Materials Chemistry

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Module - 1
Lecture - 5
Preparative Routes Un Conventional Sonochemistry Technique – II

In the previous lecture, we have been looking at the importance of Sonochemistry in material synthesis.

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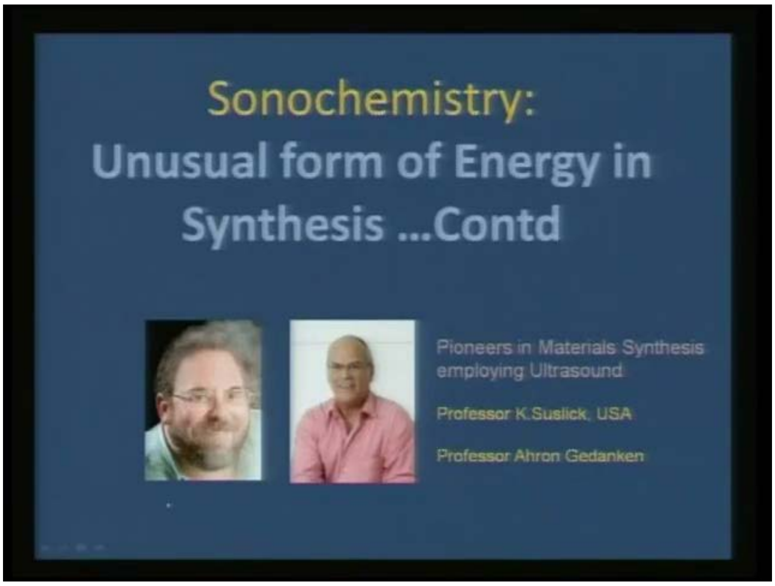

Sonochemistry:
Unusual form of Energy in Synthesis …Contd

Pioneers in Materials Synthesis employing Ultrasound

Professor K.Suslick, USA

Professor Ahron Gedanken

And we title this previous lecture as unusual form of energy in synthesis, so I will just try to quickly recap where we stopped in the previous lecture, and then continue from then on. We have shown this flow chart where the power of sonochemistry can be manifested, where if you start with a carbonyl or a nitrosyl metal salt. So, M can be anything, and if you have metal attached to carbonyl moiety or nitrosyl moiety, it is much easier to cleave the organic part by ultrasound, and thereby you can stabilize nano particles of any metal.

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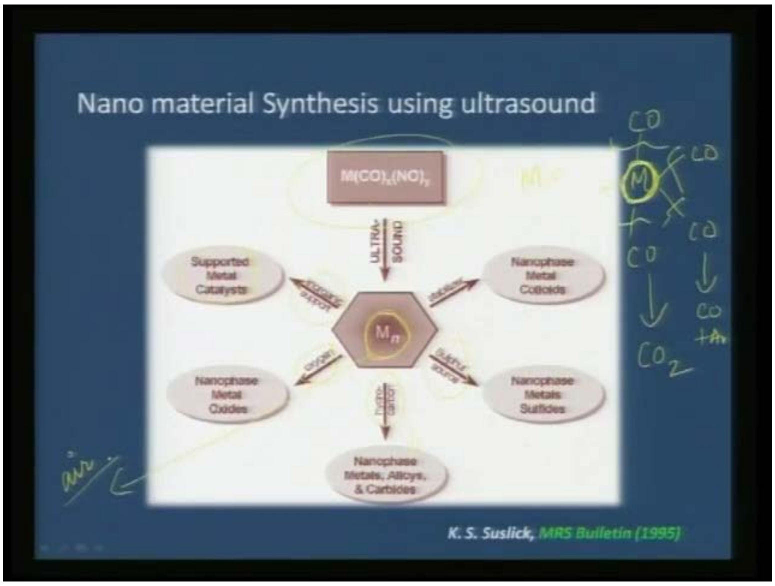

Nano material Synthesis using ultrasound

K. S. Suslick, *MRS Bulletin (1995)*

And these nano particles are very, very reactive and sensitive to atmosphere; therefore, you can stabilize it as a colloidal form. You can use sulphur source to convert it into sulphide, you can use hydrocarbon to stabilize the nano phase of this alloys or metals, and you can use oxygen to convert it into respective oxides. And also you can trap this in inorganic support like alumina, titania, and so on, to create a set of metal catalyst.

In all these cases, the corresponding end products are extremely reactive, because of the nano sized metal particles that we can get out of this. One of the main reason that, sonochemistry is still being used is because; the starting materials are very attractive. So, when you actually have metal is attached to carbonyl groups, all that the sonochemistry can do is just break these bonds. So, when you break the bonds finally, you end up with the metal nano particle, and this carbon monoxide groups or carbonyl groups usually go out as carbon dioxide, or as carbon monoxide in the presence of a carrier gas.

So, the end product is actually free from any further chemical contamination, therefore you can really rely on using the metal particles as such, without any sort of washing or other serious protocol. So, this is one of the main reasons, why we resort to sonochemistry for getting real ultra powders. And another way that we can ascertain that these powders are really nano is when you expose it to air, they decompose immediately into corresponding oxide, indicating that they are very reactive powders.

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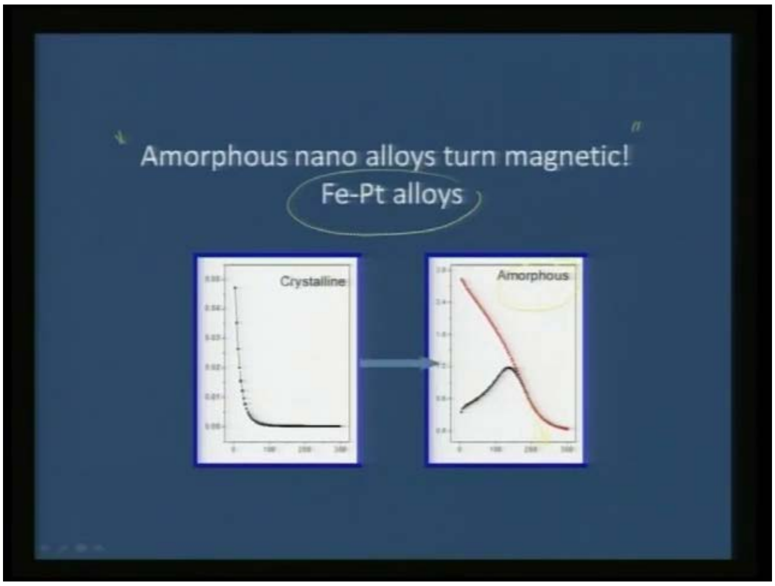

Amorphous nano alloys turn magnetic!

Fe-Pt alloys

Now, in the previous lecture, we looked at one of the examples of the cobalt platinum alloy, and how this alloy affects both the amorphous property, as well as crystalline property. Today’s lecture I would like to concentrate little bit on iron platinum alloys, as I would titled it here, the amorphous alloys of iron platinum, when they are prepared sonochemically they actually turn magnetic.

What is unusual here, in the iron platinum phase diagram which will see shortly, there are regions where when platinum is doped across the series, there are some limiting compositions where the alloy turns non magnetic. So, when there is a magnetic, non magnetic phase usually the properties would vary, but what we see in amorphous alloys of iron platinum, irrespective of the composition of platinum everything is turning magnetic. And this is one of the view graph which shows that ((Refer Time: 04:32)) amorphous alloys are turning magnetic, and the Tc seems to be somewhere around 240 Kelvin.

How does the iron platinum alloy look, you can see from this TM view graph that almost all the particles are mono sized, and of the order of 1 to 3 nanometers, this is very difficult. Because, usually when we generate such nano phase alloys, you end up with agglomeration, and as a result to stabilize this sort of alloys, usually we resort to some stabilizing agents or surfactants. But, what we see here is that, even without surfactants you can clearly isolate such alloys, and one fascinating feature is throughout the TM samples, we keep observing this sort of self-assembled pattern of iron platinum alloys. And they are held together in some sort of form, but nevertheless they seem to have almost a mono size when prepared.

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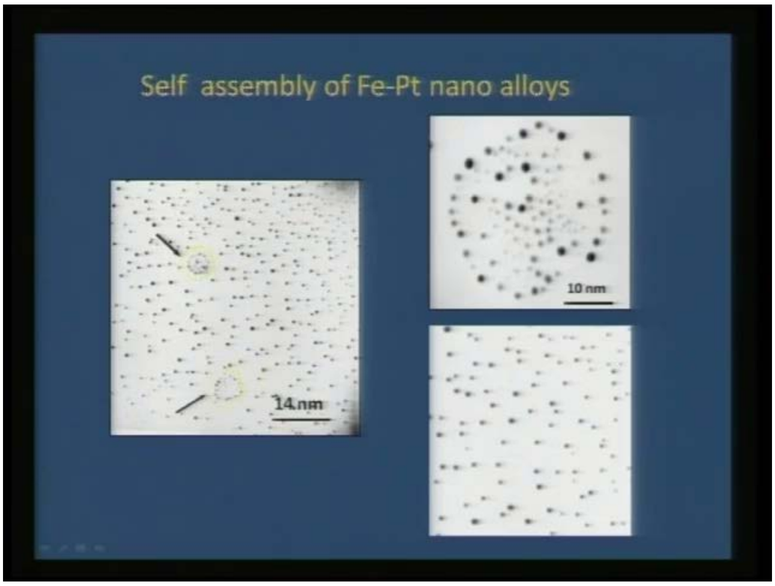

Self assembly of Fe-Pt nano alloys

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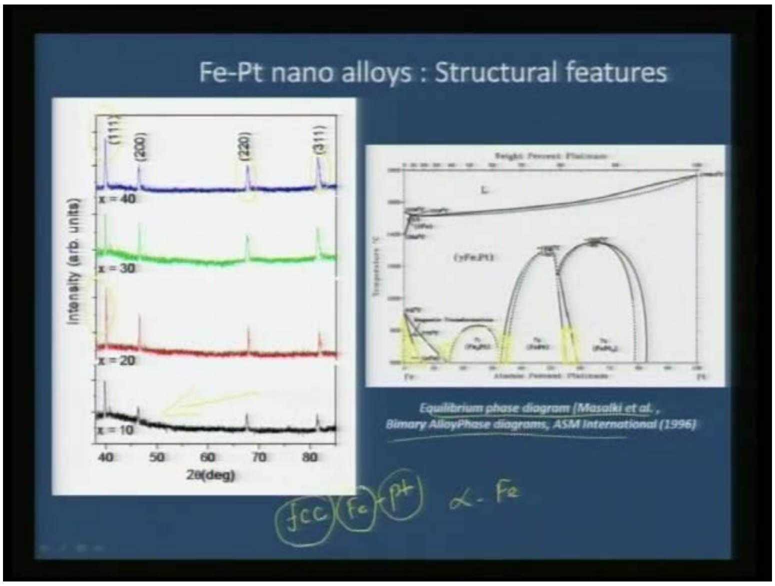

Fe-Pt nano alloys : Structural features

Equilibrium phase diagram (Masalki et al., Bimary AlloyPhase diagrams, ASM International (1996)

Now, if you look at the X-ray diffraction pattern, you can see here, they show not absolutely amorphous, but with more and more of platinum there seems to be some crystallization process that is happening. But, without platinum you can see that this is a typical amorphous phase, as seen from the X-ray diffraction pattern. And you can see these prominent peaks are emerging out due to platinum, as you increase the ratio to 40 percent of platinum.

