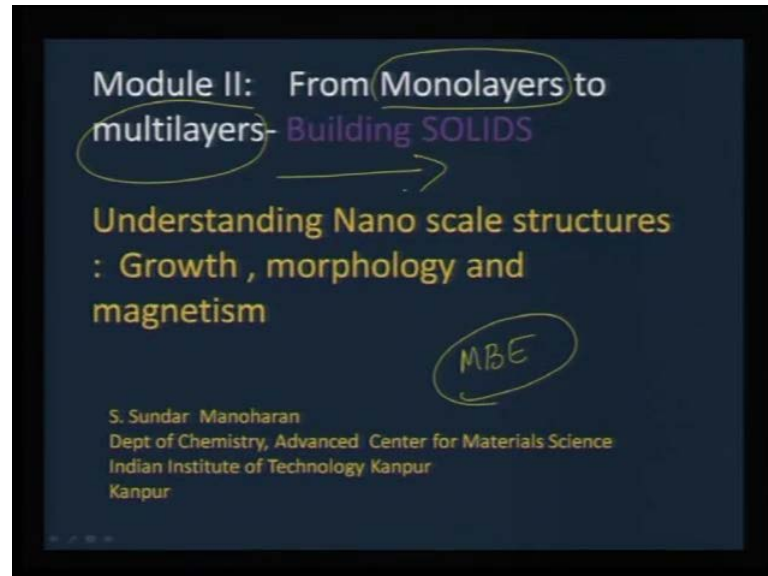
And also I have highlighted, whenever you look for Meta stable phases or unusual oxidation states in oxides, you can always resort to a very, very important approach that is hydro thermal. And I have also shown in this view graph, these are beautiful crystals of CrO_2 which is used in magnetic recording industry, and how gems can also be made selectively using hydro thermal condition.

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We looked at all the requirements for making compounds with different morphology, and composition and how hydro thermal route can help us resolve this.

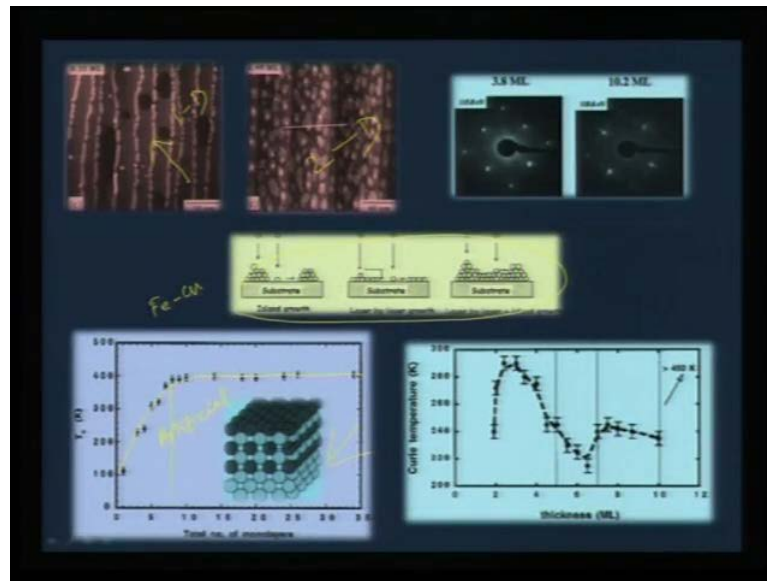
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We also looked at several combination of techniques in physical vapor method, one of the most important one that we saw is the use of molecular beam epitaxy, which we call as MBE. And in this MBE approach I have shown you examples of how to start from the scratch, you can put atomic layer by atomic layer to even develop a single unit cell, and then you can go for multi layers, so that is what we call it as mono layers. So, mono layers to multi layers, and then you can transcend to a three dimensional lattice.

So, just with few atoms deposited on a single crystal substrate, what is the magnetic origin of any material that we can talk about. For example, a iron for that matter alpha iron is a bcc which is a magnetic material whereas, gamma iron is a fcc compound, but it is not a material of choice, because it is non magnetic. But, once we construct we can see what is the minimum thickness that is needed when you grow it on a single crystal, when it transcends from fcc to a bcc compound. And I have shown you how critically we can monitor, and thanks to all the characterization tools that are available through which we can easily map a atomic level deposition. And from going from one mono layer to other mono layer how the magnetic influence happens.

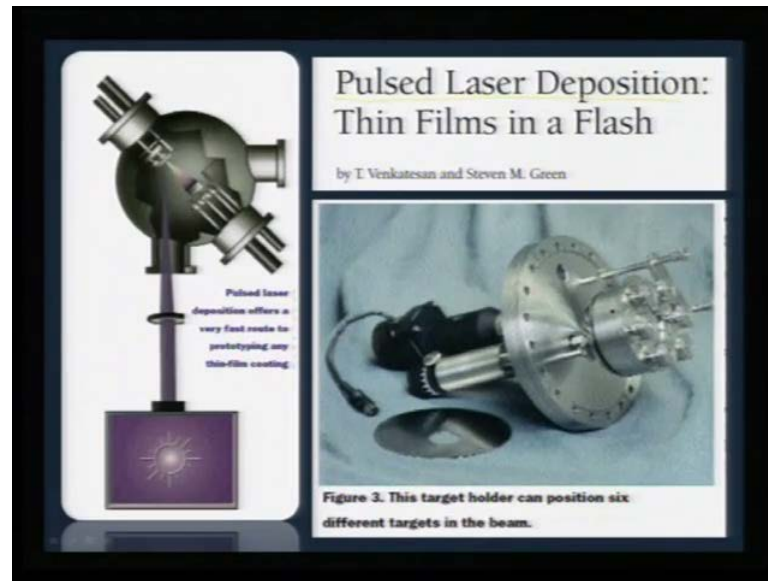
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And as an example I have shown the different growth mode, it can go through a ILEN mode, it can go through a two dimensional mode, it can go through ILEN plus layer by layer mode. And if that is the case, then how we can realize different materials for example, I talked about one dimensional wires, I talked about two dimensional wires or two dimensional films and also I had talked about artificial layers of two immiscible alloys.

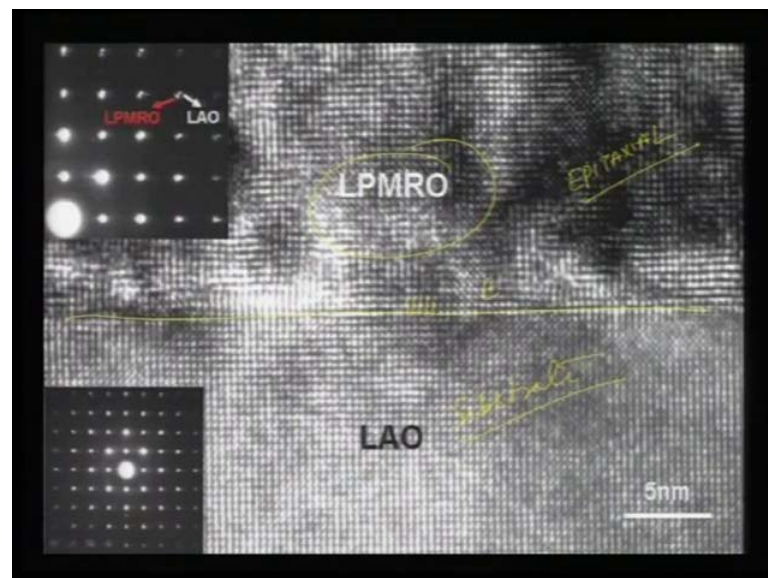
For example, iron copper is the example that I have shown, how two elements which are not miscible at all can be made to form as an alloy, if you can forcibly grow a layer by layer growth of two dimensional layers. So, this is one classic example where you see, if you start with just one atomic plane, if you keep on going then you can get a bulk property somewhere around 8 to 10 mono layers. So, this is one of the very grand demonstrations of how you can control in atomic scale, a deposition to realize unknown alloys which are not known in mother nature.

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And also I have highlighted the use of another very useful technique, which has actually covered almost all the range of materials that one can think of to translate from a bulk to a thin film form that is pulse laser deposition. And how this pulse laser deposition operates, what are the limits to it, and what is the condition in which we can do it, and most of the thin films that are being studied for device application today, specially from oxide electronic point of view it is all governed by pulse laser deposition, because it is very versatile and we can easily modulate the conditions for making oxide electronics.

