

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

Module - 1
Lecture - 7
Preparative Routes Unconventional Microwave Technique

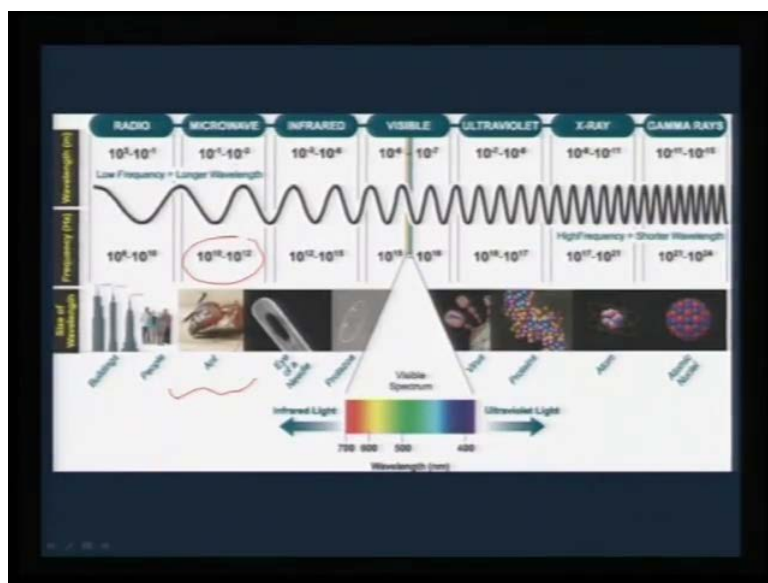
We have been looking at the synthetic aspects of materials, in the past few lectures. And there is a significant divide between chemical approaches and nonchemical approaches.

(Refer Slide Time: 00:33)



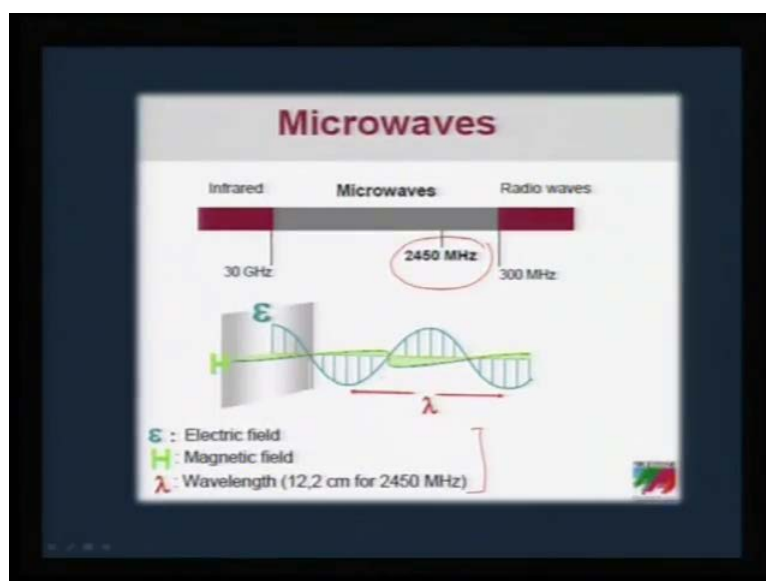
I have highlighted to you in one of the earlier lectures about, sonochemical synthesis where, we use ultrasound waves to synthesize materials. In this lecture, I would like to focus on microwave processing of materials and mainly this is coming under the category of unconventional wet chemical approach. As you would see, in the following slides how electromagnetic radiation can be effectively used for synthesizing materials. So, in the next few slides, let me highlight to you the importance of electromagnetic radiation interaction with matter, and how this can be usefully exploited for making materials, just to familiarize yourself where we stand.

(Refer Slide Time: 01:25)



As far as this approach is concerned, in the electromagnetic spectrum, this is the microwave region and the size of wavelength of this order, where it is from centimetre to millimetre, a size of ant we can say. And the frequency is of the order of 10 power 10 to 10 power 12, therefore it is usually categorized under Giga Hertz or Mega Hertz. And one of the longer wavelength region, next to radio wave and therefore, this is sandwiched between radio wave and infrared. And as you know several of this electromagnetic radiation can be used, either in the study of synthesis or in the study of spectroscopy of the materials.

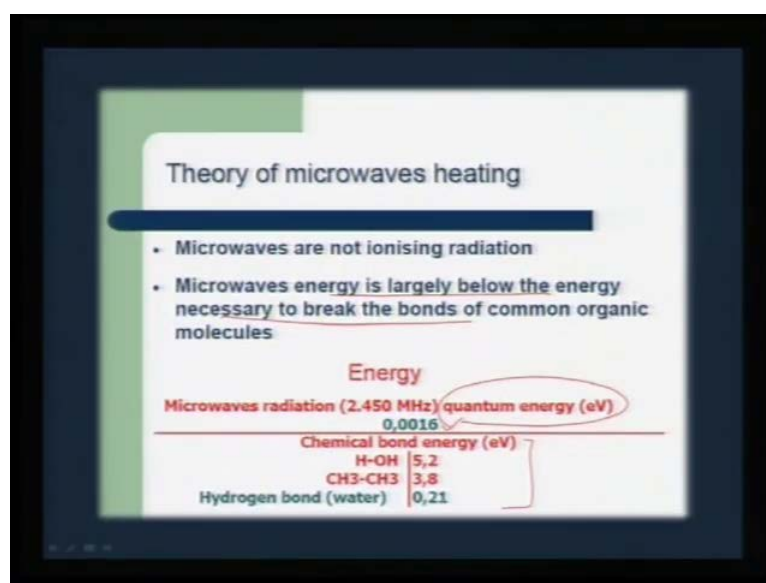
(Refer Slide Time: 02:21)



As we saw from the earlier slide, microwave is placed between radio wave and infrared, usually the region that is of more interest for material synthesis is this 2.4 Giga Hertz region. And just another mention, about this electromagnetic wave is you have two vectors, one is a electrical vector and a magnetic vector, which are perpendicular to each other and that constitutes your electromagnetic wave.

Therefore, if a material processes some dipole, then the electric field component has to interact with the matter or if the material has a moment, magnetic moment, then the magnetic vector of the electromagnetic radiation should interact with such a matter. So, either way when electromagnetic radiation is interacting with molecules or materials, there will be some response of different order. So, that way we will be actually, using the electrical vector of the microwave radiation to interact with matter, and we would see in the next few slides, what governs this interaction.

(Refer Slide Time: 03:37)



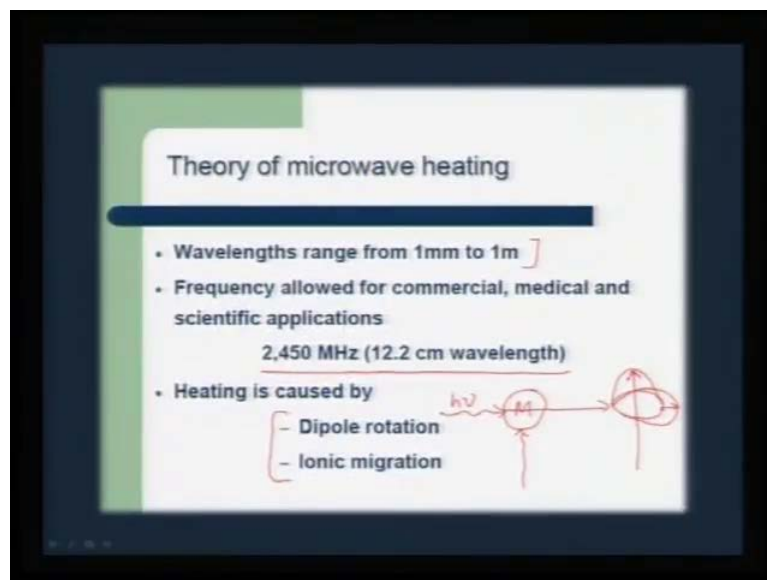
As far as the theory of microwave heating, microwaves are not ionizing radiation, they are soft, therefore this is not a ionising radiation, but largely this can be used to excite or lift the potential energy of the molecules. So, when the potential energy of a molecule is lifted up, then the kinetic energy barrier or the energy barrier that is restricting between, the product and the reactant will be lowered considerably.

So, we are trying to use the potential energy of this molecule, to overcome the energy barrier in order to give, resultant products. As you would see microwave energy is

largely below the energy necessary to break bonds, therefore it is not going to make or break any bonds, but it is going to interact. But, the heating effect does not come from breaking of bonds.