Now, if you look this equilibrium phase diagram, which was proposed by Masalki and co-workers, and this is available in the binary alloyed phase diagrams published by ASM international. Now, if we see here, there is a region up to 15 percent or so you can see that in this region the alloy is actually non-magnetic. And there is a region here where alloy is non-magnetic, and there is also a region here where alloy is non-magnetic, and there is another region where alloys turn non-magnetic.

So, there is a transformation from ferromagnetic to non-magnetic, ferromagnetic to non-magnetic, so if one can prepare across the series the alloys, we can look at the magnetic property and see whether it is really resembling that of the equilibrium phase diagram. So, in the next slide ((Refer Time: 07:13)), we can see here this is what happens, when you heat this iron platinum nano alloy, as you would see in the previous slide that it is amorphous.

But, once you heat it to 900 degree C, you can clearly see the fcc pattern stabilizing, so this is an fcc iron platinum alloy that is formed. As you know when you heat it to high temperature, iron is actually transforming to alpha n phase or alpha iron which resembles a bcc phase. But, even at high temperature, we are able to stabilize fcc iron, and this is because of the not only the effect of platinum, but also it is the effect of sonochemistry. Because even for undoped 1, we are able to stabilize fcc pattern, so the formation of Meta stable phase is one of the real trump cards of sonochemistry; mainly because you are able to get the as prepared powder which is amorphous in nature.

Now, if you carefully look at the VSM data or the magnetism M versus T plot, here we have in the y axis we have plotted the magnetization, and in the x axis we have a temperature sweep. So, if you actually do this both in ZFc, as well as Fc, this is the 0 field cooled curve, and this is the field cool curve. And as you see here the blocking temperature is somewhere here, which means there are lot of anti-ferromagnetic interactions, so if you do not cool your sample in magnetic field.

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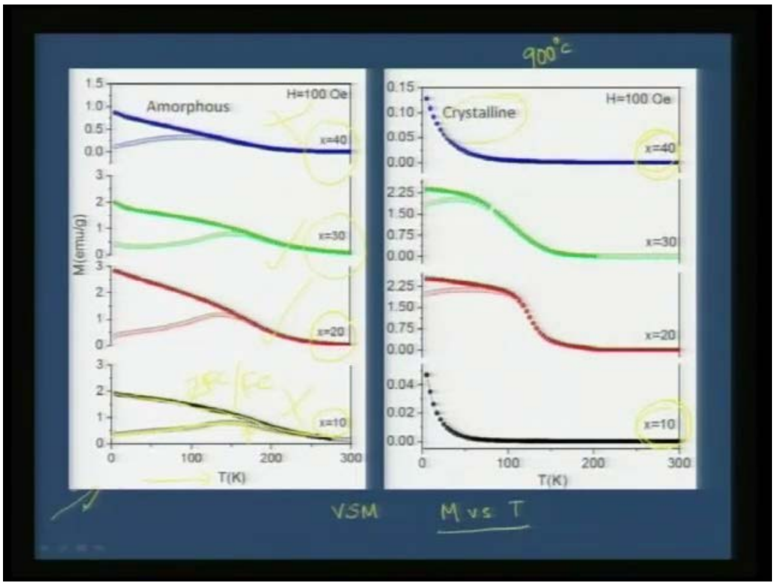

Then you see this sort of anti-ferromagnetic interactions maneuvering the ferromagnetic ordering, but if you cool the sample in the field which is called field cooled, then you can see here that it is turning ferromagnetic. And this is not there only for X is equal to 10, you also see the same trend for X is equal to 20, 30, and 40. So, irrespective of any composition, you see iron platinum, amorphous alloys are magnetic across the doping concentration.

If you quickly remember, the equilibrium phase diagram that we saw, ((Refer Time: 09:55)) these two regions are supposed to be magnetic according to the phase diagram, whereas, these two are not supposed to be magnetic. But, irrespective of that in amorphous phase all the compositions are turning magnetic. Whereas, if you look at the crystalline phase, which is the 900 degree sintered samples, when you do the M versus T curve, you can clearly see that the X is equal to 10, and X is equal to 40, they are immediately turning non-magnetic.

So, this is according to the equilibrium phase diagram whereas, in this case we see it is against the prediction of the equilibrium phase diagram. So, what we can say that although in bulk the compositions are known to show order, disorder transformations leading to magnetic, and non-magnetic phases. In amorphous form the interactions are totally different; as a result you get magnetic phases throughout the entire doping concentration of platinum. This is one of the fascinations of studying nano particles, because when the band gap is altered, when we try to play with the finite size effects; then you can clearly manipulate or bring a drastic change in the magnetic property.

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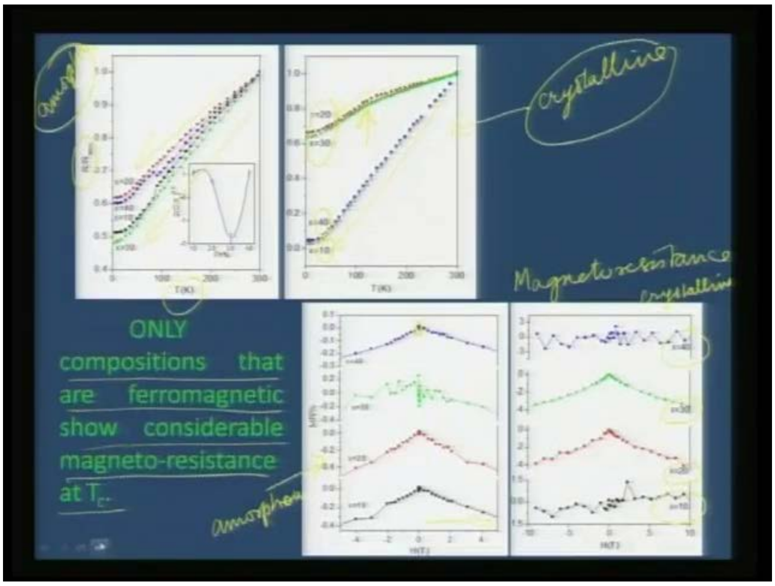

ONLY compositions that are ferromagnetic show considerable magneto-resistance at T_c.

And the same is true, if you try to do rho versus T plot that is the conductivity plot, in case of amorphous alloys as you can see all the compounds are showing same metallicity, and it is very clear they show a periodic metallic transformation. Whereas, the crystalline phases, those which are magnetic namely X is equal to 10 and 40, which is magnetic in amorphous form, they are non-magnetic in crystalline forms.

Therefore, they show a different resistivity pattern compared to X is equal to 20 and 30 which is magnetic according to the phase diagram. And as you would see here in this rho versus T plot it is linearly decreasing, whereas in the case of the true magnetic phases, you can see there is a small change in the slope, specially in the place where there is a Tc. As you would see here ((Refer Time: 12:36)), I just want to point out, because the Tc is somewhere here, as a result you would see a small inflection here going hand in hand.

So, the magnetic phases show a different rho versus T behavior compared to the amorphous pattern, so these are the surprises that we can see. And also if you correspondingly take these compounds ((Refer Time: 13:00)) amorphous and crystalline compounds and if you can make a solid, you sinter it below the crystallization temperature as I showed for cobalt platinum. You have to do that DSC curve and below that crystallization temperature, if you can sinter the compact and if you can do magneto resistance studies, this is for the amorphous pattern or for the amorphous sample.

You can see in amorphous sample almost all the samples show this sort of a MR behavior meaning, the resistance is maximum, but as you sweep the field the resistance drops down. So, even though the magneto resistance ratio is feeble, not of a very high order, but you can see in all cases it is turning that way. Whereas, in the crystalline phases, in the crystalline compounds you can clearly see the non-magnetic phases do not show any magneto resistance. Whereas, the 20 and 30 percent which shows a magnetic transition, they respond nicely and they show magneto resistance behavior.

So, this is going hand in hand, only compositions that are ferromagnetic show considerable magneto resistance at Tc. So, this is a conformation that there is definitely influence of the size effect, when we study the magnetism and electronic property, and you see a systematic change when you go from amorphous alloys to crystalline alloys. Therefore, as we title in the earlier slide, truly iron platinum nano alloys have the potential to turn magnetic against the equilibrium phase diagram predictions, mainly because of the influence of sonochemistry.

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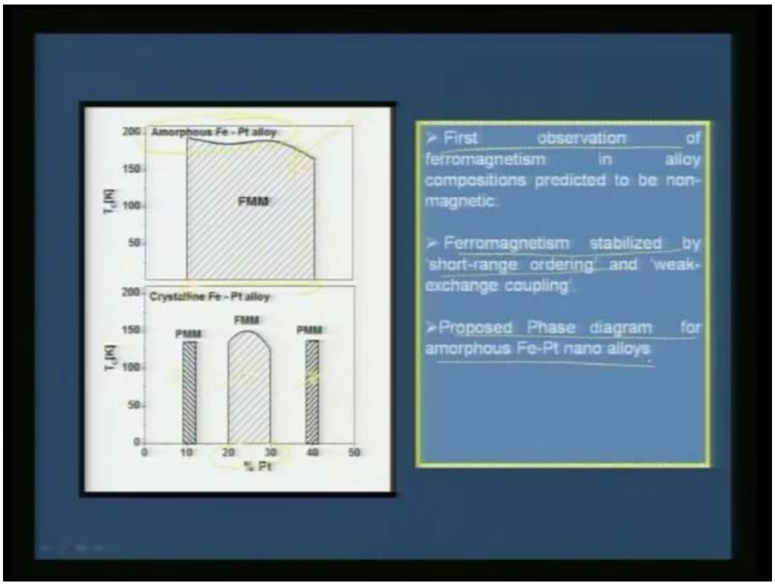

- First observation of ferromagnetism in alloy compositions predicted to be non-magnetic.
- Ferromagnetism stabilized by 'short-range ordering' and 'weak-exchange coupling'.
- Proposed Phase diagram for amorphous Fe-Pt nano alloys

So, therefore, we can even go one step further to sort of propose a new phase diagram for amorphous alloys. So, in crystalline alloy this is a paramagnetic metal, in this phase it is a paramagnetic metal, but in our study we can show that the entire region, so from 10 to

40 is actually turning ferromagnetic metal, this is the beauty of studying the amorphous phase. And we can even go one step further to say, this is the first observation of ferromagnetism in alloy compositions, which are turning magnetic, which is predicted to be non-magnetic. Ferromagnetism is actually stabilized by a short range ordering, and weak exchange coupling; and the proposed phase diagram for the amorphous iron platinum nano alloy is entirely different from the crystalline and platinum phase.