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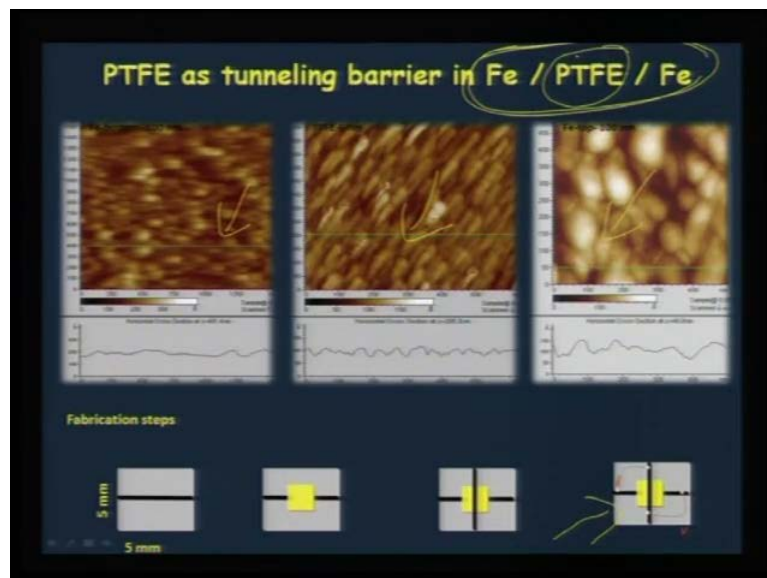


Just to show one view graph of what we have discussed earlier, we can make very sharp interfaces between a substrate this LAO, Lanthanum Aluminate is a substrate whereas, lanthanum manganese oxide is the material that you are. And you can see very clearly each dot is nothing but, a atom and on each atom you can see the regularity with which the lattices are growing, and we call this as a epitaxial growth. So, epitaxial growth can be affected on a very, very sophisticated way in a atomic level dimension, especially when you adopt a pulse laser deposition view.

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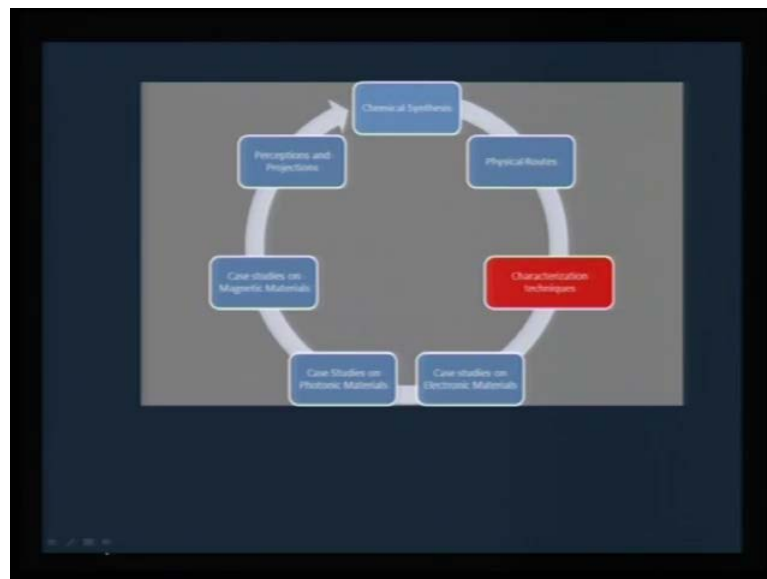
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And another equally useful technique that I have projected in this course is pulse electron deposition, this is not just confined only to metallic materials; but the chief advantage of this is to extend to any sort of material including semi-conductors and insulators.

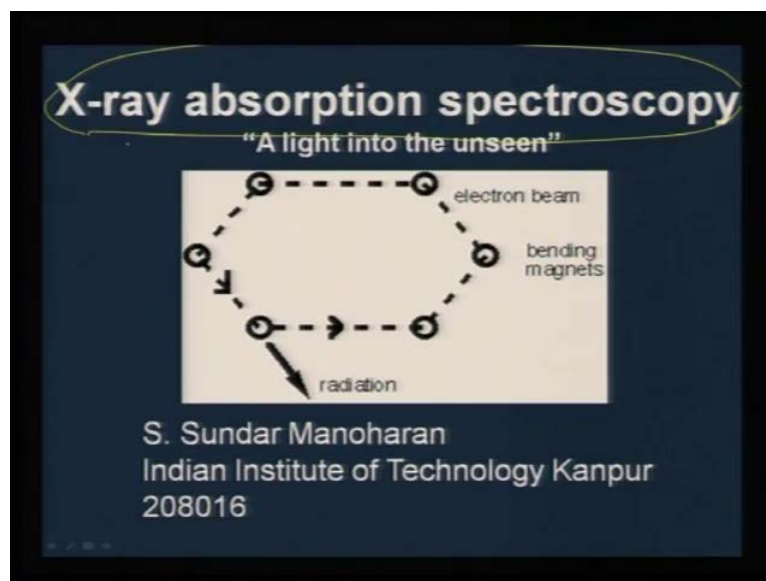
As an example I have also shown to you how the process can be made, and one example that I have discussed earlier is to bring in a rich chemistry between organic and inorganic interface. Ion, PTFE ion this is a trilayer how we can make such devices here, these are fabricated at IIT. And you can see that each of the layers have a very clear morphology from the AFM pictures, and this sort of trilayer devices can be made to even observe the critical dimension that is needed for this tunneling magneto resistive device to operate. And I have also shown that, what is the thickness limit at which this device can be made, and how difficult it is to control this thickness, because you are talking about a two dimensional growth.

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And then we have looked into many useful characterization techniques, I specially limited to some which are very sophisticated, and they carry rich information into any material that you study. So, in characterization techniques we have looked at several issues, basically on X-ray diffraction, but I have also looked in looked more carefully into X-ray absorption studies, which is a light source experiment. And what are the principle behind this X-ray absorption spectroscopy, and what is that we infer out of it, we have seen that in detail.

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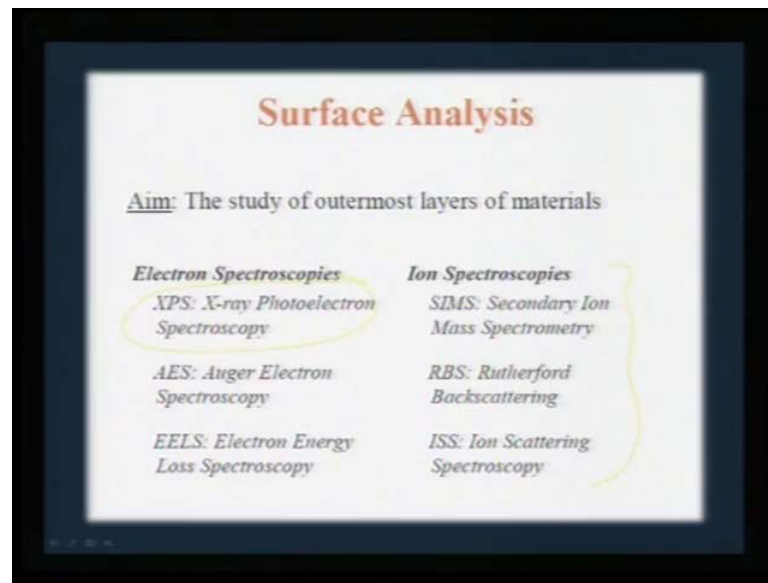


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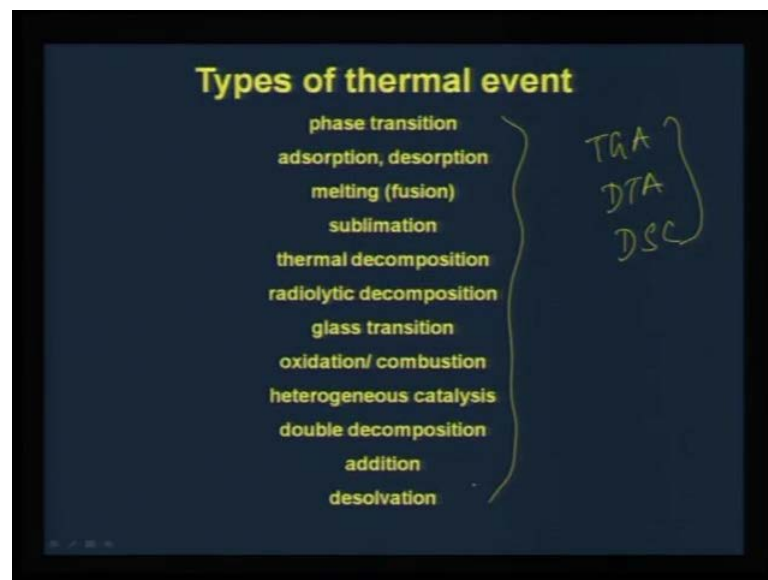
And the source for X-ray absorption spectroscopy is a synchrotron radiation, where your beam is accelerated and it comes out with very high kinetic energy. As a result you have very higher resolution even to atomically very, very low level percentage of material is there in your compound, then you will be able to resolve it with lot of certainty. So, we have seen how a synchrotron source is different from a traditional X-ray source that we use in our X-ray diffraction techniques, and what information that, we can get out of it.