So, if you compare the quantum energy, that is available from microwave radiation, let us say 2.5 Giga Hertz, then you are talking about a very low electron volt energy, and this energy is not sufficient to break any bonds. For example, think of a hydrogen oxygen bond 5.2 e V or hydrogen bonding in water is of 0.21, so even it cannot overcome the hydrogen bond. Therefore, the secondary effects of microwave interaction with matter is what is going to bring about synthesis, therefore this is not a bond making or a cleaving process.

(Refer Slide Time: 05:19)



So, when we think of the wavelength of such microwaves, you can think of the dimensions to be, 1 millimetre to 1 metre that is why in conventional microwave ovens that we have in our kitchen. You actually have a perforation a metal foil in front of you, which is having very fine holes less than 1 millimetre, so as to give you some transparency for you to see what is going on inside. At the same time, it will avoid the leak, of the microwave from coming out of the commercial oven.

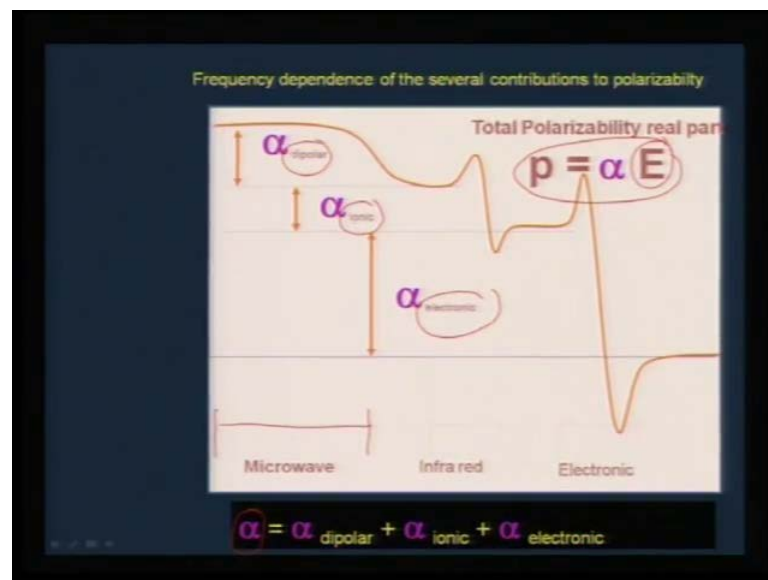
A frequency allowed for commercial and medical and scientific application is of this order, therefore it will not easily come through, this small openings that is available in the conventional or commercial ovens. There are many ways that, we can interpret the

heating, but there are 2 specific causes by which, microwave heating can be achieved, as you know, the molecule when you keep a molecule, in a electrical field.

Let us say $h\nu$ then the molecule actually undergoes deformation in other words, there is polarization, suppose it is in the access molecular access, then this particular molecule will deform like this and thereby, it will induce a polarization. So, the molecule will actually deform in the axis a molecular axis, when light is supplied, therefore there is a polarization in this form and suppose we apply the light in this direction, electromagnetic radiation, then the deformation will happen in this form. In any way, we actually have a polarization, that is induced and this is anisotropic in nature.

So, this dipole will actually rotate or this dipole will oscillate with the microwave frequency, as a result there will be interaction between the material molecule or any solid for that matter with matter. And once dipole is introduced it will bring about a net polarization, and this net polarization is the governing factor for in the interaction of microwave energy with the material. And therefore, there will be two mechanisms, which will actually govern, we will see in the next few slides.

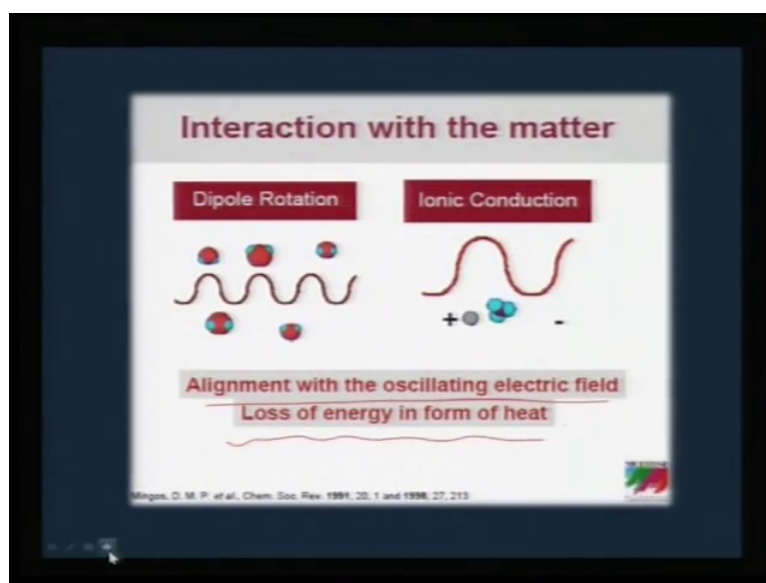
(Refer Slide Time: 07:51)



So, the frequency dependence of the several contributions to polarizability can be mapped up this way the power loss, microwave power is therefore, proportional to the electric field and alpha comes as a proportionality constant where, alpha is nothing but polarization or polarizability. And this net polarization is actually governed by three

factors; one is dipolar polarizability and ionic polarizability and electronic polarizability. But, if you actually look at the frequency mapping and what are all the polarizability factors that become active in the microwave region. So, if you look at the microwave region here, the dipolar and ionic contributions are maximum. And therefore, the interactions of the microwave radiation with matter is principally governed by these two mechanisms.

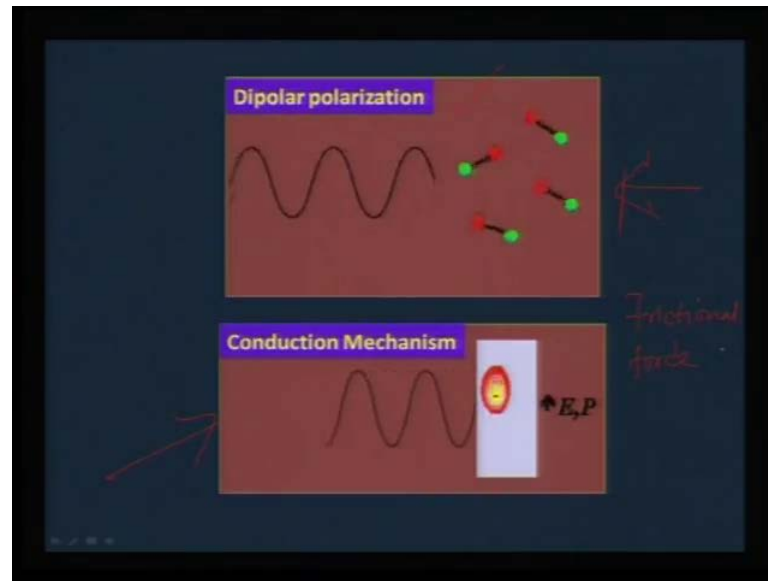
(Refer Slide Time: 08:55)



So, dipole rotation is to do with the dipole that is oscillating in a molecule, when it is kept in a electric field or it could be the ions, that are coupling with the electromagnetic radiation. And therefore, they will oscillate according to the frequency, alignment with the oscillating electric field and therefore, there is loss of energy in the form of heat, which forms the mechanism.

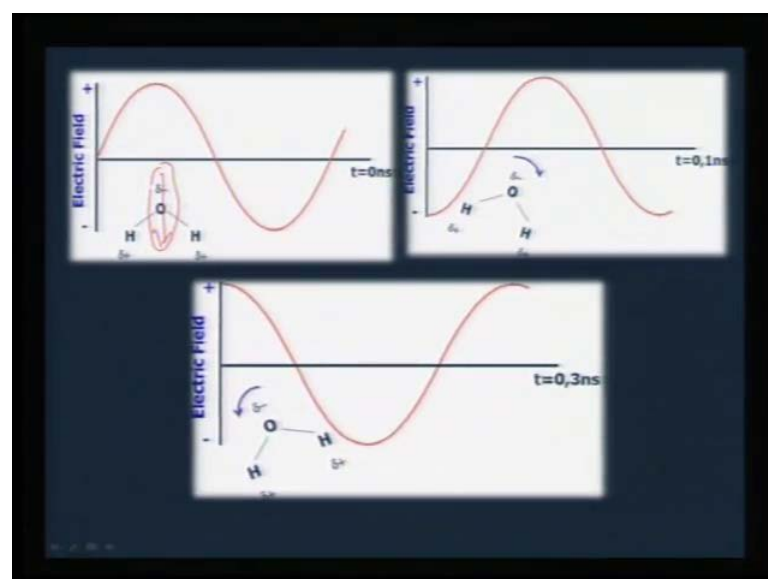
The animation of this is given in this cartoon, as you can see here when microwaves come, the dipoles actually oscillate in this fashion, they do not rotate, but they oscillate with the phase. So, when you bring any molecule in phase with the frequency of your microwave, then they start oscillating with keeping phase with the electromagnetic radiation. So, this is to do with a dipolar polarization, and in the case of conduction mechanism, it is the ions that oscillate with the electromagnetic radiation.