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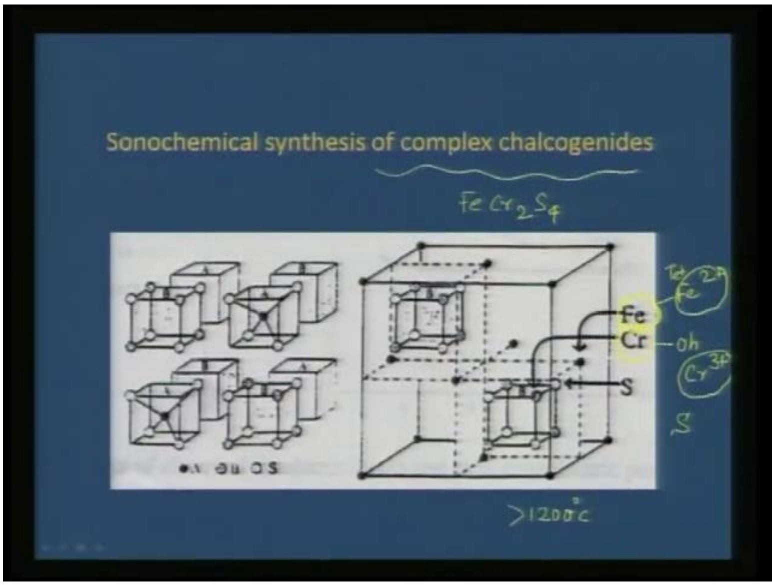

Sonochemical synthesis of complex chalcogenides

Now, to give you another variation and to stress the beauty of sonochemical approach, I am going to show you one example of how complex metal chalcogenides can be formed. For example, if you take FeCr2S4, this is a chalcogenides, this is crystallizing in a spinel phase, and this is a typical representation of spinel, where in a cube there are 8 octants. And each one has a specific metal to oxygen ratio and distribution, and iron occupies all the tetrahedral holes, as Fe2 plus.

And chromium occupies all the octahedral holes as chromium 3 plus, and the close packing is actually done by sulphur atoms, therefore in a cubic closed packed sulphur close packing of this chalcogenides. You actually have the chromium occupying the octahedral void, and iron occupying the Fe2 plus void. And as you would see here ((Refer Time: 17:17)), this is one of a very complex oxides where selectively each of these ions have to go and occupy therefore, preparation is a major challenge. Most of these spinels are prepared above 1200 degree centigrade, now we can try to see if sonochemistry can be used to prepare this oxide.

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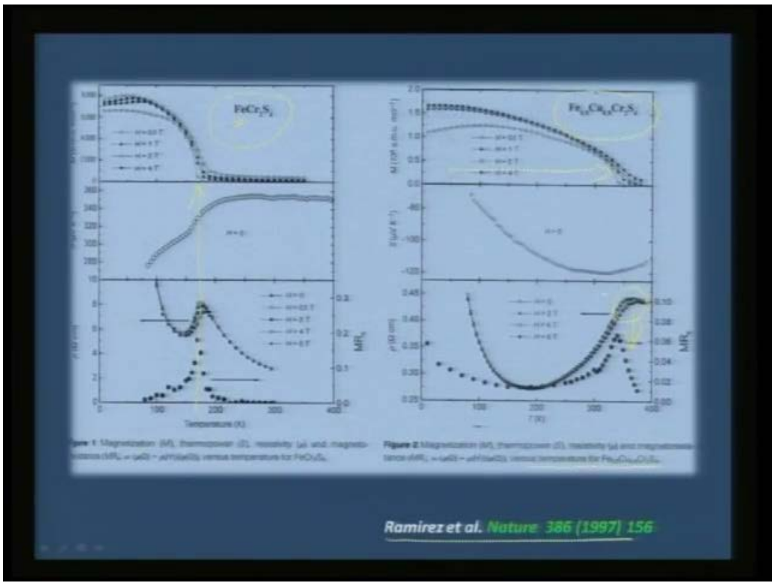

Ramirez et al. Nature 386 (1997) 156

Now, what is the reason why this became prominent, this particular composition was reported by Ramirez and co-workers in US, in the year 1997, where they predicted that these particular groups of compounds are showing unusual magnetism. And unusual electronic property leading to a very large change in magneto resistance values, as you would see here iron chromium sulphide can be formed, and they show a typical ferromagnetic loop somewhere around 180 Kelvin.

And you can see here that, this is the magneto resistance plot for a typical iron chromium sulphide, but if you are going to dope 0.5 of copper instead of iron, then you are talking about iron copper chromium, copper chromium spinel. So, in a solid solution containing equi atomic ratio of iron and chromium in this spinel, you can see from 180 Kelvin, the Tc is actually pushed above room temperature. So, in that case it becomes a very good candidate for magneto resistance effect.

Now, typically you can see there is a colossal change in the resistance, in this particular composition, therefore this was reported to be a very good CMR, colossal magneto resistive compound. And also because it shows Tc above room temperature, this can be thought or explode for commercial applications.

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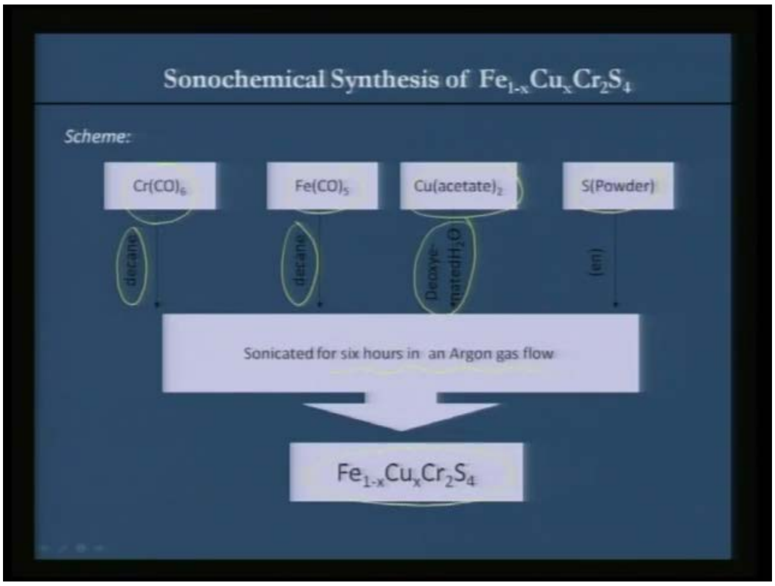

Sonochemical Synthesis of $Fe_{1-x}Cu_xCr_2S_4$

Scheme:

$Cr(CO)_6$

$Fe(CO)_5$

$Cu(acetate)_2$

S(Powder)

decane

decane

Deoxygenated H_2O

(en)

Sonicated for six hours in an Argon gas flow

$Fe_{1-x}Cu_xCr_2S_4$

Now, having this as a motivation, if you try to attempt preparing this iron copper chromium spinel using sonochemistry, this is the protocol that one would follow. You can take chromium hexacarbonyl in decane, iron pentacarbonyl in decane, and copper acetate. Because, copper does not have a copper carbonyl compound, therefore you take this and you try to dissolve it in deoxygenated solution of water, where you try to bubble this with argon or nitrogen and saturate the water, and then you dissolve copper acetate.

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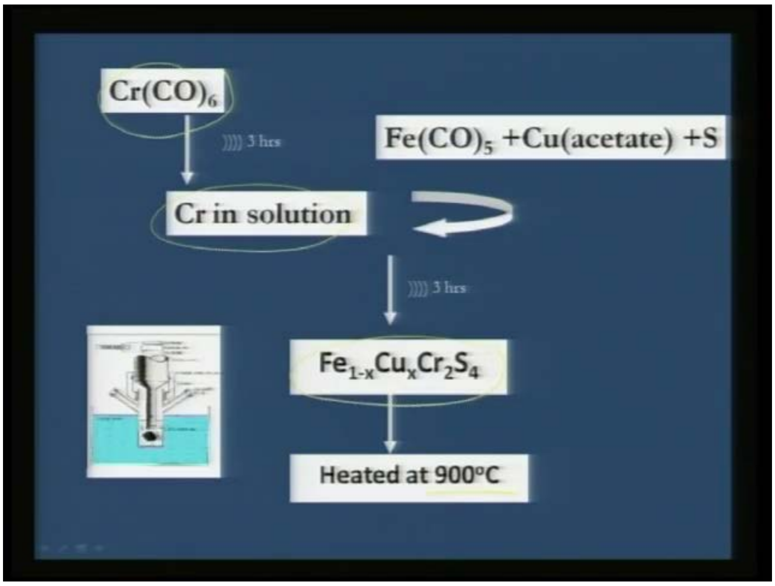

$Cr(CO)_6$

))))) 3 hrs

$Fe(CO)_5$ +Cu(acetate) +S

Cr in solution

))))) 3 hrs

$Fe_{1-x}Cu_xCr_2S_4$

Heated at 900°C

Then you can take ethylene diamine with the sulphur powder, and if you can sonicate it for 6 hours in organ flow, we can expect some sort of a black residue, and incidentally that happens to be that of iron copper chromium sulphide. So, this is the protocol that we follow, we do not just mix everything together, first we take copper chromium carbonyl, sonicate for 3 hours, then you get a black solution which will be like this. And then this chromium is now added to iron pentacarbonyl, then you get the iron copper chromium sulfite, and then because this is amorphous, you try to heat this at 900 degree C.