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And we also looked at other surface analysis techniques which are there, I could not deal with these techniques ion spectroscopies in detail for want of time. But, we have looked more carefully into another technique that is XPS, X-ray photo electron spectroscopy.

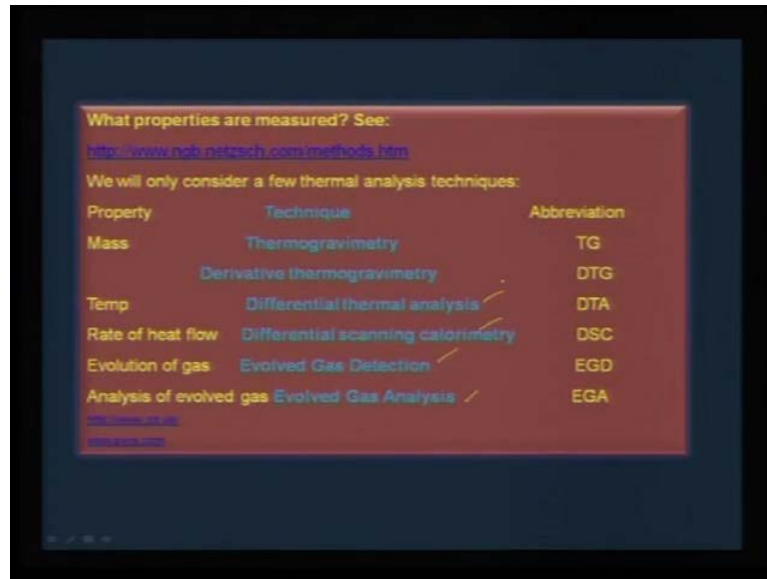
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And then I have also discussed about a fairly simple technique, which does not called for much material preparation. Or sophisticated instrument which is thermal analysis, we call it TGA combined with DTA, and DSC all this are a combined thermal analysis techniques by which we can get several useful informations which are listed here. And I

have discussed in details how this thermal analysis technique although it looks very, very simple it can provide rich evidences into the mechanistic approaches of material synthesis. Even in this lecture I have shown you how zinc benzothiazole complexes, give a clue to why we can easily dope manganese on zinc oxide. And we have seen all this principles in detail with examples.

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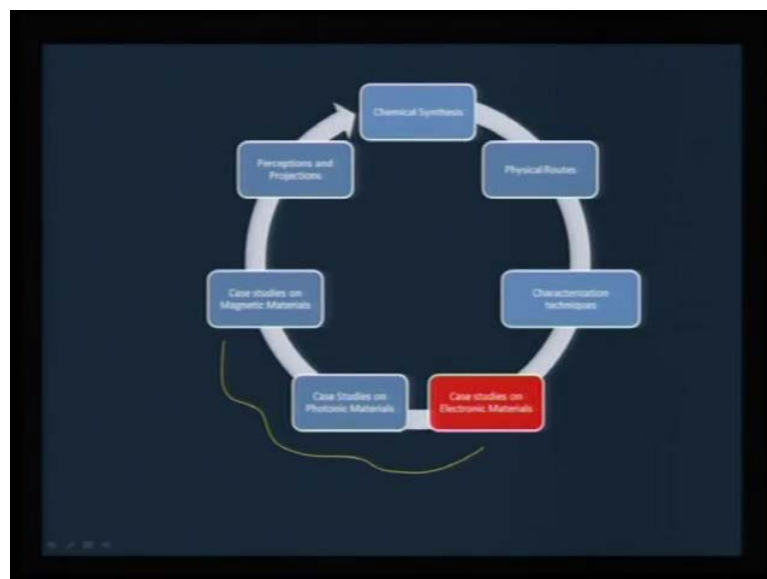


What properties are measured? See: <http://www.nob.nettech.com/methods.htm>

We will only consider a few thermal analysis techniques:

Property	Technique	Abbreviation
Mass	Thermogravimetry	TG
	Derivative thermogravimetry	DTG
Temp	Differential thermal analysis	DTA
Rate of heat flow	Differential scanning calorimetry	DSC
Evolution of gas	Evolved Gas Detection	EGD
Analysis of evolved gas	Evolved Gas Analysis	EGA

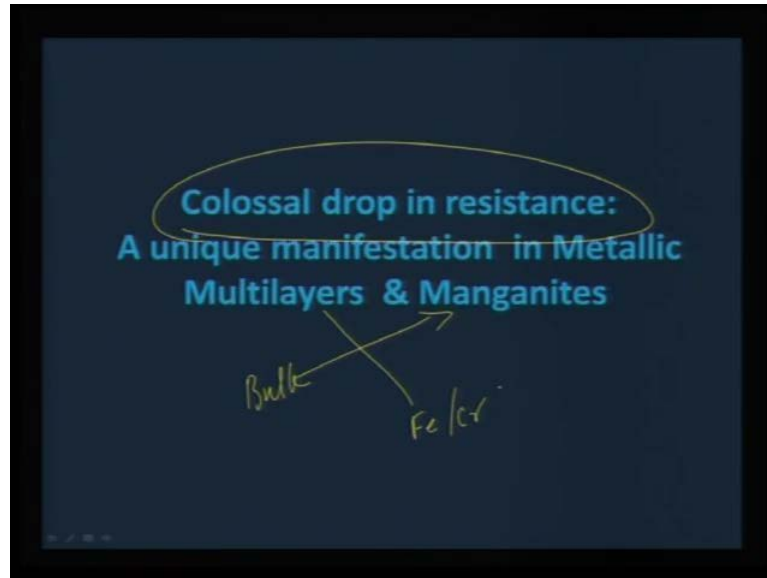
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And lastly we have taken up several case studies of different materials, which are functionally important some materials are important from the electronic properties, some

from the photonic properties, and some from magnetic point of view. And we have taken you through a course of case studies where in each lecture we have discussed, one particular group of materials.

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And here we have highlighted colossal drop in resistance in a series of compounds, one in bulk and which is actually related to manganites, three dimensional manganites. And we have looked at multilayers, this sort of combination of iron chromium which also paved way through several noble prize winning work. And today whatever we are handling in terms of iPod or many of the memory storage devices are mainly due to the phenomena of magnetoresistance. And I have shown you several examples of how we can study these compounds.

One of the compounds that show a huge drop in resistance is this perovskite manganites, which I have distinctly mentioned as a genie inside a small lattice, is just a small unit cell. But, the rich chemistry that you understand by doping the manganese site and the lanthanum site brings about several combinations of electronic and magnetic features. Therefore, we have studied that in detail and just to remember what is important, we just coined 3 letters called x r d, just to easily remember x r d; x for the amount of doping that you can do, r for the average size that governs the perovskite, and the dimensionality how we can tune the magnetic property in these materials.

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Perovskites: 'The Genie inside the lattice'

ReO_3
Rhenium Trioxide

- The XRD factor
 - 'x' factor: double exchange
 - '<r>' factor: Charge ordering
 - 'd' factor: Tuning the T_c

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Effect of magnetic field

The diagram illustrates the effect of a magnetic field on a layered material. It shows two 3D block diagrams at the top, each with a purple top layer and a teal bottom layer, and arrows indicating magnetic alignment. Below these is a 2D cross-section showing alternating layers with blue and orange arrows representing magnetic moments. To the right is a graph of Resistance (R) versus Magnetic Field (B). The graph shows a peak in resistance at zero field, which decreases as the field increases in either the positive or negative direction, forming a symmetric, inverted parabolic-like curve.