(Refer Slide Time: 09:22)



In either case, as you would see here this oscillation, actually brings about frictional force, so when there is frictional force with the neighbouring molecules, there comes heating. So, this is not a breaking of bond, but the heating actually comes from frictional force that is coming from the dangling of these bonds, as a result a local heating is generated. So, this local heating actually maximizes, a uniform heating in the whole material, rather than the heating coming from one particular direction. Therefore, this particular heating effect that is generated due to microwave is much more special than, any other form of heating.

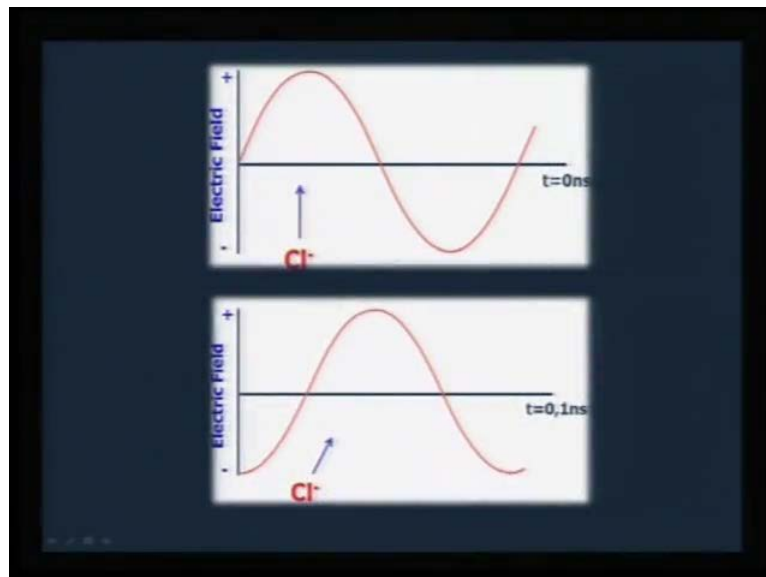
(Refer Slide Time: 10:55)



So, this is another way that we can construe, how this water is getting heated in a conventional microwave, if you just put water within 30 seconds or so you get it boiling hot and this is how it is. There is a permanent dipole here, because of this polarization of charges and this is the axis perpendicular to the molecular axis, and molecules actually will be rotating in this fashion.

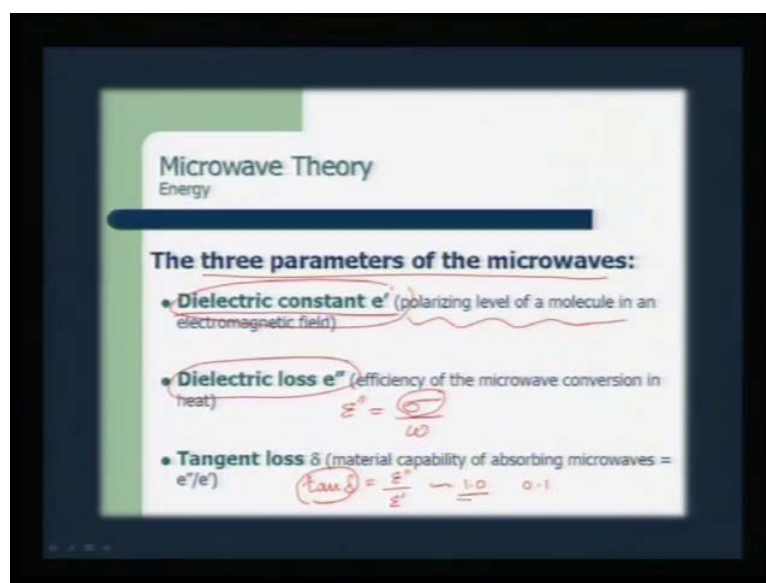
So, molecules will rotate and then again it will go back, so it is more of oscillation not a continuous rotation, it is more of oscillation of this form and this oscillation will actually heat other neighbouring water molecules. So, when there is a global effect, where all the water molecules are oscillating with each other, then the frictional force, actually brings about the heating.

(Refer Slide Time: 11:49)



And same is true for the ions, so the ions do also oscillate in phase with the microwave radiation producing heating. So, when we think about this heating, do we have any numbers that we can look at, and what is the factor that governs the heating of these materials, there are three parameters that we should bear in mind. And we need to moderate this, in order to get maximum heating effect, one is dielectric constant ϵ' and this is to do with the material itself that is interacting with microwave.

(Refer Slide Time: 11:57)



And this dielectric constant is dependent on the polarizing level of a molecule in a electromagnetic field. Sometimes, if you have a molecule with a permanent dipole, then already it is polar, therefore it will couple. But, if you have some molecules may be may be a non polar molecules or aprotic molecules, and then those will actually have a induced dipole moment in the microwave, therefore that will also interact.

So, the essential factor is the epsilon or ϵ' , which is unique of the material itself and the second factor is dielectric loss ϵ'' , and this is the efficiency of the microwave conversion into heat. And this ϵ'' is nothing but conductivity over frequency and therefore, we can call or we can have a measure by which the interaction of the microwave radiation with the material can be gauged. And this is given by $\tan \delta$, and this $\tan \delta$ is nothing but ϵ''/ϵ' .

So, this is called as tangential loss or loss tangent and loss tangent is nothing but the material capability to observe microwave. So, if loss tangent is approximately close to unity, then you say that is maximum capability of the material to absorb, suppose it is less than 0.1, then it is a material, which will couple very poorly. So, if you have a data for tangential loss, then you can easily map, what sort of material can be used for the reaction, and you can fine tune on the frequency to effect this. In case of polar compounds, actually your conductivity is more compared to ω , therefore your $\tan \delta$ will be very close to 1.

(Refer Slide Time: 14:41)

Dielectric Parameters

Dielectric loss tangent: $\tan \delta = \frac{\epsilon''}{\epsilon'}$

Dielectric loss: ϵ''

Dielectric constant: ϵ'

Solvent	$\tan \delta$	Solvent	Medium	$\tan \delta$
ethylene glycol	1.350	DMF		0.161
ethanol	0.941	1,2-dichloroethane		0.127
DMSO	0.825	water		0.123
2-propanol	0.799	chlorobenzene		0.101
formic acid	0.722	chloroform		0.091
methanol	0.659	acetonitrile		0.062
nitrobenzene	0.589	ethyl acetate		0.059
2-butanol	0.471	acetone		0.054
2-butanol	0.447	tetrahydrofuran		0.047
1,2-dichlorobenzene	0.280	dichloromethane		0.042
NMP	0.275	toluene		0.040
acetic acid	0.174	hexane		0.020

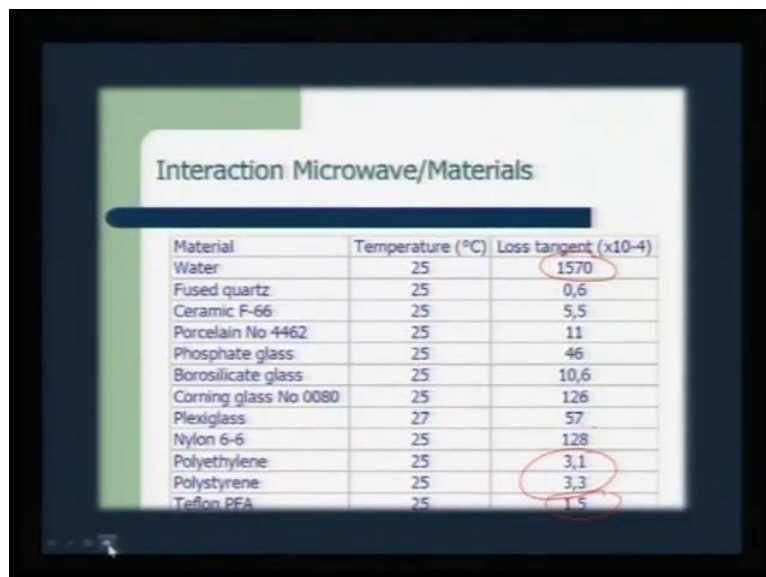
So, the dielectric parameters are governed by this equation as we saw, tan delta is equal to ϵ'' by ϵ' , we call this as dielectric loss, we call this as a dielectric constant of the material and this is the loss tangent. And if you can map several of this compound which coupled with microwave, we have three categories, one is strongly coupled molecules, and the one which tops the order is ethylene glycol, where the tan delta is of the order of 1.350.