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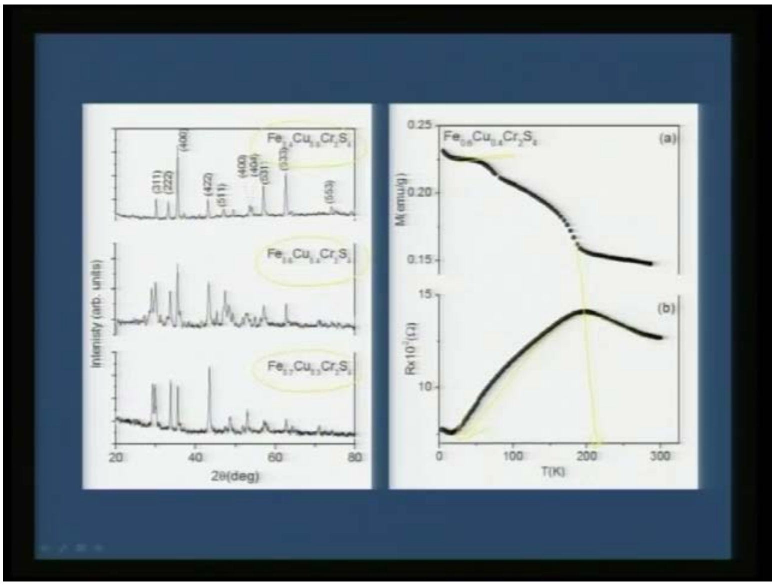

And one would see a very clear evolution of this chalcogenide coming from a simple protocol of sonochemistry. So, you can see, play around with variety of compositions of iron copper in this spinel, and what we have found here is for a optimum concentration of 0.6, 0.4 you can get the Tc to be around 200. And then that also shows a typical metal to insulator transition going with the Tc, therefore one can easily prepare such oxides.

But, what is fascinating is, if you try to take the 30, 70 composition of iron copper, then you see the transition to be, to come somewhere above room temperature. Actually if you do the rho versus resistance versus temperature plot, you would see a typical graph like this. But, if you try to blow up this area you can clearly see that, there is a metal insulated to metal transition that is happening which is going with the magnetic property.

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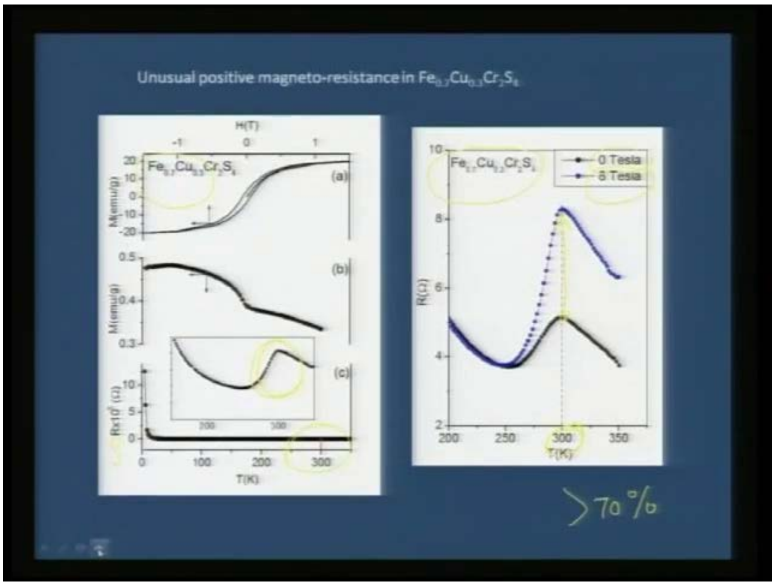

Unusual positive magneto-resistance in $Fe_{0.7}Cu_{0.3}Cr_2S_4$

So, in such case, if you take this particular composition and try to measure the resistance both at 0 Tesla and at 8 Tesla. You can see that there is a huge drop in resistance of this order, which means there is more than above 70 percent of magneto resistance is observed above room temperature for this particular composition, this is reported for the first time in the literature.

So, this is not actually going with the report of Ramirez in nature, because there they have worked on a 50, 50 composition. But, definitely what we find here is that, the there could be a inherent sulphur, a non stoichiometric which can actually induce this sort of huge change in the resistance. Not only that you see here ((Refer Time: 22:57)) that when you apply magnetic field, then the resistance is higher compared to the resistance at 0 Tesla which means the magneto resistance here is not negative, but it is positive.

So, what is reported is a negative magneto resistance, but what we see here is a positive magneto resistance at room temperature, therefore this is also typical of the method that we adopt to prepare the sulfurs. So, this is reported for the first time it has appeared in journal of applied physics, in the year 1990, in year 2008.

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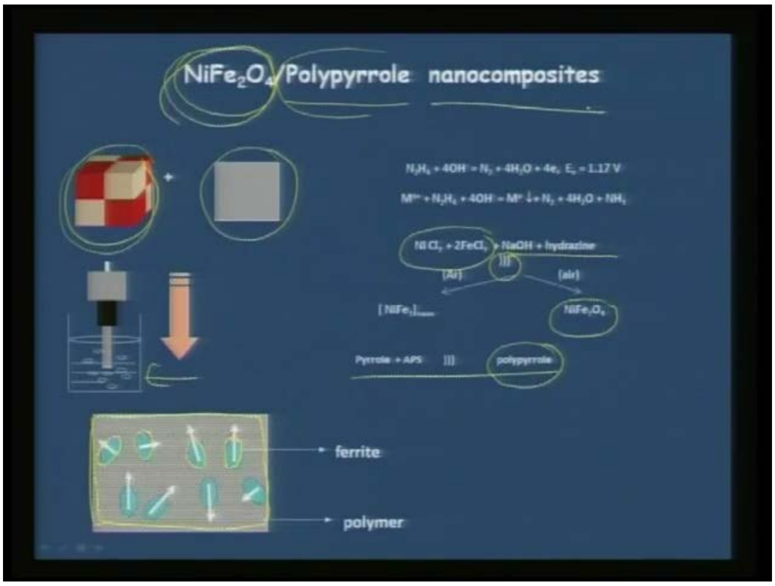

$NiFe_2O_4$/Polypyrrole nanocomposites

$N_2H_4 + 4OH^- = N_2 + 4H_2O + 4e,\ E_o = 1.17\ V$

$M^{n+} + N_2H_4 + 4OH^- = M^0\downarrow + N_2 + 4H_2O + NH_3$

$NiCl_2 + 2FeCl_3 + NaOH$ + hydrazine

)))

(Air) $[NiFe_2]_{nano}$

(air) $NiFe_2O_4$

Pyrrole + APS))) polypyrrole

So, I will also take you to another example, where we are actually trying to study the electronic conductivity of oxide polymer nano composite. So, what is beauty here polypyrrole is a conducting medium, and if you can coat this polypyrrole which is a good conductor. And intrinsically if you can coat this nickel ferrite nano particles, then you can actually effect the conductivity of this nickel ferrite, because nickel ferrite is ferromagnetic, it is actually used as a spin injection layer in the magneto resistive device now a days.

And nickel ferrite is a insulator, so if you want to see some sort of a magneto resistance effect, then one can try to intrinsically coat this with polypyrrole. So, how can you do that, there is a protocol by which one can apply, if you take pyrrole and APS and you sonicate, it is possible to prepare polypyrrole. Therefore, you take polypyrrole, you try to polymerize pyrrole in side to as and when you are trying to generate nickel ferrite.

So, you are generating two things, you are taking the salts of nickel, and you are trying to sonicate it by reduction, hydrazine method. So, as you are generating nickel ferrite you are also trying to in side to polymerize, so both are happening in a single pot that is what we have mentioned it here. So, you have a polymer support, and then you have a nickel ferrite a spinel which is generated, and all in one chamber.

And in that case, the sort of mechanism that we foreseen is you get nice nickel ferrite particles, and these may be randomly oriented. But, they are actually embedded or intrinsically coated in a polymeric matrix; so you actually generate a nano composite of this choice.

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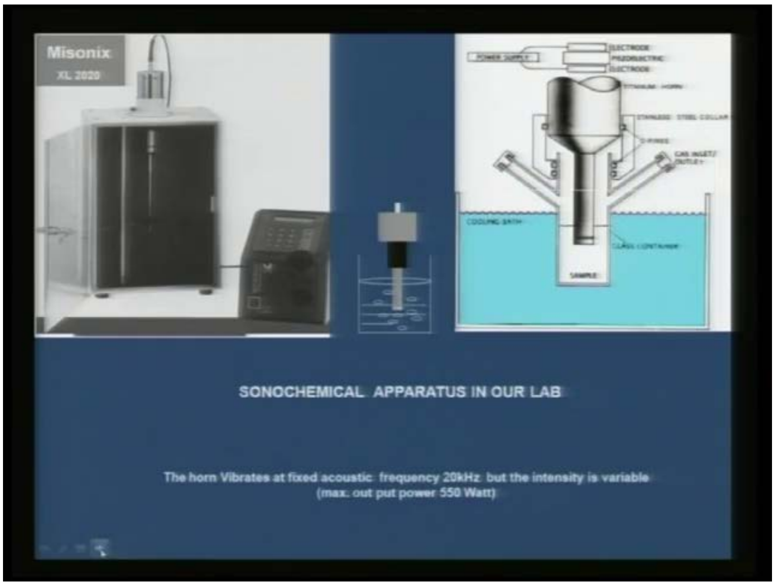

SONOCHEMICAL APPARATUS IN OUR LAB

The horn Vibrates at fixed acoustic frequency 20kHz but the intensity is variable (max. out put power 550 Watt)

And as I have discussed in the last lecture, this is the machine that we use in our laboratory and this is the cartoon of the sonochemical cell that we use.

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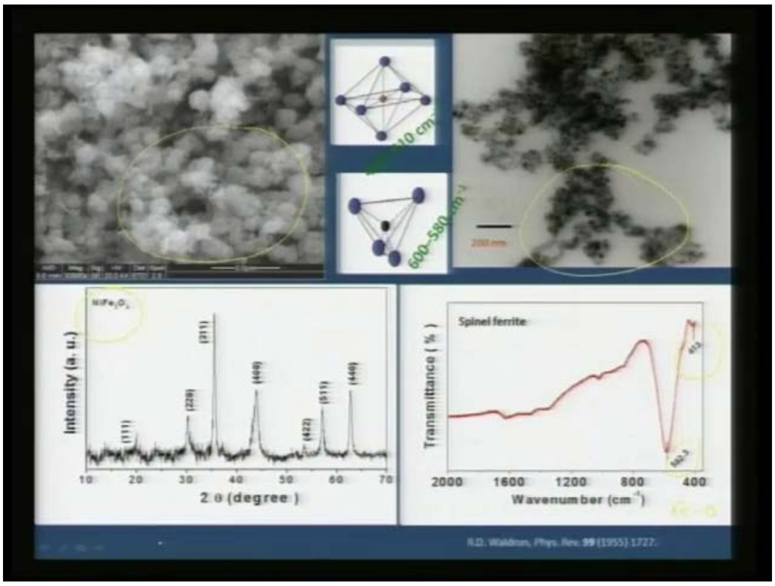

R.D. Waldron, Phys. Rev. 99 (1955) 1727.