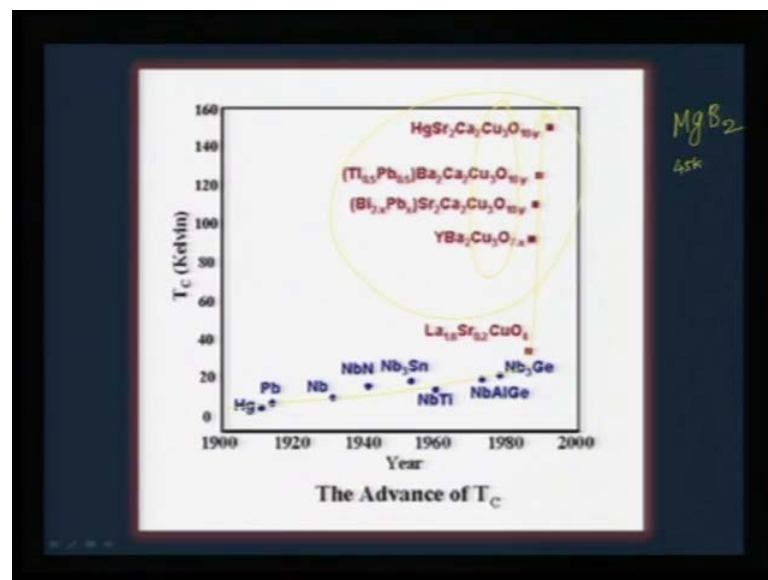
And also I have highlighted to you, how this compounds the multi layers are useful in rotating the magnetic alignment. So, with the magnetic field and without the magnetic field, how a anti ferromagnetically aligned material gets ferromagnetically aligned in a one direction; as a result you see a drop in resistance as a function of field.

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And this is the magneto resistance, so we have seen that in detail and also we had 1 lecture exclusively to highlight, the need for a super conductivity, because it effects the electric sector, power sector in a greater way.

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And we have seen how chemistry has played a vital role in bringing about new discoveries. As you see here these are all alloys or intermetallic, which has shown super conductivity below 3540 Kelvin, for very long time, for over 70 years we have lived with this intermetallics. But, thanks to the materials chemistry which has really sky rocketed

this T_c in just 2, 3 years time starting from 1986, where we have seen a tremendous improvement in highlighting the high T_c story.

And as you see here, the T_c has now reached up to 160, but this is not enough for functional applications and to realize room temperature super conductivity, we need to look for newer material although the cuprates have by and large held this excitement for long time. But, we are actually running short of ideas, we are not able to improve more than a 3 layer cuprate morphology, as a result we are not able to transcend beyond 160 Kelvin for a long time.

So, what is need of the r is a room temperature super conductor which can show absolute resistance without any resistance, and that can actually transcend to be the material of choice. So, lot of research is still going on, there are some excitements along the way like magnesium bromide, has shown a view that borides can also offer excitement in the same field. But, this is not enough, because magnesium boride shows T_c below 45 K and that is not enough, so to stick on to the story of high temperature super conductivity. We need to look for something which can go much more closer to room temperature, so such research has to be engineered and materials chemistry will be very important.

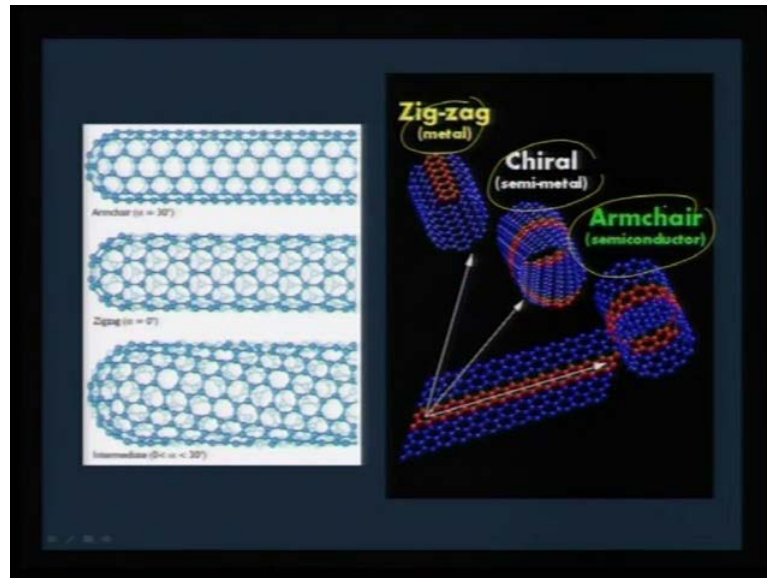
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We also looked at another important field that is the new carbon additives in the carbon family. And we also saw the emergence of fullerenes, nanotubes and graphane which has

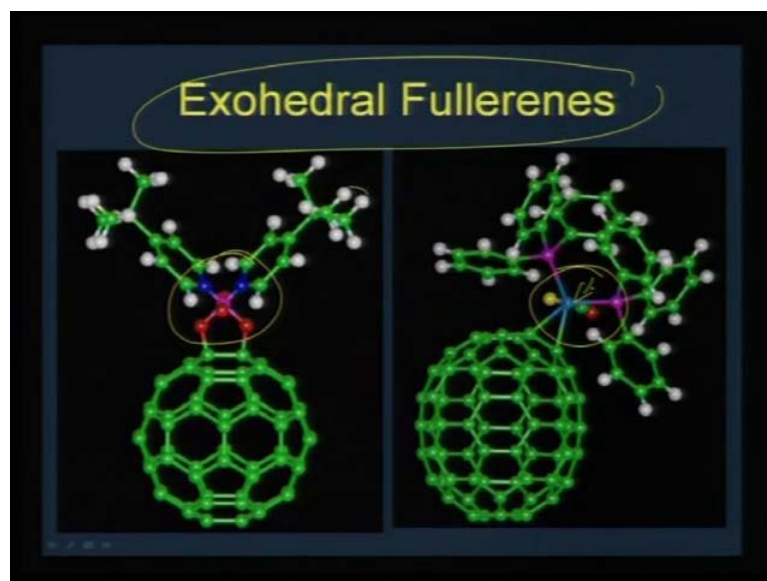
added to our, traditional understanding of graphite and diamond. And we looked into several aspects of this structure, properties that are related.

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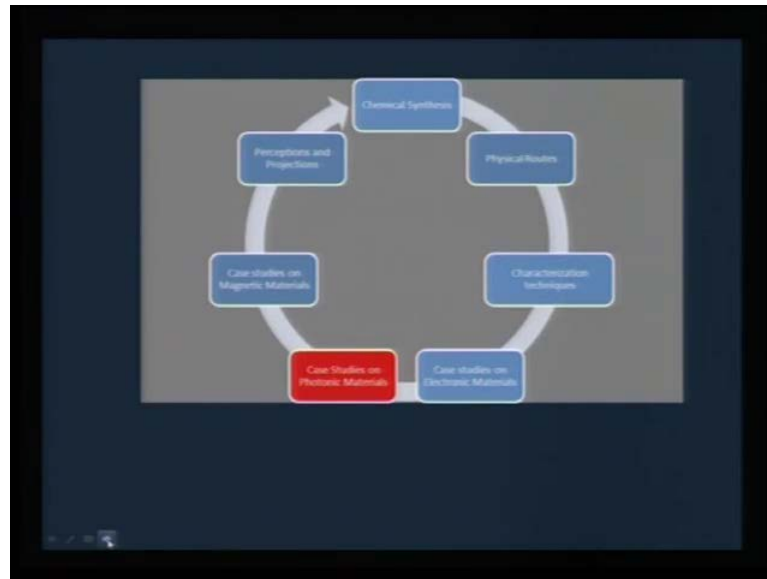
We looked at how the way the nanotubes are rolled from a simple two dimensional carbon sheet, how we can get a semi metal or metal or a semiconductor carbon nanotubes, and whether it is a single wall or a multi wall all depends on how the configuration is...

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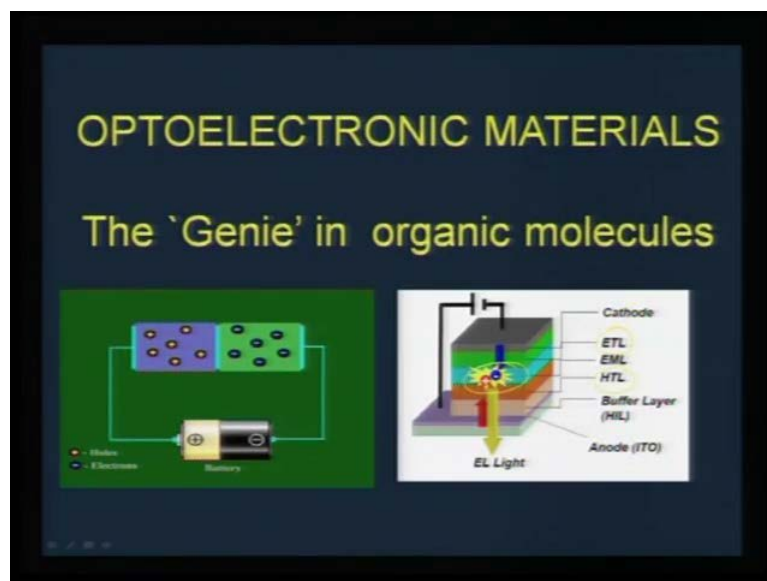
And to make this more useful for other applications, we have also looked at the several substitutions that can go; one is exohedral fullerenes where you can actually cap it with some metal centers, in order to use this for applications. So, these are called exohedral fullerenes this is one with the osmium as a core, the other one with the iridium as a core, we have to design new materials for functional applications.