So, and as you would see, these are all polar compounds, most of these polar compounds are very close to unity, therefore these are best microwave absorbers. But, if you go further down, you can see region where, there are some molecules or organic solvents, which are medium coupled. So, therefore, they may not really bring about the necessary heating effect as you would see, and there are other ones which are very reluctant to couple with microwave. Therefore, the tan delta value gives us a measure of what sort of combinations that you can choose for microwave synthesis.

Here are some more materials, which gives you the tangential loss factor, as you would see here, water is a better candidate compared to some of the polymers here. And Teflon for that matter, Teflon is very reluctant, therefore Teflon can be used as an inert material even to conduct many of the reactions, for that matter in conventional microwave synthesis, Teflon tubes are used or Teflon boards are used or Teflon bombs are used. So,

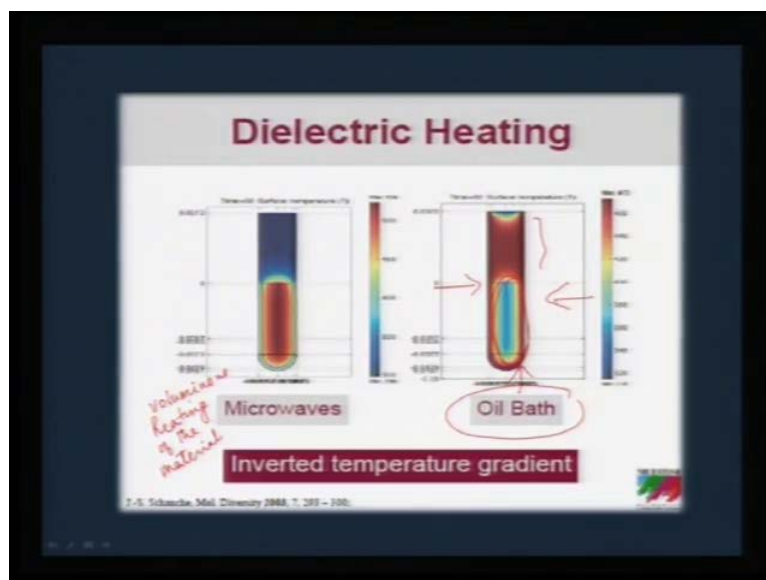
mainly because they do not interact with microwave, so this can be used as a substrate or a holder for conduction reactions.

(Refer Slide Time: 16:01)



Material	Temperature (°C)	Loss tangent (x10 ⁻⁴)
Water	25	1570
Fused quartz	25	0,6
Ceramic F-66	25	5,5
Porcelain No 4462	25	11
Phosphate glass	25	46
Borosilicate glass	25	10,6
Corning glass No 0080	25	126
Plexiglass	27	57
Nylon 6-6	25	128
Polyethylene	25	3,1
Polystyrene	25	3,3
Teflon PFA	25	1,5

(Refer Slide Time: 16:50)



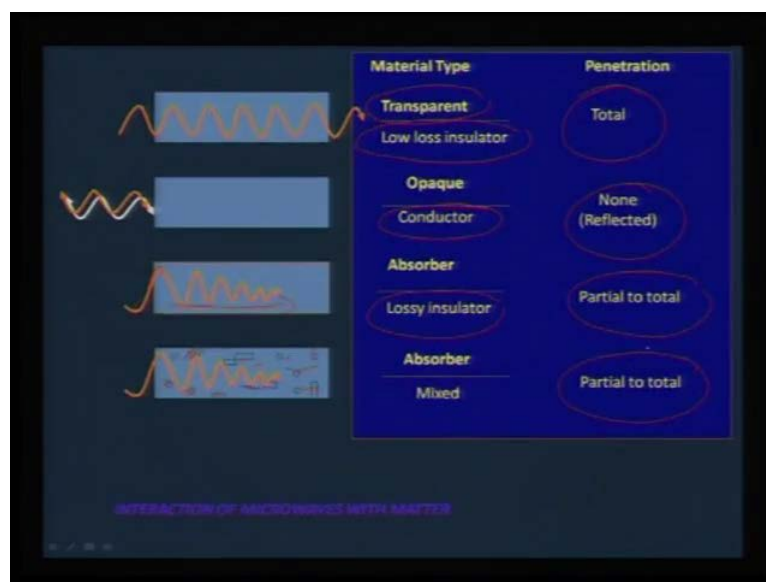
So, the tangential loss a factor is one measure by which we can gauge what sort of material can interact with microwave. Now, when we look at this dielectric heating, we need to understand that, the dielectric heating really brings about a drastic change compared to the conventional heating. For those who are familiar with organic synthesis

usually, all the reactions are conducted in oil bath or in sulphuric acid bath, because you can go up to 350 degree centigrade maximum to conduct your reactions.

But, if you look at the zone that you try to generate usually there is gradient here, and temperature gradient is maximum in this region and you do not see, the voluminous heating that is happening in a conventional oil bath. Or even if you have a electro heating furnace, the heating will come from all sides and therefore, there will be a clear temperature gradient and voluminous heating cannot be achieved. Whereas in the case of microwave, because it depends on the dielectric parameters of the material.

There is voluminous heating, in the material and therefore, there is no temperature gradient that you would see. And as a result, if you are looking for any phase separation or any other possible impurity formation, this can be very easily avoided in microwave heating, compared to electro heating. So, this is a very, very crucial dividing principle between microwave heating process and the conventional process, which really makes this a very good candidate to try a variety of reactions.

(Refer Slide Time: 18:48)



So, when we think of using this microwave heating for synthesis, we need to understand what can be the holder, what can be the vessel, in which we can use. Therefore, we should use a vessel, which is actually transparent to microwave, which means it does not interact with microwave. So, it will allow the microwave to pass through, but react only with the sample, therefore, if you have a low loss insulator for example, and this low loss

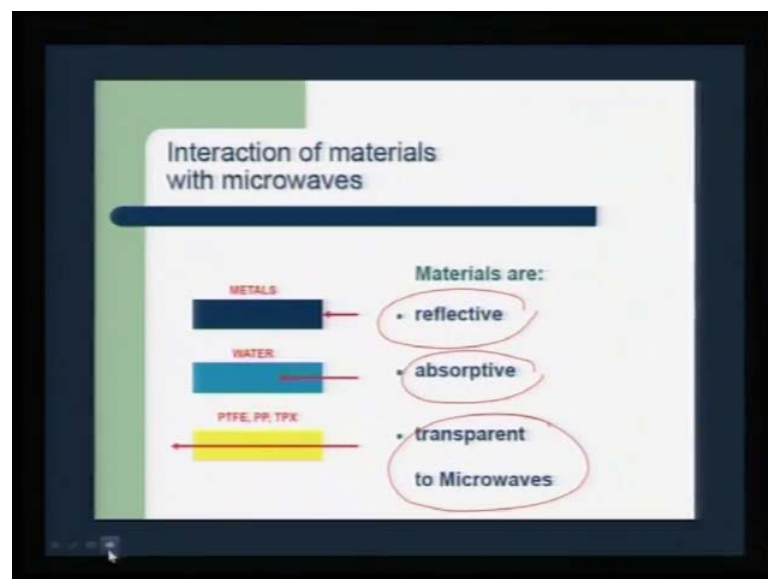
insulator are transparent to microwave, as a result the penetration is total, so glass for example or any ceramics, they are transparent to microwave, so heating can be very well achieved.

So, crucibles of glass or something made of silica or alumina this can act as a very good agent, even Teflon can act as a very good agent, for microwave to go through. Metals, actually coupled with microwave, therefore they are opaque it wouldn't allow the microwave to pass through, so it gets reflected. And that is why, you have a shield in your commercial microwave, which is a metal shield, therefore it will actually reflect the microwave to the centre of the cavity.

As a result the material, that you want to heat can be effectively heated, therefore metal is a opaque a candidate and as far as the absorbers are lossy insulators can allowed partially the microwave to go, as you would see it propagates, but then it gets dampened.