Individually if we prepare this spinel ferrite and the polypyrrole, we can characterize it before we make a composite out of it. And typically the particles are of the order of 20 to 30 nano meter, you can see the Tm morphology of this nickel ferrite nano particle, and you can see the SEM of the nano particles. And they are more like waferic clusters of a oxides which are present. And typically you can see the iron oxide stretching frequency which is characterized by this, and also the spinel pattern which is emerging from the XRD. So, all we can clearly say is that we have a clear proof that we can make a nickel ferrite nano powders.

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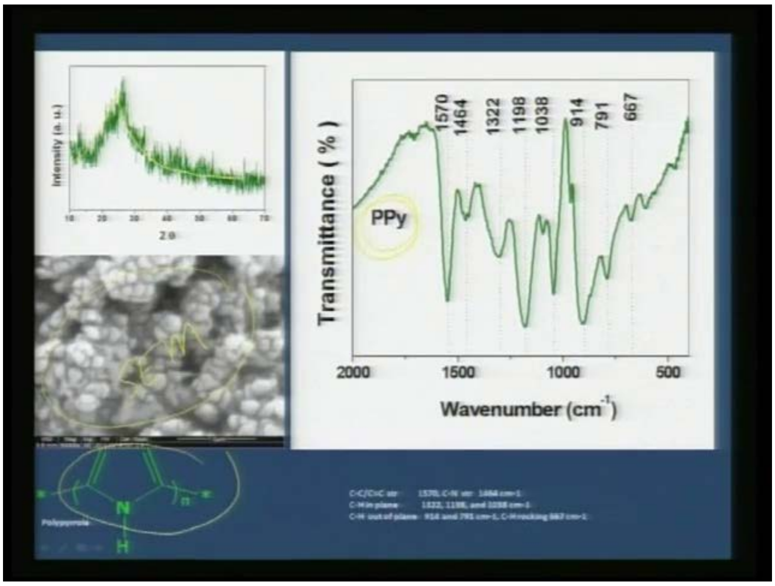

C-C/C=C str 1570, C-N str 1464 cm-1

C-H in plane 1322, 1198, and 1038 cm-1

C-H out of plane 914 and 791 cm-1, C-H rocking 667 cm-1

And similarly, we can make polypyrrole out of sonication, take a pyrrole and sonicate it this is the a SEM feature, which clearly shows that you can get fine particle polypyrrole either as a very thin film form which can be coated on the sides, or you can isolate this as a powder. And this will not be crystalline, because you can see here it shows a typical X-ray amorphous pattern, because it is a polymeric unit, nevertheless the IR shows typical stretching frequencies for polypyrrole. So, individually using sonochemistry we can establish the synthesis of both ferrite and the polypyrrole.

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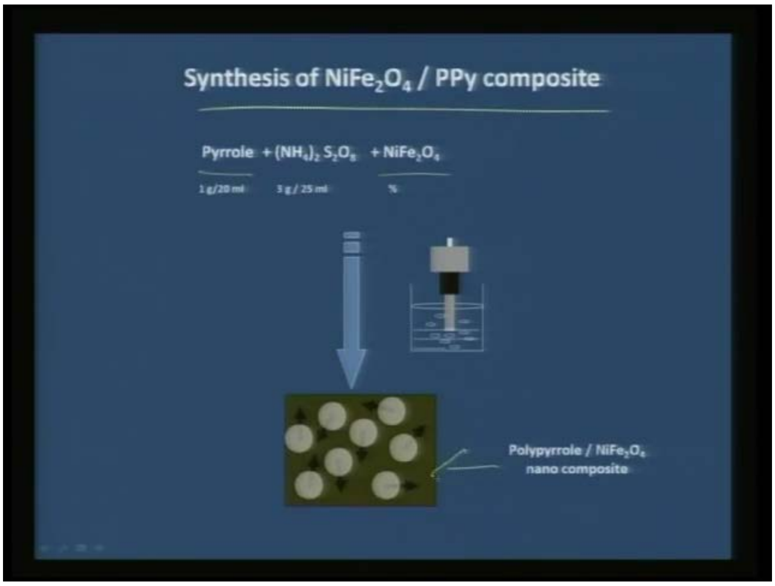

Synthesis of $NiFe_2O_4$ / PPy composite

Pyrrole + $(NH_4)_2S_2O_8$ + $NiFe_2O_4$

1 g/20 ml　3 g/25 ml　%

Polypyrrole / $NiFe_2O_4$ nano composite

Now, we can go one step further to prepare these composites, and as I already discussed with you, take pyrrole then nickel ferrite, and try to in situ polymerize then you can get this sort of composite.

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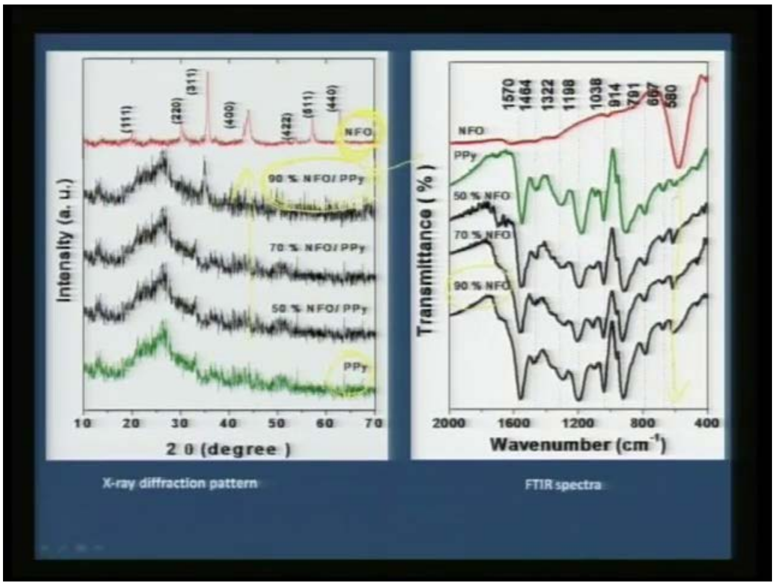

X-ray diffraction pattern

FTIR spectra

And this is typical a X-ray graph for the composite, as you would see here PPY which is the polypyrrole without any loading of nickel ferrite. And as you keep loading nickel ferrite even up to 90 percent of nickel ferrite in polypyrrole, you still see a amorphous pattern that is the beauty. What that means, that there is a intricate mix of the pyrrole over every single particle of nickel ferrite as a result, you do not see any X-ray pattern for nickel ferrite.

Whereas just the nickel ferrite prepared by sonochemistry gives a clear XRD pattern, so even with 10 percent, in other words even with 10 percent of polypyrrole, you can surface coat this powders effectively, so as to mask the crystallinity. So, it is possible to surface coat all this nickel ferrite particles using polypyrrole. And in that way you are actually bringing about a conducting media between any two given nickel ferrite particle.

Because, the outer cluster coating that is happening due to pyrrole is actually a conducting matrix, and this is also clearly proved by the IR pattern, this is the typical stretching pattern for nickel ferrite, and you would see only with 90 percent of nickel ferrite you see this intensity of the peak growing. So, this clearly proves that you can intimately coat the nickel ferrite particles with polymer.

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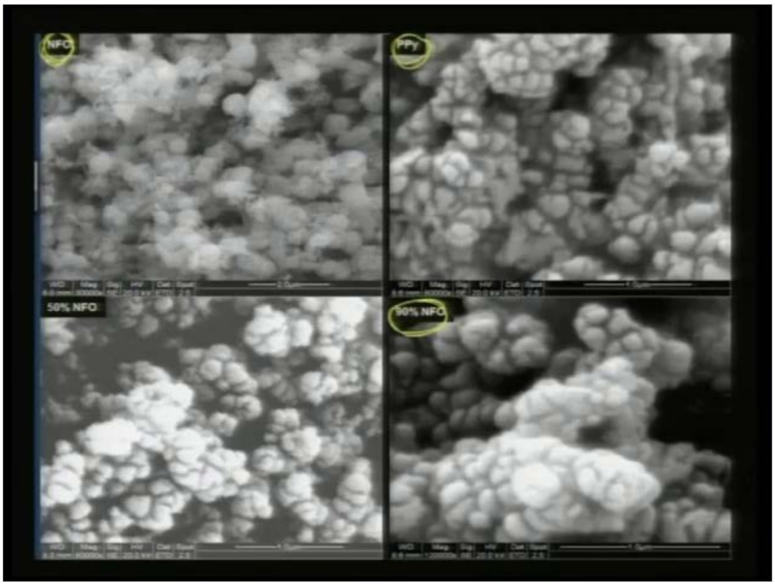

And you can also see that, there is typically no change in the morphology for polypyrrole and even 90 percent nickel ferrite; which means the morphology of the polypyrrole is retained even for a 90 percent composition whereas, nickel ferrite has a different SEM image.

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Transmission electron micrograph of ferrite (left) and nanocomposite with 50% ferrite loading (right)

In the next slide, you can see the TM pattern of this nickel ferrite, this I have already shown the as prepared one, and how the ferrite loading alters the particle size of this composite.