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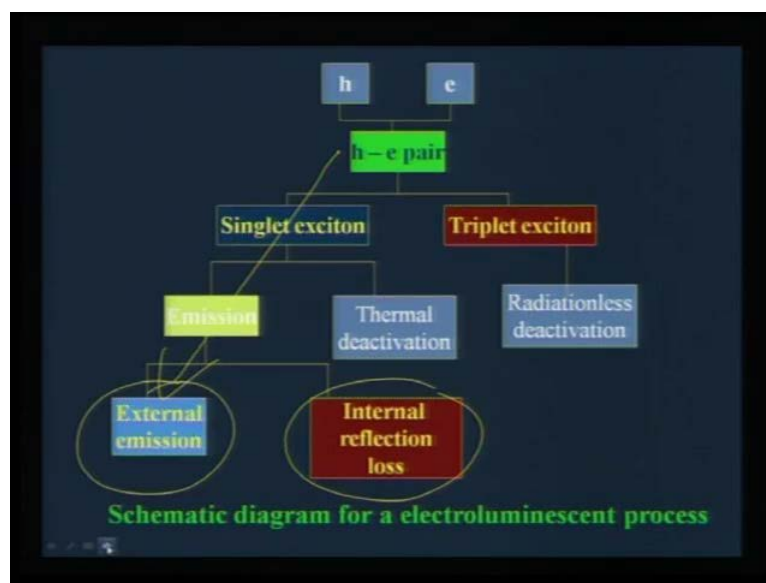
We also have looked into some of the examples of photonic materials.

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And we understood from couple of lectures on organic photonics, how this organic molecules can be used for oled applications. One such important example is the emissive layer which is very much responsible for tuning color in organic LED's, and what is the role of the whole transport layer, what is the role of electron transport layer? And how materials synthesis is very important in designing different molecules.

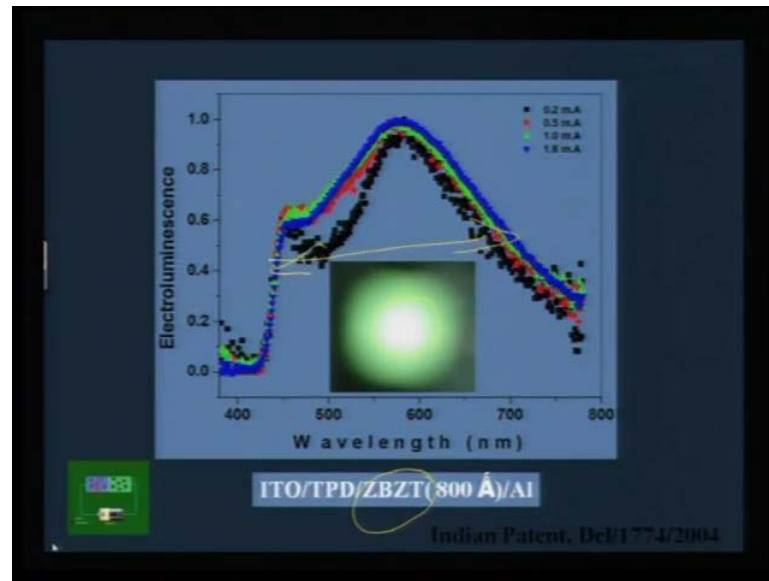
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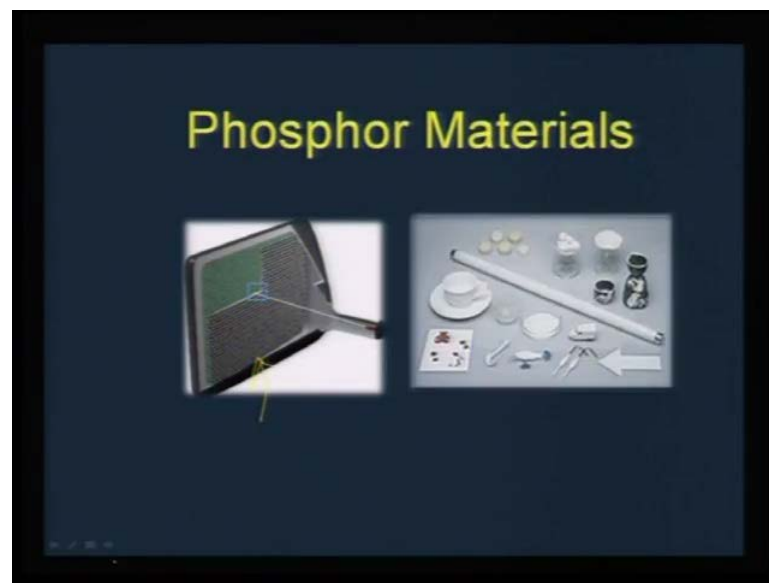
We have looked into the basic understanding of how this oled operates, and apart from all this internal reflection loss how we can improve on the quantum efficiency which we harvest from the singlet exciton. So, we looked into the EL process which is responsible for getting a very good LED response.

And we have seen also several examples to show, how important device making is crucial in a LED structure, because what you see as a photo luminescent behavior of a particular compound need not necessarily be translated to a electro luminescent behavior. For example, if you take the case of zinc benzothiazole as a active material, you see it can give a white light against a green light which is predicted, mainly because of the broadening that happens in the oled structure, and that is reflected due to a phenomena called Xemplex.

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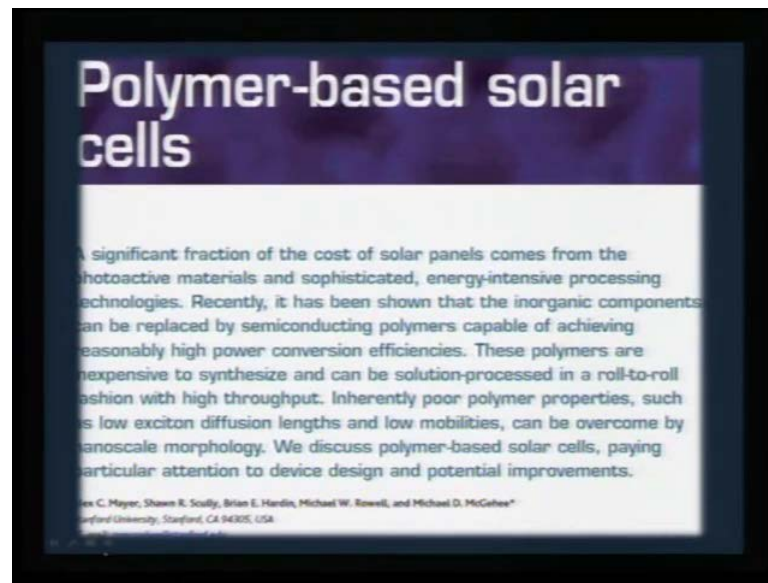


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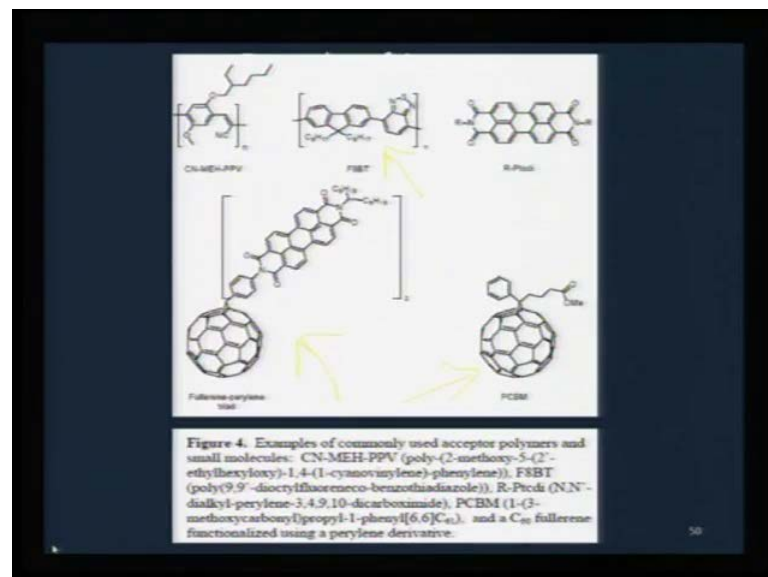
So, although you can make material making a device has its own demand and therefore, that is very crucial, so the engineering part or it of the device fabrication point of it has to go hand in hand with the material tuning. And therefore, materials synthesis is going to be very, very important, and then we also looked at several examples of phosphor materials, how they are used in today's CRT applications, and what are the need for it.