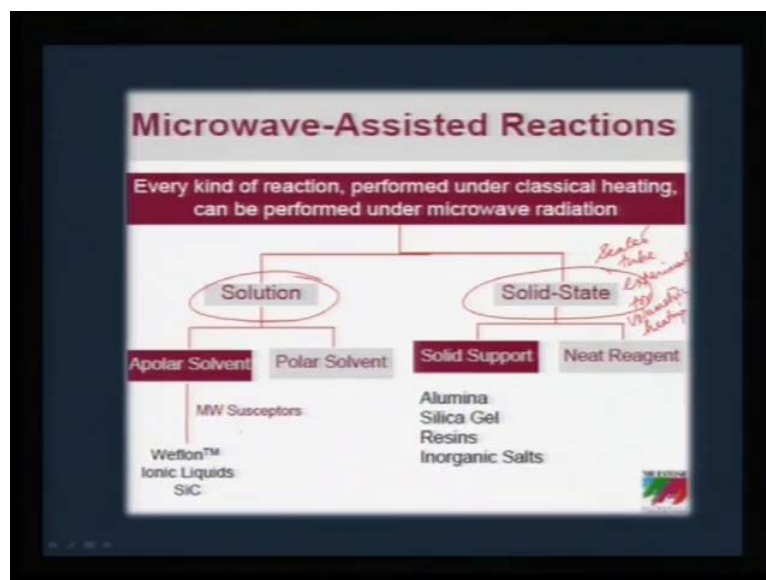
And therefore, the penetration is partial to total or if you have, in such lossy insulators, some metal ingredients like this as you would see here, then this can actually allow microwave to get absorbed. And therefore, you can achieve a partial or total penetration. So, this gives us some idea, about the range of material that you can choose, those which are opaque to microwave, and those which are transparent to microwave.

(Refer Slide Time: 21:11)



And as a result, we can say reflective ones are metals, water is a very absorptive metal, and those which are transparent to microwave are polymers. Polymeric stuffs are microwave transparent, therefore you can use that as containers.

(Refer Slide Time: 21:29)

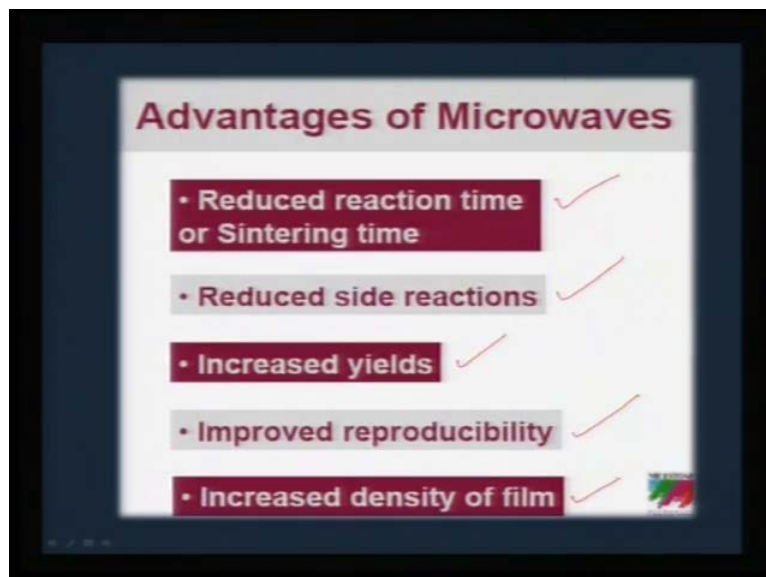


Now, every kind of reaction performed under classical heating methods can be performed under microwave radiation, therefore this sort of chemical synthesis is actually categorized as microwave assisted reactions. And in microwave assisted reaction, you can aim for both solution approach as well as solid solution approach. So, if you want solid state reactions, that is also possible, suppose you are bringing two solids and this has to be formed, usually such reactions are aimed at, under sealed vacuum conditions.

So, vacuum sealed capsules can be used for bringing about, solid state reactions to bring the solid interaction into closer proximity, because usually when solids coupled with microwave, there will be a plasma generated. And this plasma can bring about a voluminous heating and therefore, this is done in sealed tube experiments mostly, for volumetric heating. So, we can actually go for any sort of reactions there, neat reagents are possible, as well as solid supports are possible, so variety of solid state reactions can be achieved. Similarly, solutions we can try with aprotic solvents or aprotic solvents and polar solvents. In case of aprotic solvents, we need to induce some sort of microwave

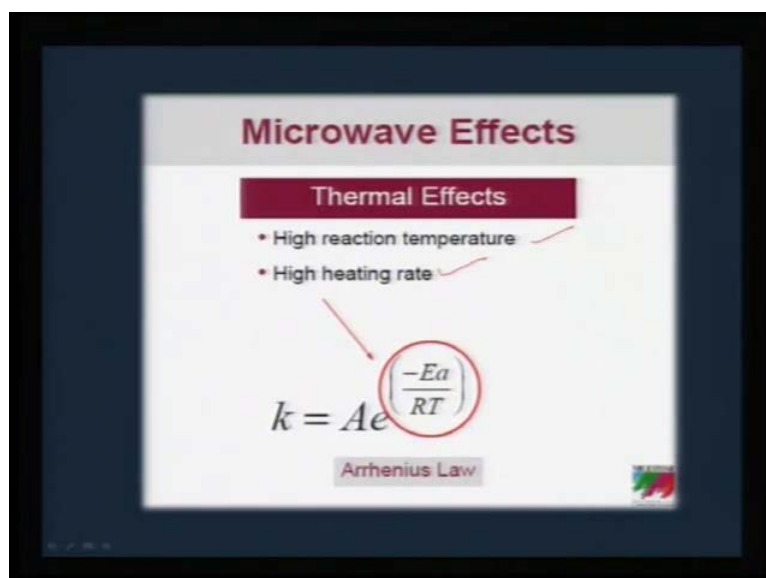
susceptors, which will actually bring about the microwave coupling, therefore either of this range can be achieved.

(Refer Slide Time: 23:21)



So, what are the advantages of microwave heating, why we have to use microwave heating, number one it is reduced reaction time or if you think about sintering, I will come to this issue later in some of the examples. We can tremendously lower the reaction time scale and we can also avoid side reactions, therefore microwave heating is more selective and specially in organic synthesis.

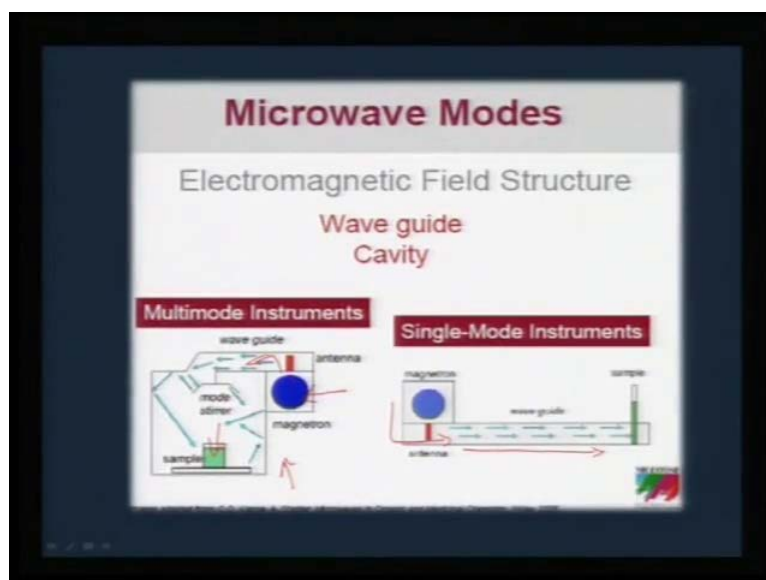
(Refer Slide Time: 24:21)



In today's lecture, I will not be able to give you more examples on organic synthesis, I will concentrate more on inorganic materials. And another thing is, it is more specific in nature and therefore, increases the yield of the reaction and it gives improved reproducibility and also increase density of film, when we try for some film fabrication approaches.

So, when you look at microwave effects, one of the main ingredients there is the thermal effect, in this microwave heating, which achieves a high reaction temperature at a high heating rate. And therefore, it affects the energy of activation, so the reaction rate can be fastened by orders of magnitude. So, because of this, we try to use the thermal effects as a source to speed up the reaction.