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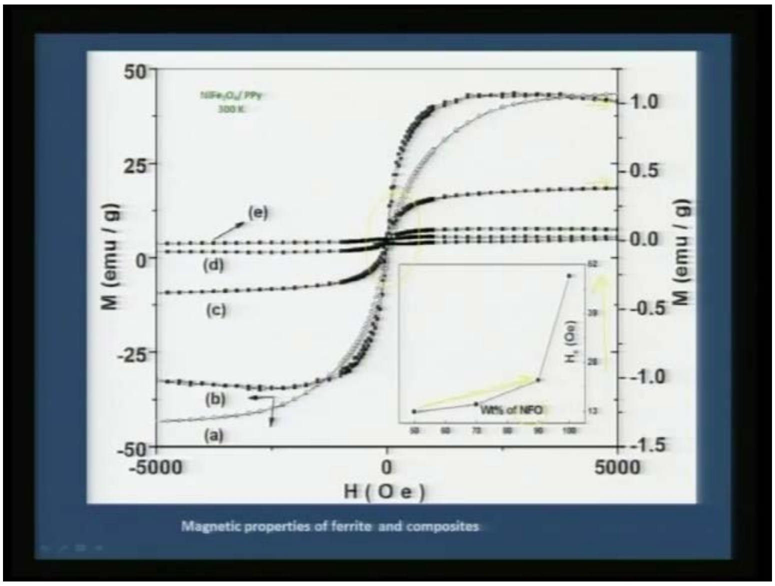

Magnetic properties of ferrite and composites

And the magnetic property shows a very clear systematic change with the increasing loading of nickel ferrite, you can see the magnetic signal is changing and a very clear loop is seen in the middle, and typically indicating these are soft magnets. And if one would plot the loading concentration of nickel ferrite, as a function of the coercivity one can say that there is a plateau between 50 to 90 percent.

So, the coercivity does not seem to be largely affected by the coating, so although there is very small variation from 20 to 20 oersted. So, the coercivity does not seem to be varying much, although the magnetic moment is sufficiently different in the polypyrrole coated nickel ferrite powders.

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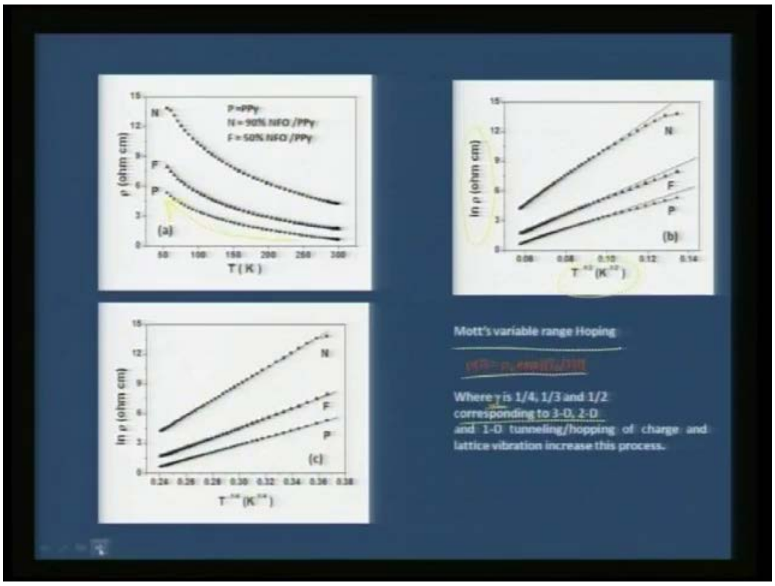

Mott's variable range Hoping

[illegible]

Where γ is 1/4, 1/3 and 1/2 corresponding to 3-D, 2-D and 1-D tunneling/hopping of charge and lattice vibration increase this process.

And you can also make a plot of the resistivity versus temperature plot, showing that they all are magnetic, and they are ferromagnetic, as well as they are conducting only at low temperature. You see this upturn in resistance mainly that is coming, because of the conduction mechanism, therefore if you plot log rho versus T to the power minus half. This is typically a model related to Mott's variable range hoping, and if you make a plot of this, you can see that there is almost a good agreement over the entire range for these particles.

Indicating that, there is a 3 D variable range hoping when there is larger doping of nickel ferrite whereas, with lean doping of nickel ferrite. The gamma value that is the parameter for variable range hoping differs from 1 by 4 to half indicating that it goes through a only tunneling, when the loading concentration of nickel ferrite is very less. So, we can make a very systematic analysis of how the properties are varying with respect to nickel ferrite loading.

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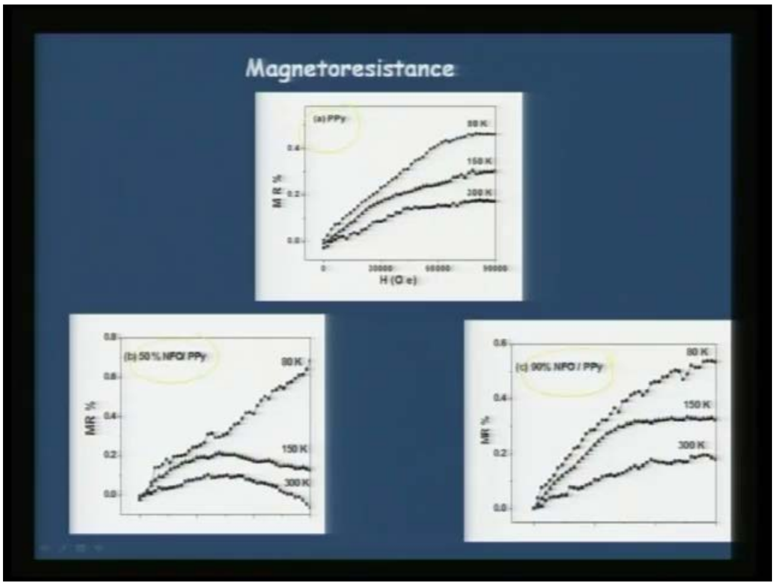

Magnetoresistance

And we can also try to see, whether this has any pronounced effect on magneto resistance, we have seen that although magneto resistance is not highly altered. Yet that seems to be a systematic change for a 50 percent or a 90 percent doping compared to polypyrrole. So, in terms of magnetic influence definitely it does change whereas, the magneto resistance does not seem to be much altered with the nickel ferrite loading.

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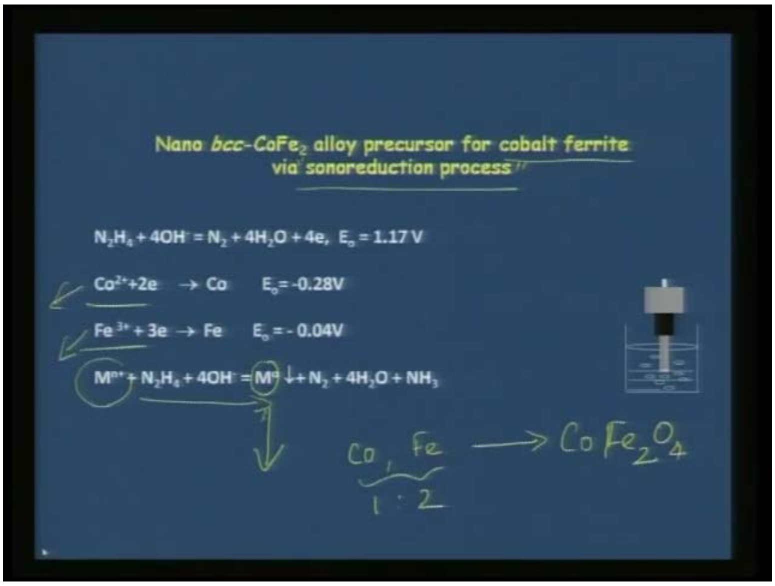

Nano *bcc*-$CoFe_2$ alloy precursor for cobalt ferrite via sonoreduction process

$N_2H_4 + 4OH^- = N_2 + 4H_2O + 4e,\ E_o = 1.17\ V$

$Co^{2+} + 2e \rightarrow Co \quad E_o = -0.28V$

$Fe^{3+} + 3e \rightarrow Fe \quad E_o = -0.04V$

$M^{n+} + N_2H_4 + 4OH^- = M^0 \downarrow + N_2 + 4H_2O + NH_3$

$\underbrace{Co, Fe}_{1:2} \longrightarrow CoFe_2O_4$

And one more example that we can think of is, using this we can prepare n number of ferrites using a sonoreduction process. So, far I told you how we can prepare alloys, and how we can trap these alloys, and how we can try to make composites with polymer support. Here is one example, where we can use a different variety of chemical processes, but coupled with sonochemistry.

Therefore, we coin this as sonoreduction, because this is typically a reduction process, where you take a metal salt and try to reduce it with hydrazine to prepare the corresponding nano metal. But, what is interesting is the influence of sonochemistry on the resulting metal powder seems to be enormous, even though you are using a conventional chemical reduction route.

So, let us take the case of iron or cobalt, now this can be reduced into corresponding cobalt or iron powder in sonochemistry, but you do not have to resort to any carbonyl or nitrosyl compounds of iron or cobalt. You can take simple metal salts, instead of costly carbonyl or nitrosyl starting material, and you can reduce it to corresponding metal. Now, what will happen suppose I take cobalt, and iron, and my final aim is to prepare cobalt Fe2O4 which is final. So, which means I will take these two salts in the ratio 1 is to 2, and then I will try to reduce it and oxidize this to cobalt Fe2O4. There are interesting things that are happening which we will see in the next slide.

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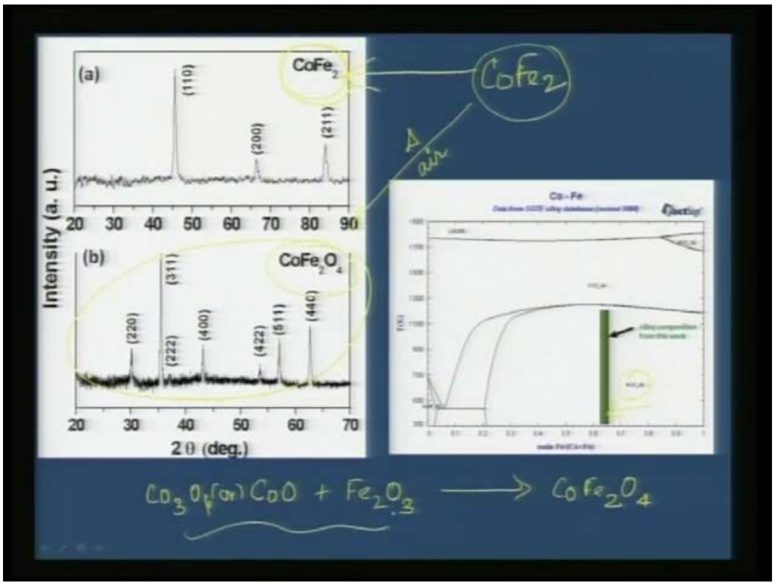

Co_3O_4 (or) $CoO + Fe_2O_3 \longrightarrow CoFe_2O_4$

So, we will see in the next slide, how this ferrites can be made, as you would see from this two X-ray pattern interesting things happen. Now, when you take the cobalt and iron salt, and when you try to reduce it instead of passing oxygen, if you are going to do this in argon atmosphere, and if you are going to change to oxygen or air, you can see the corresponding end products are not essentially the oxide.