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And one other lecture, we looked more closely into polymer based solar cells and what are the applications of that, how a traditional solar cell will behave. And what are the parameters that we should look for to fine tune the materials, so that we can get maximum efficiency.

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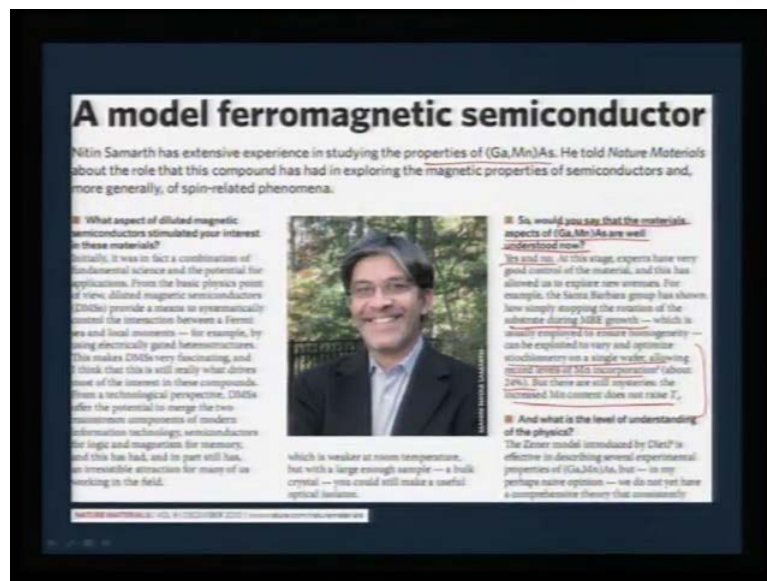


And we looked at some of the popular compounds that are used as acceptors and donors, which can generate excitons. For example, this is a hybrid molecule of fullerene that is used as an electron acceptor; PCBM is used as an electron acceptor. And this sort of

fullerene molecules is actually used as a electron donors, and how the combination of these will affect the solar energy conversion. And the last of all that we have seen in solar cells is the dye sensitized solar cell, and that seems to have a greater efficiency than any of the hetero junction solar cells.

And we have also looked into other examples of materials which are promising for application in solar cells. In essence if we look at both the electronic materials and the photonic materials, what is the fork ascend what do we have to look forward to and where do we go from here. There are some useful articles which has appeared in nature materials, and other nature magazines which I just want to highlight 1 or 2. Just to show what are the limitations that we face in today's materials chemistry, and what are the challenges that are ahead of us.

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Here is an article on a model ferromagnetic semi conductor interview with the Nitin, has brought about the need for understanding the material synthesis. And here is a prediction on gallium nitride doped with manganese which shows ferromagnetism, and this has been studied as a model compound for all the dilute magnetic semiconductors. When he was asked about one question, whether materials aspect are well understood as of now, what Nitin has to say is that it is as a no.

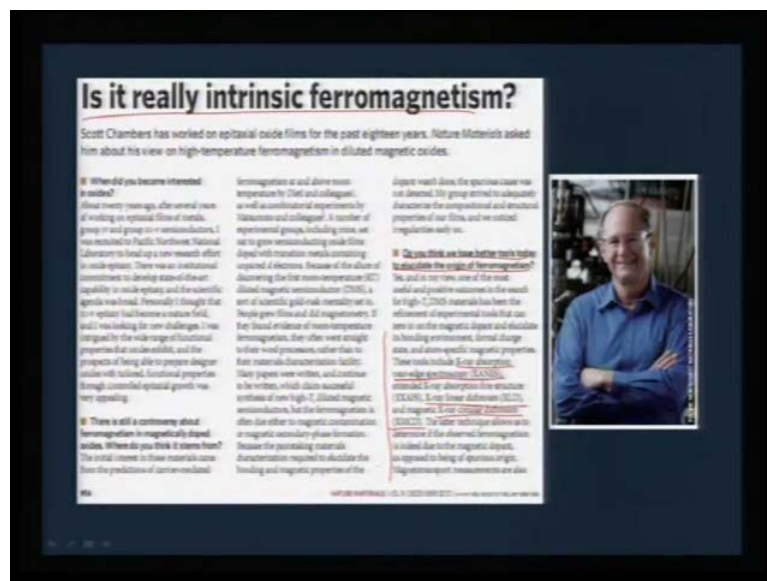
Because, what he has found is that under very high sophisticated a fabrication conditions, a very clean dilute magnetic phase could be made. And in other cases it has been a

controversial results therefore, what he says is growth based on MBE method seems to be by far the safest route, were you do not get into any issue of external impurities adding to the confusion. Therefore, what is important that we need to understand in understanding ferromagnetism at room temperature in semi conductors.

We need still more refined parameters both from characterization point of view, as well as from synthesis point of view. But, what has been told, so far is that using MBE they have attempted even to dope up to 24 percent of manganese in gallium arsenide, but yet what they could not understand is even though they increased the doping level, they could not increase the T_c .

Because, if it has to obey the Vegard's rule, then with more and more of manganese doping in the semi conductor, you should have seen a little bit of linearity in the increase in T_c which they have not found. So, lot more sophistication is needed to elucidate the origin of room temperature ferromagnetism.

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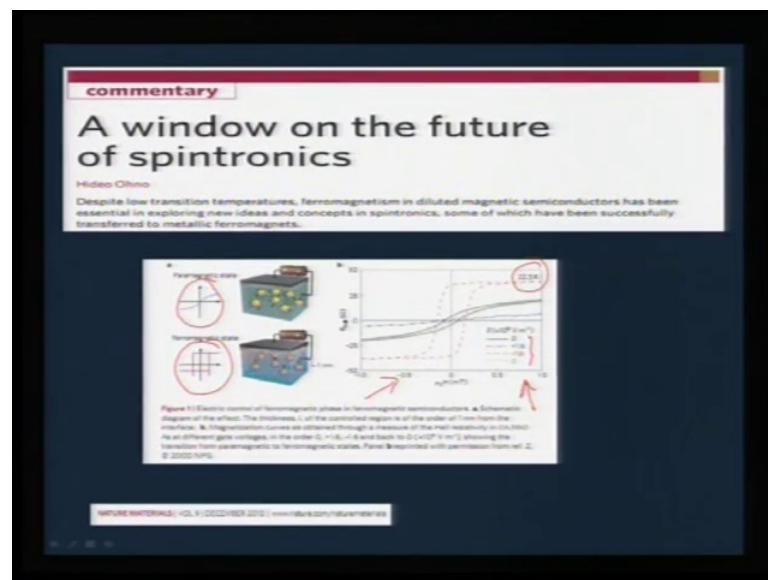


And here is another interview with Scott Chambers who has worked on semi conductors for a very long time. And question asked to him is the magnetism in dilute magnetic semi conductors which is truly ferromagnetic, and one of the question that was posted to Scott is do you think we have better tools today to elucidate the origin of ferromagnetism, and the answer is yes. And he says in my view one of the most useful and positive outcomes

in the research of high Tc DMS has been the refinement of experimental tools that can 0, in on the magnetic dopant and elucidate the bonding environment.

The characterization tools that he has highlighted or X-ray absorption studies as I highlighted to you in the previous slides, then X-ray linear dichroism, X-ray circular dichroism, because that is the one which will tell whether the light that is coming out of this photonic material is plane polarized or not. Therefore, you need such very critical diagnostic tools to understand, if truly what we are talking about magnetic semiconductors is true or not. So, we can sort of say that the research is matured in order to understand, whether there is a intrinsic ferromagnetism or not or whether it is coming from any external impurities as we suggest.