(Refer Slide Time: 24:51)

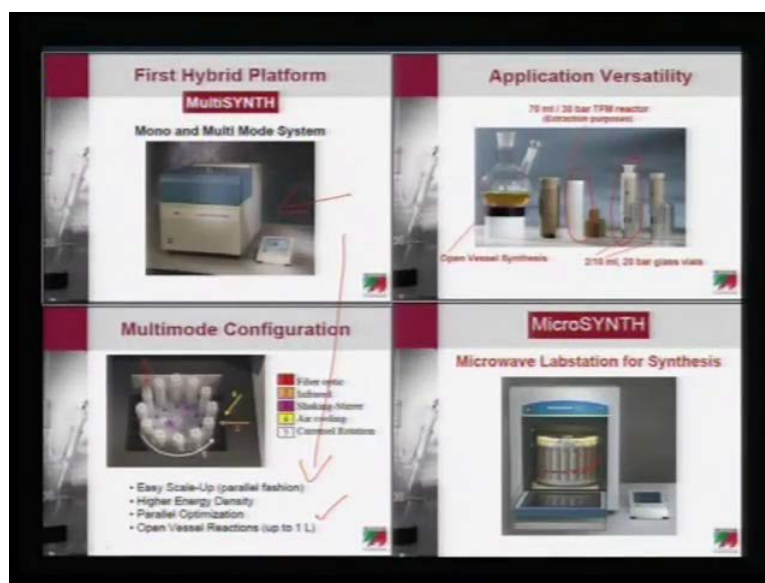


And the way that we can do that is of two forms, either we can go for a single mode cavity instrument or multimode instrument. What we have in our kitchen microwave is actually a multimode instrument, where you have a magnetron, which will generate your microwave. And this is guided by a wave guide and this will finally, lead to open cavity where it will be confined, it will get scattered everywhere but then reflected so as to concentrate only on the sample.

So, this is multimode cavitations and single mode instruments are also available, where you generate microwave and this is actually channelized through a wave guide only to heat at a particular sample. For organic reactions, this sort of single mode cavity

instruments is also possible, I will show one or two commercial instruments, which can do the job. And as you would see, microwave is also the source material for electron spin resonance, where a magnetron will generate microwave and that is actually guided through a wave guide to the sample. So, single mode instruments are already in use, but multimode instruments actually helps us with larger amount of samples.

(Refer Slide Time: 26:19)



There are different versions of microwaves that are available, I do not mean to promote only Multisynth equipments, but there are several other commercial instruments that are available. I will show some, which are used in our own laboratory for reference, but this is a very good sum up to show, what sort of features can be achieved. We can go for mono or multimode using this sort of cavity and if you look at the inside view picture, you can actually do a scale up of that with the many containers here.

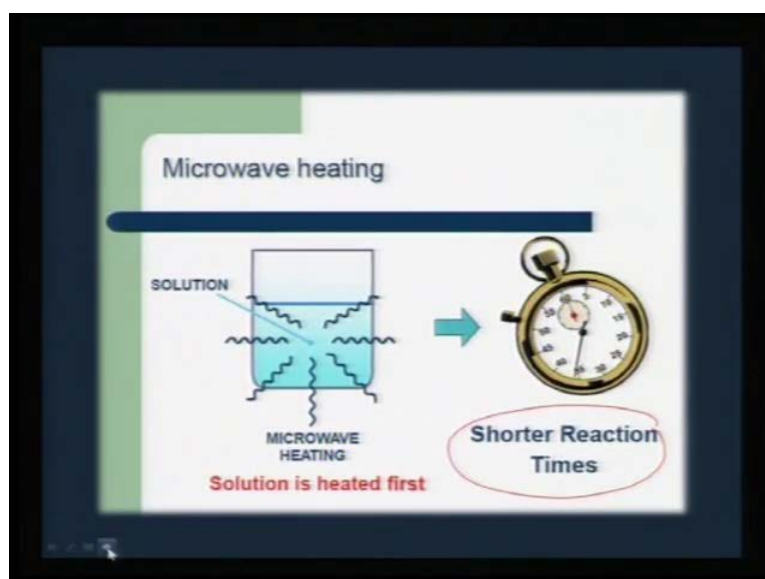
So, you can go for a easy scale up, in a parallel fashion and you can also engineer open vessel reactions. For example, these are for open vessel synthesis, these are Teflon bombs, that can be used for high pressure vessel studies. As you can see, this can be kept inside a bomb and then can be mounted here. So, this looks more like a lab station, where you can have a parallel synthesis of several units of your sample tubes placed simultaneously and therefore, you can scale it very easily.

(Refer Slide Time: 27:37)



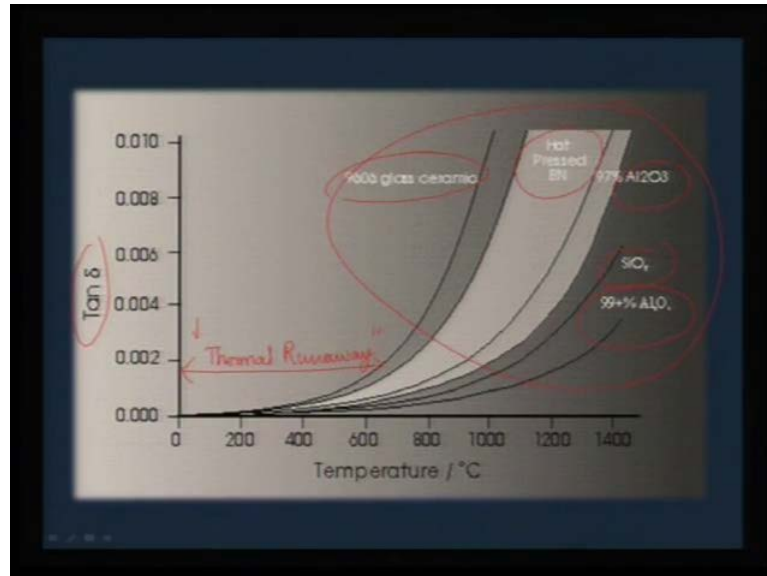
So, from a simple multimode cavity, you can achieve many things, one you can look this more like a muffle furnace but then you can do open system reactions. If you want, you can even purge, the system with gas. So, this is possible or you can do closed system, as you can see this is confined to a bomb and we can try to measure the pressure release there. So, parallel screening can be made and Teflon bombs can be housed like this, so either, you can do open system or closed system reactions.

(Refer Slide Time: 28:15)



And the best word here, in microwave heating is the shorter reaction scales, reaction time and as a result, the solution actually gets a uniform heating. So, we can go for any sort of reactions that, we are looking for.

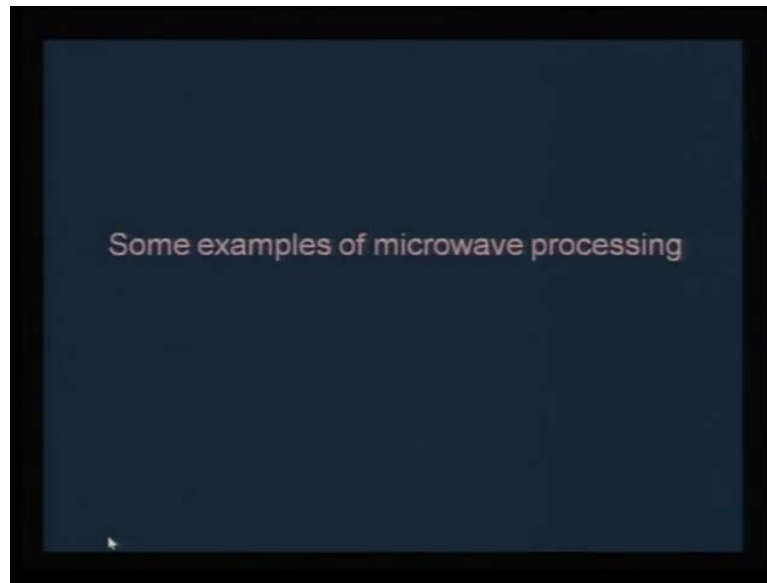
(Refer Slide Time: 28:34)



But, when we come to solids, we need to understand, that it is not as simple as the solution process, as you would see here, this is a good example of a glass ceramic and this is a hot pressed boron nitride, this is alumina, this is silica, and this is again 99.9 percent alumina. In all this if you look at the tangential loss factor, these are very low and you need to expose these materials for a longer time scale. In order to really achieve a considerable amount of microwave absorption and this region, in such insulators is actually referred to as thermal runaway.