For example, if you bubble it in argon atmosphere, the X-ray pattern that you get is peculiar, and it is quite different from what we expected as cobalt Fe2O4. So, if you carefully look at this pattern ((Refer Time: 36:05)), this amounts to CoFe2 which is a ferromagnetic alloy. And in the literature there is no way that you can make this alloy using a wet chemistry route, you would always end up with a oxide. And the only way that you can prepare such a alloy is by conventional metallurgical route, where you can use a crystal growth method or so to grow a CoFe2 alloy.

But, it has never been reported in the wet chemistry approaches to isolate a cobalt Fe2 alloy of this form with a clear single phase. What is the advantage, if you can prepare such alloys, then it is possible for us to make any sort of shapes of these alloys, because it is easy to make the samples of any shape with alloy compared to a oxide. So, if you could make it into a rod shape or a pellet shape, then you can correspondingly try to decompose this into the corresponding ferrite.

For example, if I now take this alloy and try to heat it in air, then what I expect is a spinel ferrite which is nothing but CoFe2O4. So, this is one of the first time that we could ever show that such alloy, we are talking about CoFe2, and this is based on the mole percent of this. So, you are actually talking about a alloy composition somewhere here, which is supposed to be actually bcc, but what we are getting is actually a fcc CoFe2 alloy. And this is the first time we have demonstrated that using sonochemistry, you can prepare alloy of any nature if you can do this reaction just in argon.

So, if you instead of taking argon, if you directly bubble through either air, compressed air or if you can do it in oxygen atmosphere straight away in one shot, you can actually get CoFe2O4. As you would know, the conventional solid state method you take CoO plus Fe2O3, and when you heat it this can be either CoO or Co3O4 for that matter, then the corresponding oxide would be CoFe2O4, if you take in stoichiometric proportion. So, this is the conventional way of preparing, but for the first time we could observe that cobalt ferrite can be made even using a amorphous alloy as a precursor.

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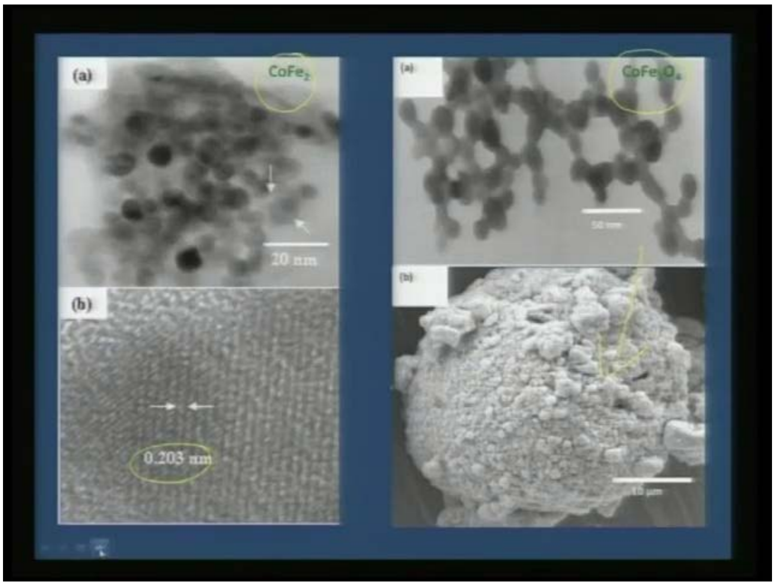

And you can see here this is the morphology of CoFe2 alloy, and this is the morphology of CoFe2O4, and this is the SEM pattern of the oxide powder that we can prepare. And these are the cobalt Fe2 nano particles which are prepared, and the dimensions of the lattice spacing exactly matches with that of the Fe2 phase, therefore we can clearly prove that it is so.

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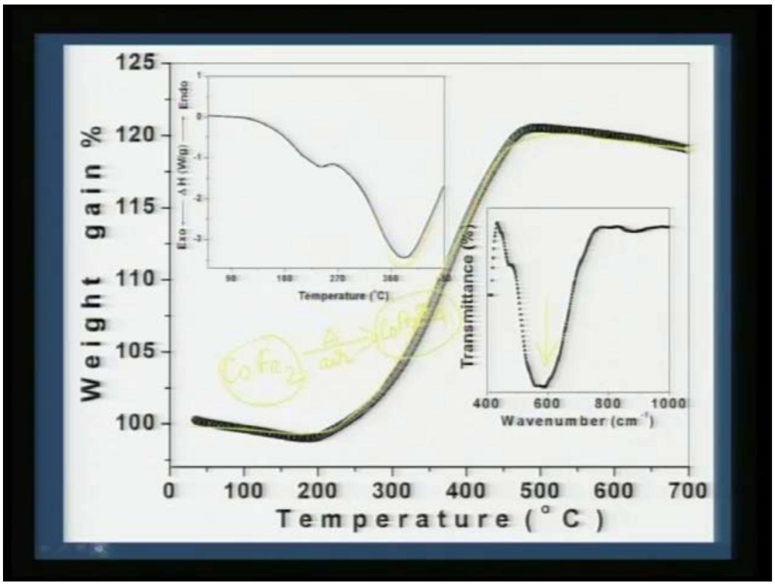

But, from a chemist point of view it is much easier for us to ascertain, whether it is really the alloy or the oxide itself. How do we do that, take the alloy powder that you prepare, and try to do TG, so usually we are all familiar that TG we always think about weight loss, when you heat any sample. But, if you are actually going to take CoFe2, and if you are going to heat it in air, then you would not expect a weight loss, but you should expect a weight gain.

Because, it is going from CoFe2 to CoFe2O4, therefore it has to be a weight gain, and as you can see here interestingly it shows a clear increase in weight. And this weight gain say from 100 to 121 exactly corresponds to the weight gain that you would expect out of CoFe2O4. So, just simple TG technique can be used to ascertain what is exactly going on and by this way we have make sure that you are exactly isolating a alloy powder of this form.

And you can also see corresponding to that is a typical endothermic conversion, because there is a weight up take due to conversion from alloy to oxide, so that is clearly seen in the DTA curves. And we also see the formation of the oxide is pronounced due to this typical stretching which observes at 600 centimeter inverse, conforming that the oxide formation is indeed correct.

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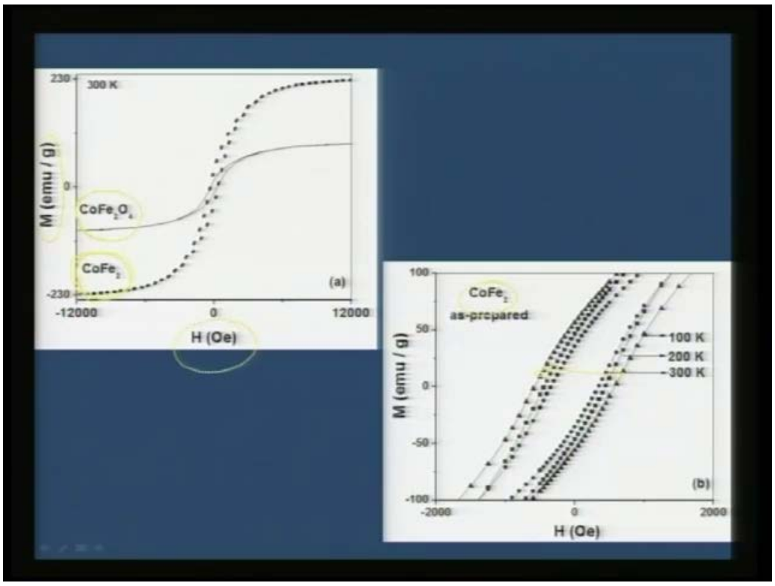

And we can also clearly distinguish between the alloy and the oxide powder, if you take a typical M versus H loop, the alloy composition will have more moment compared to the oxide composition. So, you clearly see the change in the magnetization values between the alloy and the compound. And as you see here the change in the coercivity also it is there, for the alloy as prepared powder, if you are going to do a temperature sweep saying that this is truly a ferromagnetic alloy.

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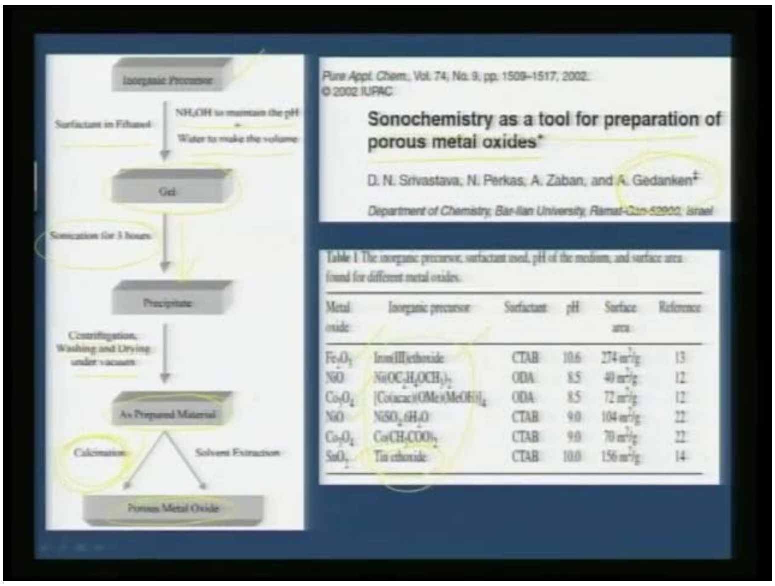

Inorganic Precursor

Surfactant in Ethanol

NH_4OH to maintain the pH

+

Water to make the volume

Gel

Sonication for 3 hours

Precipitate

Centrifugation, Washing and Drying under vacuum

As Prepared Material

Calcination

Solvent Extraction

Porous Metal Oxide

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Sonochemistry as a tool for preparation of porous metal oxides*

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Table 1 The inorganic precursor, surfactant used, pH of the medium, and surface area found for different metal oxides.