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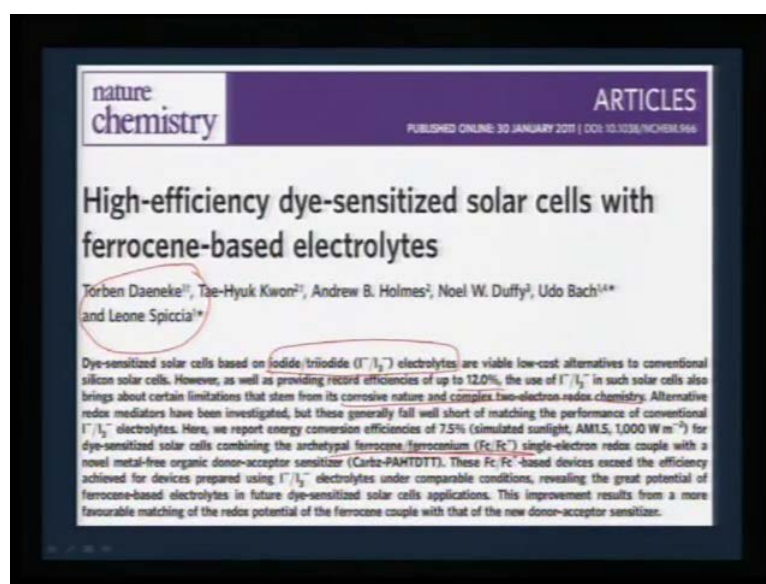


And here is another commentary made by a Ohno and co-workers, window to the future of spintronics, were he says that a paramagnetic state of a material can be driven into a ferromagnetic state by electrically driving that to be a ferromagnet. And this is the principle of a dilute magnetic semi conductor, and if we call any material to be truly a dilute magnetic semi conductor, then it has to display a behavior of this sort. Where with different operation voltage you can see a ferromagnetic loop is emerging at a critical temperature of 22.5 K.

So, if you design any material and you truly call this to be a dilute magnetic semiconductor, then it has to show voltage dependence of resistance against field and

this is a resistance against field plot which shows a hysteresis with different gate voltage. So, this is one of a important signature that we should have in mind, when we try to generate a magnetic material and this material is supposed to be a room temperature ferromagnet, then this is the sort of response that you would look for.

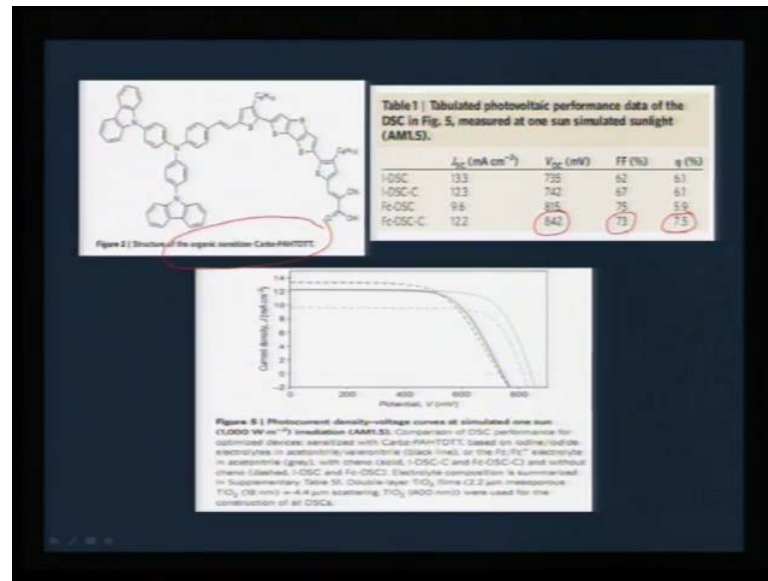
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And another important area that has been recently highlighted is high efficiency dye-sensitized solar cell, about which we have talked in the earlier slide with ferrocene-based electrolytes. As you know in dye sensitized solar cell, we have the electrolyte which is usually a iodide electrolyte. And one of the reason that this has a severe limitation, although you have a very good efficiency of the order of 12 percent is that, it is corrosive in nature and therefore, it is more complex in understanding the redox chemistry there.

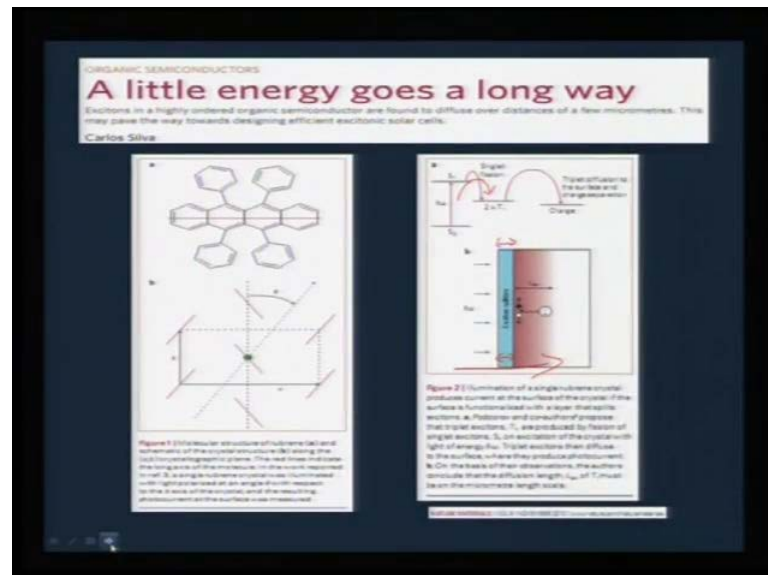
So, this is a group which has recently published in nature chemistry, where they have replaced the iodine, iodide, electrolyte with ferrocene, ferrocenium, single electron redox couple which is fairly a good one a stable molecule. And using this they have improved on the energy efficiency up to 7.5 percent, and these are emerging stories from dye-sensitized solar cell. And these are very practical and very easy to fabricate, but the chemistry that is going on in this dye sensitized solar cell has to be trimmed or modified in a much better way.

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This is the organic sensitizer which they have used, and one of the ferrocene based dye-sensitized solar cell seems to have a efficiency up to 7.5. Interestingly they have very good open circuit voltage, and the fill factor is up to 73 which is not a bad number, as you see from this curve.

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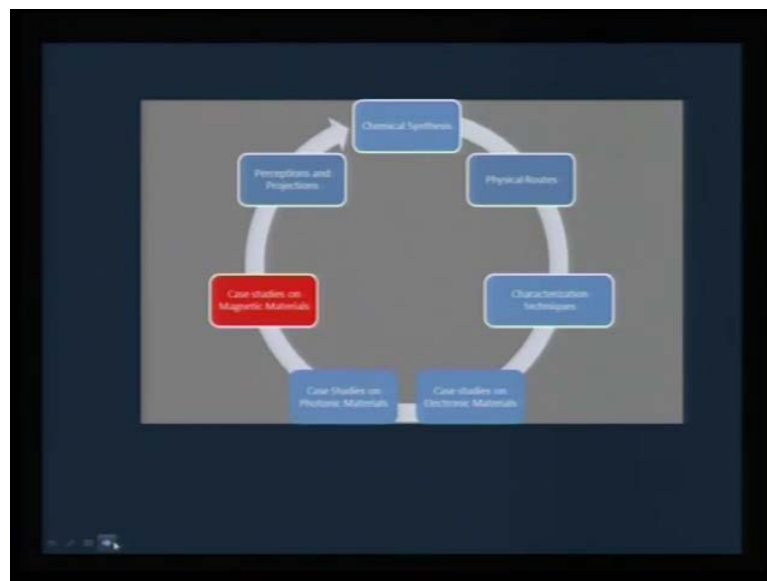


And another important advancement in the solar cell is the use of organic semiconductor, in this case it is a ruberine based one which has a symmetry, it is a symmetric molecule. And this molecule seems to be able to undergo a singlet fission into two

triplets, and this triplet seems to be increasing the photo current. Therefore, the efficiency of the solar cell is very easily manageable, or we can improve on the efficiency.