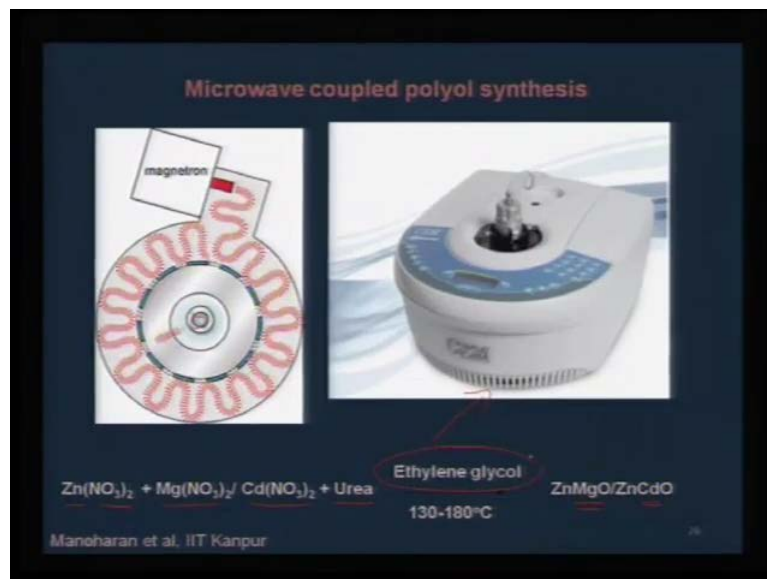
This is called thermal runaway meaning, there would not be effective coupling of microwave with this material until you generate a minimum energy or temperature. Only after the sample reaches, say 600 or 700 degrees centigrade, then you will be able to scale up or maximize on the coupling. And therefore, when you look at the insulating oxides, one of the or ceramics in general, one of the important thing that, we need to understand is it, is not as quick and fast as solution route. Therefore this thermal runaway is a very important parameter, when we are looking at solids, when they interact with matter. So, I will take you through some of the examples from now on.

(Refer Slide Time: 30:20)



Some of the examples are from our own group and let me first start with those examples.

(Refer Slide Time: 30:25)



The one thing that is very popularly used nowadays is microwave coupled polyol reaction and this is a commercial instrument that we have from cem corporation U S A and this is a voyager unit, which actually has a magnetron, which is designed in such a way, that you can get the microwave focus to the centre of the cavity here. So, this you will get a voluminous heating, only thing the size restriction is there, but you can actually

use it for, both open vessel as well as closed vessel reaction and this is the way, you can generate the microwave concentrating on the middle of the sample region.

So, let me take a issue of zinc oxide formation and we can do alloying of this zinc oxide, either with cadmium doping or with magnesium doping. And as you would see here, the reactions is very simple, you can start with the nitrate either zinc nitrate or magnesium nitrate and cadmium nitrate, as you would desire. And you can use urea, urea to hydrolyze and ethylene glycol is both used for hydrolyzing plus as a solvent, as you have seen in one of the previous slides.

(Refer Slide Time: 31:46)

The slide displays the formula for dielectric loss tangent: $\tan \delta = \frac{\epsilon''}{\epsilon'}$. It identifies ϵ'' as Dielectric loss and ϵ' as Dielectric constant. Below the formula is a table of dielectric loss tangent values for various solvents and mediums.

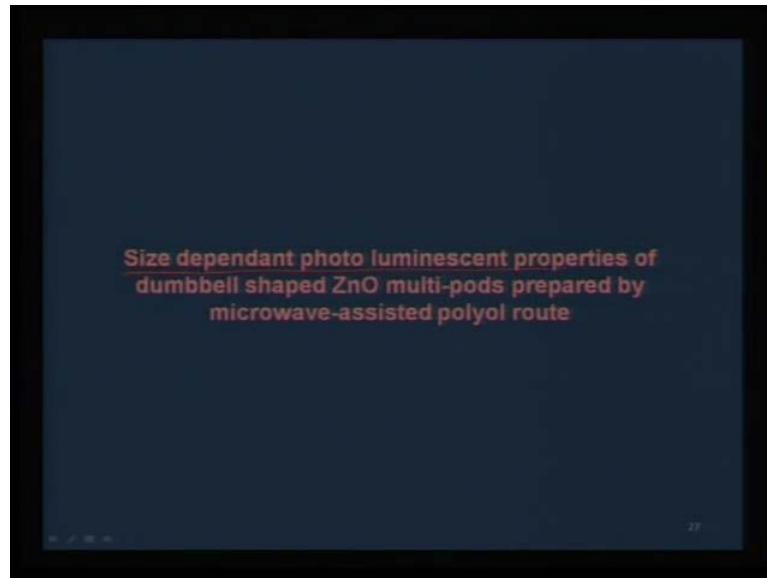
Solvent	$\tan \delta$	Solvent	Medium	$\tan \delta$
ethylene glycol	1.350	DMF		0.161
ethanol	0.541	1,2-dichloroethane		0.127
DMSO	0.825	water		0.123
2-propanol	0.799	chlorobenzene		0.101
formic acid	0.722	chloroform		0.091
methanol	0.659	acetonitrile		0.062
nitrobenzene	0.589	ethyl acetate		0.059
1-butanol	0.571	acetone		0.054
2-butanol	0.447	tetrahydrofuran		0.047
1,2-dichlorobenzene	0.280	dichloromethane		0.042
NMP	0.275	toluene		0.040
acetic acid	0.174	hexane		0.020

Ethylene glycol is actually having a strong tangential loss and therefore, this is a very good solvent that can be used for reactions. So, in this example, I will show you, how size dependent photo luminescent properties, can be generated in dumbbell shaped zinc oxide multi-pods prepared by microwave assisted polyol route, as you would see here.

Polyol synthesis involves high boiling alcohols with more hydroxyl groups, more the hydroxyl groups then the tangential loss gets maximized, therefore the alcohol can do 2 jobs, one is to reduce and the other one is to act as a solvent. And the mechanism is proposed via 2 types, one is crystallization of the metal hydroxides and dissolution of the metal hydroxides and further reduction by alcohol, to give corresponding metal nano particles. So, let us take the case of simple reaction of zinc oxide, before we consider

cadmium and magnesium doping. So, I can actually vary, the exposure of this mixture to 1 hour to 6 hours and then look at the property, to understand what really is important.

(Refer Slide Time: 31:58)



(Refer Slide Time: 32:16)

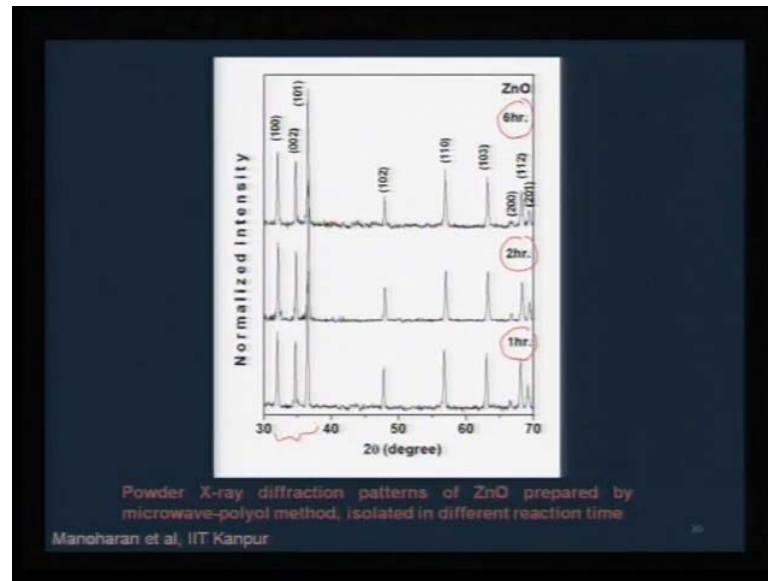
- ❖ Polyol synthesis involves high boiling alcohols with more hydroxyl groups.
- ❖ The alcohol employed serves as a solvent and a reducing agent.
- ❖ The mechanism is proposed to proceed via two steps:
 - (i) crystallization of metal hydroxides
 - (ii) dissolution of metal hydroxide and reduction by alcohol to yield metal particles/oxides (depending on the nature of the metal element)
- ❖ Further reaction continues as spontaneous nucleation and growth of the particles wherein temperature affects the growth kinetics.

$$\text{Zn}(\text{NO}_3)_2 + \text{NH}_2\text{CONH}_2 \xrightarrow[\text{Microwaves/130-180}^\circ\text{C}]{\text{Ethylene glycol}} \text{ZnO}$$

1-6 hr.

28

(Refer Slide Time: 33:12)



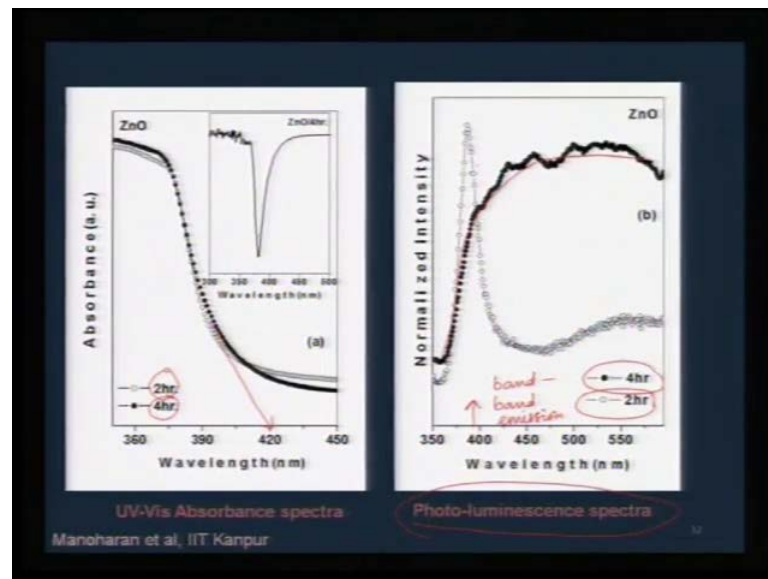
Now, in this case, you can see 1 hour exposure 2 hour exposure and 6 hour exposure gives very highly crystalline zinc oxide powders. So, there is no doubt from, the x-ray mapping, that you can see this typical hexagonal pattern, that is coming out therefore, you would not like to doubt on the x-ray purity or the composition of this oxide. But, what you should understand, that the exposure does control the particle size and as a result the other properties can also get altered.