Metal oxide	Inorganic precursor	Surfactant	pH	Surface area	Reference
Fe_2O_3	Iron(III)ethoxide	CTAB	10.6	274 m^2/g	13
NiO	$Ni(OC_2H_4OCH_3)_2$	ODA	8.5	40 m^2/g	12
Co_3O_4	$[Co(acac)(OMe)(MeOH)]_4$	ODA	8.5	72 m^2/g	12
NiO	$NiSO_4 \cdot 6H_2O$	CTAB	9.0	104 m^2/g	22
Co_3O_4	$Co(CH_3COO)_2$	CTAB	9.0	70 m^2/g	22
SnO_2	Tin ethoxide	CTAB	10.0	156 m^2/g	14

Now, as last example I would like to cover this issue that sonochemistry can be used as a tool for preparation of porous metal oxides, and this was actually exploited more by Gedanken's group. For example, you think of just technologically important iron oxide, or you think of Co3O4 or you can think of tin oxide, nickel oxide which is anti ferromagnetic. You can prepare any sort of precursors, any sort of oxides using corresponding precursors.

So, if you are thinking of Fe2O3, there are protocols by which you can prepare that nicely using iron 3 ethoxide, if you want to prepare tin oxide, and then you can use tin ethoxide. The general protocol that Gedanken's group has followed in preparing complex metal ions, or porous metal oxides start with the inorganic precursor like a ethoxide as listed here, take this with a surfactant in ethanol and try to form a gel by adding ammonium hydroxide.

So, essentially going to precipitate this as a hydroxide, so you get a gel here and gel you try to sonicate it for 3 hours, then you get a precipitate from this gel. And this precipitate you can centrifuge, you can wash and dry under vacuum, and then you can get a ash prepared compound. And this ash prepared compound and be either amorphous or it can be crystalline directly indicating that you are getting something.

So, if it is amorphous, then you try to calcine it and try to see the porosity of this metal oxides they are indeed porous. Now, this can be adopted for several applications, because there are several devices where you would like to have a porous metal oxide in such case, you follow this sort of a protocol. Whenever you do not require a porous metal oxide, then you can completely eliminate this protocol and go for a simpler one, like the sonoreduction method that I was talking about, where you just reduce it and immediately convert it into oxide, even without involving calcinations.

So, that is the beauty, because most of the wet chemical routes it involves isolation of a metal oxide, and then converting it into a crystalline phase by another protocol involving calcinations for long hours or for short time. But, what we see from sonochemical approach is, you do not even need to calcinate the compound directly by bubbling it, because of the cavitations, and because of the high temperature that you can generate locally. These compounds which prepare they are not only amorphous in the beginning, but they tend to crystallize as you sonicate it for few hours.

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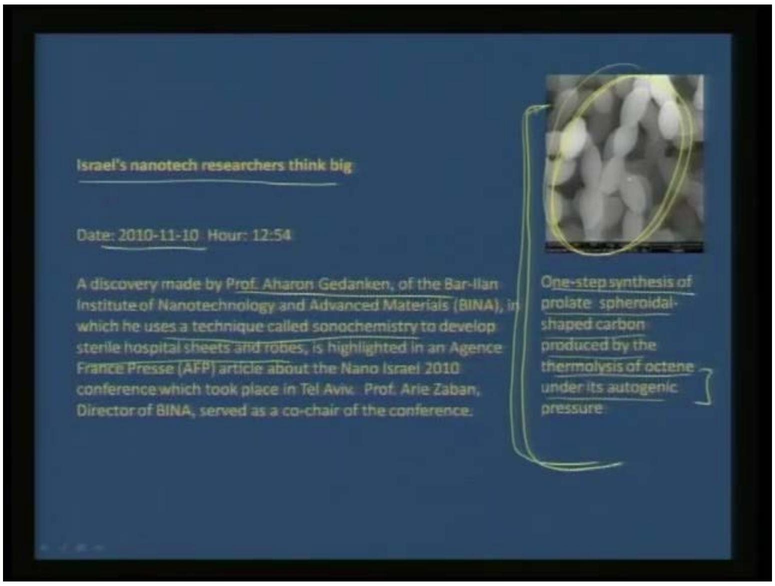

Israel's nanotech researchers think big

Date: 2010-11-10 Hour: 12:54

A discovery made by Prof. Aharon Gedanken, of the Bar-Ilan Institute of Nanotechnology and Advanced Materials (BINA), in which he uses a technique called sonochemistry to develop sterile hospital sheets and robes, is highlighted in an Agence France Presse (AFP) article about the Nano Israel 2010 conference which took place in Tel Aviv. Prof. Arie Zaban, Director of BINA, served as a co-chair of the conference.

One-step synthesis of prolate spheroidal-shaped carbon produced by the thermolysis of octene under its autogenic pressure

This is a, these are some of the news that is coming which I wanted to highlight that in Israel’s nano tech research, which was reported this month. We found that Gedanken’s group has made another contribution, where he has used sonochemistry to develop sterile hospital sheets and robes, and this has been patented; and they are trying to look for variety of applications. They have also tried to observe another interesting aspect in the recent past, which is come out in the literature, a one step synthesis of prolate spheroidal shaped carbon produced by thermolysis of octene under it is autogenic pressure.

The autogenic pressure is nothing but sonochemistry here, but what they found was when they thermolyse several of hydro carbons like octane, in this case they found that typically this particular prolate spheroidal shape of carbon, they are able to isolate. And this seems to be critical characteristic of sonicating any hydro carbon in using ultra sound, and there is lot of interesting applications that are foreseen for this sort of compounds.

So, several things are happening, it is not just a merely preparing oxides or alloys of different kind, but several other applications can be envisaged, and worked out using sonochemistry. I will also touch upon one more interesting application which I have not covered in general, under the title of material synthesis. This is another company, which is using ultra sound technology in the pharmaceutical industry.

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Ultrasound
Technology
in the Chemical
Industry

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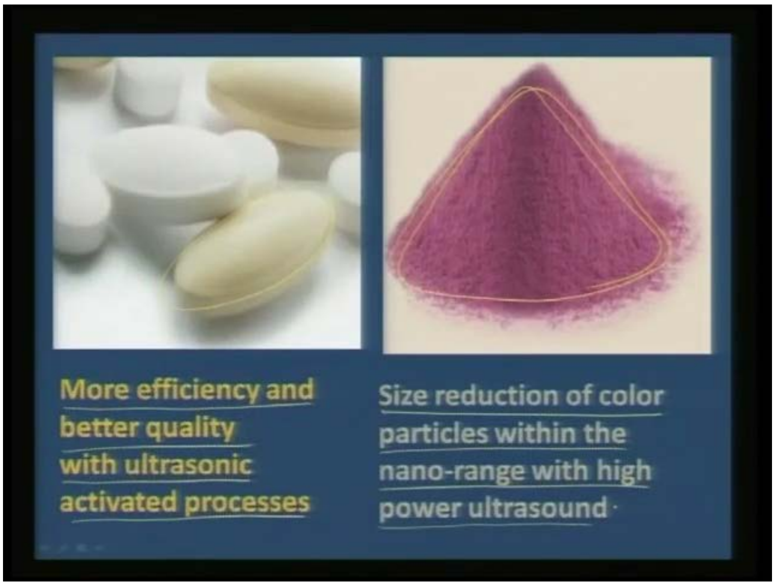

More efficiency and better quality with ultrasonic activated processes

Size reduction of color particles within the nano-range with high power ultrasound

As you would see in the next slide, more efficiency and better quality with ultrasonic activated process are envisage in the drug making company. So, drug and pharma industries are also seriously involved in using ultrasound to make good and better quality medicines. Specially when you are making tablets like this, what is critical is that you need a mono sized one to get a good compact; otherwise your tablet will crack, if you are going to have a different size range. So, a mono sized particle of your medicine is very important for pharma industry, therefore they are resorting to sonicating the sort of compounds that they are finally, planning to take it.

For example, the real drug may be actually dispersed in safe matrix, it could be a polymer or it could be a oxide, some matrix where such tablets are made. So, the base material has to be mono sized, and that is what we see here ((Refer Time: 48:16)), you can see this is one of the powder that the pharma industry makes, and size reduction or of color within the nano range is emphasized which is possible using ultra sound. So, several applications are there which are hidden, not necessarily coming out in open as a material synthesis.

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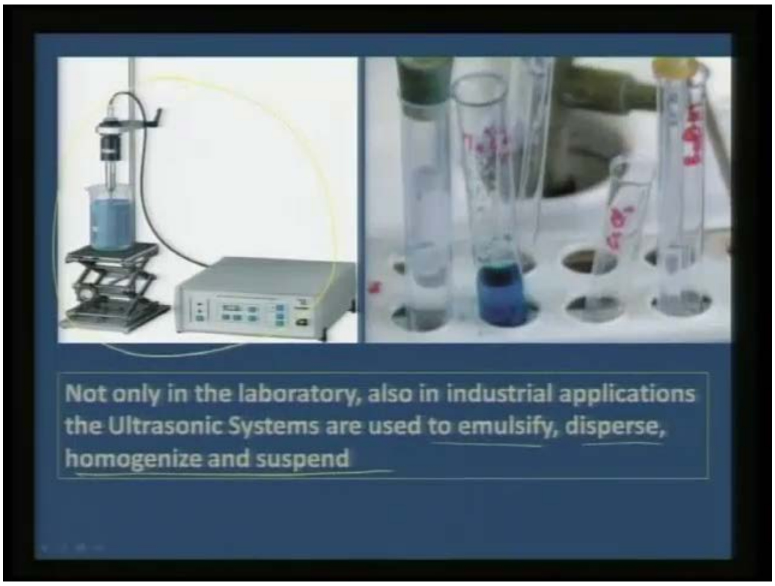

Not only in the laboratory, also in industrial applications the Ultrasonic Systems are used to emulsify, disperse, homogenize and suspend

And therefore, in the last two exercises I have told you, how the ultra sound can be used, this is again a view graph of how the pharma industry is actually using ultra sound. In emulsifying, in dispersing, in homogenizing, the compounds ultra sound is regularly used; and this is one of the simplest setup that any laboratory can afford to manipulate or to engineer new materials. So, I have highlighted in the last 2 lectures, how ultra sound can be used for materials synthesis. But, as you would see from the history, it was the organic people who have exploited in the earlier years how to prepare organic molecules.

And how to make some conversions very effective, and also improving yield, and they have come out with some theme saying that, a only cation reactions, involving cations are speeded up by ultrasound, free radicals are effected by a ultrasound. And lot of understanding is there now in the organic synthesis on the use of ultrasound, and also in the last 2 lectures I have highlighted several examples of how we can make inorganic solids using ultrasound waves. So, I stop here and we will continue with other non conventional chemical routes in the next few lectures.