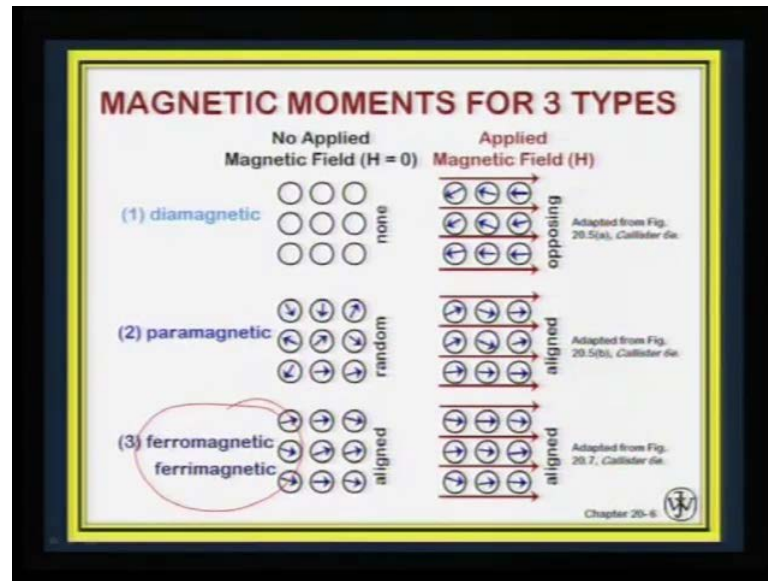
The point here that we need to understand is, if we can get very good photo current and then we need to form this ruberine layer in a very, very critical dimension and the dimension of this has to be nearly in a 2 to 10 nanometers. So, control of this ruberine which is a organic film, and to control in that dimensions is the challenge. So, if we can do that, then we can bring about a new generation of a solar cell with organic semiconductors like ruberine. So, there are lot of forecast, and new developments that are coming, in this fashion which needs to be taken into consideration. We also looked at another important module on magnetic materials.

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Mainly we tried to look at the various group of magnetic materials, and then we looked specific examples of ferromagnetic materials which are useful for functional applications. And then we also looked in this module into several classification of this ferromagnetic materials, and one of the example that we touched upon is the magnetic storage.




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MAGNETIC STORAGE

- Information is stored by magnetizing material.
- Head can...
 - apply magnetic field H & align domains (i.e., magnetize the medium).
 - detect a change in the magnetization of the medium.
- Two media types:
 - Particulate: needle-shaped $\gamma\text{-Fe}_2\text{O}_3$. +/- mag. moment along axis. (tape, floppy)
 - Thin film: CoPtCr or CoCrTa alloy. Domains are ~10-30nm! (hard drive)



recording medium

recording head

Simulation of hard drive courtesy Martin Chien. Reprinted with permission from International Business Machines Corporation.

Adapted from Fig. 20.18, Callister 6e. (Fig. 20.18 from J.J. Lemke, *MRS Bulletin*, Vol. XX, No. 3, p. 31, 1999.)

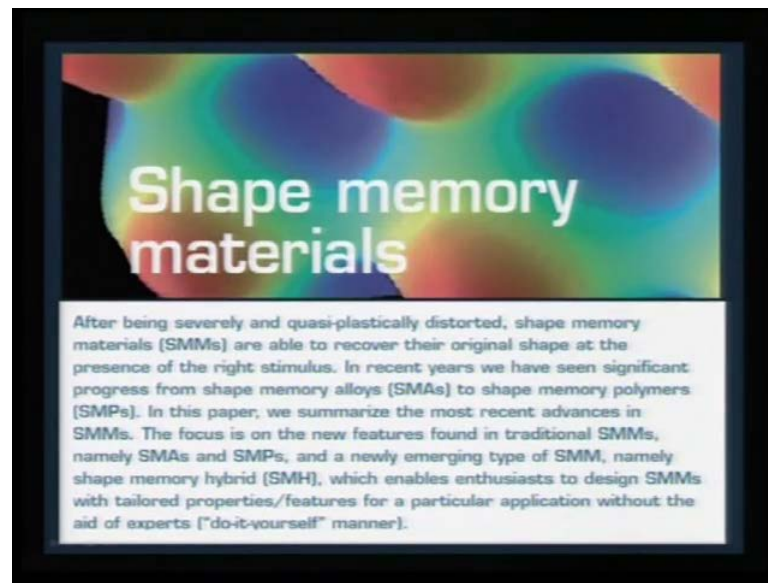
Adapted from Fig. 20.19, Callister 6e. (Fig. 20.19 courtesy P. Ragner and N.L. Head, IBM Corporation.)

Adapted from Fig. 20.20(a), Callister 6e. (Fig. 20.20(a) from M.F. Kim, S. Guruswamy, and K.E. Johnson, *J. Appl. Phys.*, Vol. 74 (7), p. 4646, 1993.)

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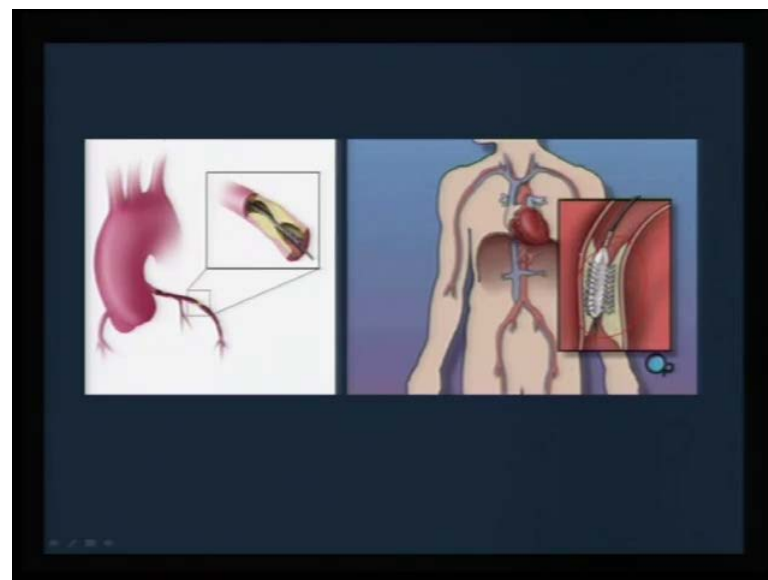
And how particulate mediated materials, and the thin film mediated materials can affect the magnetic storage in a larger way.

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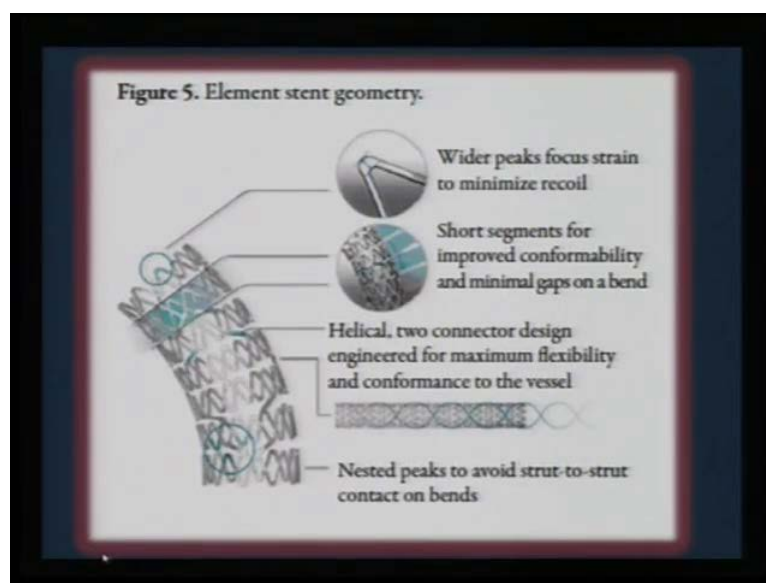
And another important application of this magnetic materials is the shape memory alloy, which has found application in variety of areas including biomedical devices.

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We also looked at how the cardio vascular stents are made of these shape memory alloys, which can actually hold a very critical technology with high degree of specificity. And we looked at examples of how this shape memory alloys can be used for various design of this material.

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And this is one of the other a view graph which we have seen in one of the earlier course, showing what is critical about the design of this shape memory alloys.

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Lastly I would like to conclude by acknowledging all the people who are involved in this course, specially I would like to record my thanks to ministry of human resource and development, who have taken extra pain to bring this lectures on a web based mode, video based lectures. So, that many people can be profited I hope that these lectures on materials chemistry would be useful.

And especially want to record my thanks to NPTEL organizers the nodal point has been IIT Chennai, I want to thank the coordinator and the director of IIT for letting me do this course, and it has been a challenging time. So, I want to record my appreciation also to administration at IIT Kanpur, who have provided a very excellent recording studio. And the friendly atmosphere provided by the NPTEL crew at IIT K has been fantastic, and we have enjoyed their courtesy especially recording and editing has been superb.

So, I want to place my record, thanks on record for all that they have invested, and I hope that these series of lectures that I have provided would bring some perception into the challenges that a chemist will face in a materials world. And how important a simple chemistry principle can take you long way into applications, so I just conclude with this and also thanks to the viewers.