(Refer Slide Time: 33:47)



And that is what you would see from the other cartoon here, at 1 hour you can see the they are almost forming a sort of pods multi-pods of zinc oxide and you do not seem to see any secondary effects or any phase separation here. Therefore, these are quite impressive 1 hour and a 2 hours seemingly, these multi-pods have grown in size, but when you go to 4 hours and 6 hours, the sort of length scale of these multi-pods are vanishing. And they are going more into smaller crystallites when you go for 6 hour time scale, so does this growth factor or the shape and size of the zinc oxide nano rods.

(Refer Slide Time: 34:37)



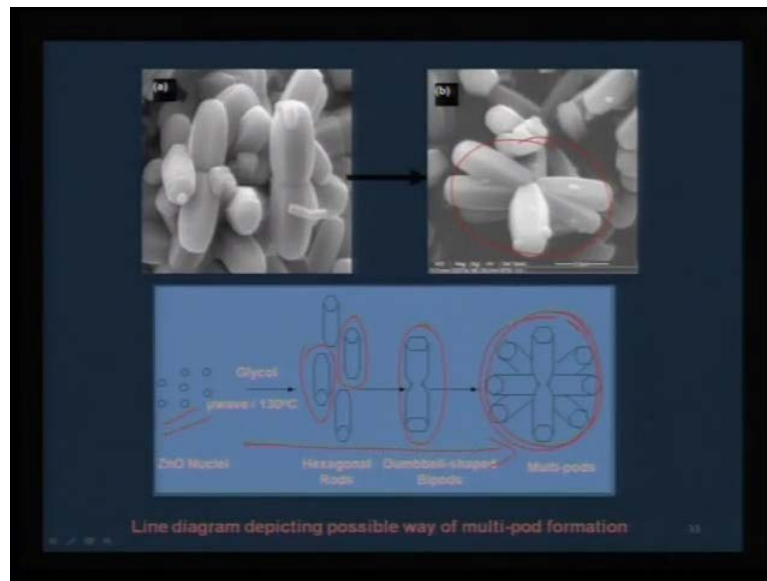
Do they have any influence on the property, if you look at the absorbance for a 2 hour exposed mixture and a 4 hour exposed mixture, you would see, the optical band gap is nearly the same. So, you would not think that, there is anything extraordinary happening, but if you look at the photoluminescence spectra of the 2 hour sintered 2 hour exposed and 4 hour exposed mixture, you can clearly see the photoluminescence is totally different.

In 2 hours exposed case, you get a very characteristic sharp 380 nano meter band, which is nothing but your band to band emission. Emission and this is exactly, what is needed as far as zinc oxides are concerned, but when you expose it further, the subsequent nucleation actually brings about defect chemistry into zinc oxide, as a result you do not see this 280 380 nano meter peak. But, you see a dominant surface induced defect

induced emission, as a result you do not see this characteristic 380 nano meter peak anymore.

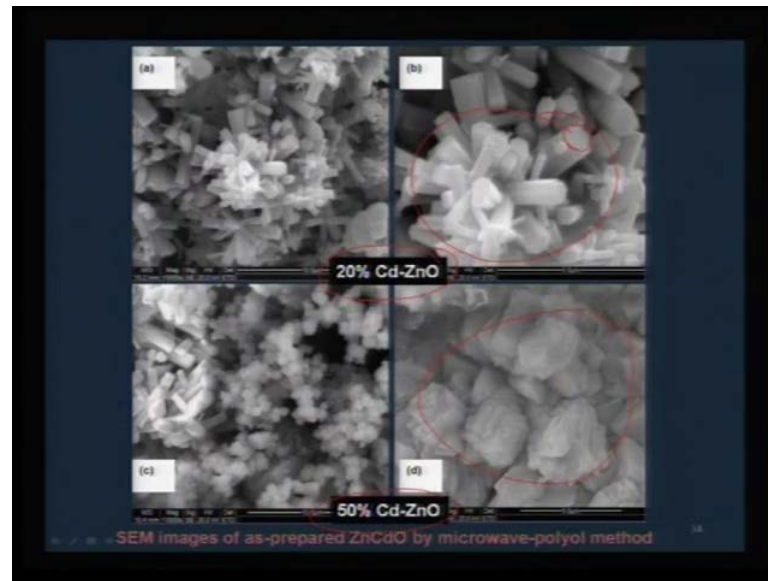
Therefore, the way you expose the mixture or the starting material to microwave, it may not show macroscopically any defects, but it subsequently will induce, some amount of defect chemistry into it. Therefore, this study would help us to understand, how much of microwave exposure is needed, to control the physical properties.

(Refer Slide Time: 36:24)



As you would see the growth of these multi-pods are also kinematic in nature, initially this zinc oxide nuclei's are formed and this they form subsequently, single nano rods and these nano rods get fused like a dumbbell shaped ones and this dumbbell shaped rods further, they get fused like this fashion into multi rods. And all this is a kinetically controlled and therefore, if you want to stop the defect chemistry, then you need to stop at a particular size. If you go for a very long exposure, probably you will get very interesting facets of zinc oxide rods, but essentially they lack, in clarity as far as the photoluminescence property is concerned.

(Refer Slide Time: 37:15)



Similarly for cadmium, let us say if you would, we can achieve easily doping, for 20 percent and 50 percent cadmium oxide and x-ray will not give you any clue, but once you see here, the carefully, the S E M feature. These are all zinc oxide rods, you can see the hexagonal feature on the top of this rod, but for 50 percent, you do not see the same morphology.

(Refer Slide Time: 37:44)

Metal Hydroxide/oxide	Decomposition Temperature (°C)	Heat of Formation ΔH° , (KJmol ⁻¹)
Zn(OH) ₂	125°	-641.9
ZnO	-	-350.5
Cd(OH) ₂	232°	-560.7
CdO	-	-258.4

Decomposition temperatures and heats of formation of Zn-, Cd- hydroxides and oxides

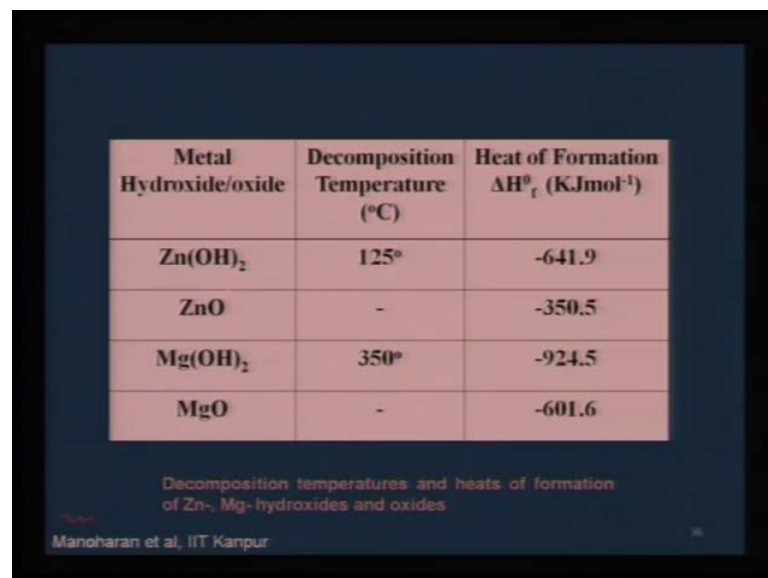
Manoharan et al, IIT Kanpur

And if you carefully look at the decomposition temperature and the heat of formation of these oxides, we can get a clue, for zinc oxide the decomposition temperature of zinc

hydroxide is only 125 degree. And therefore, it is very easy for us to get zinc oxide nano rods whereas, when we dope cadmium into it, cadmium hydroxide is initially formed and for cadmium hydroxide to get subsequently reduced to cadmium oxide, it is very reluctant, because the temperature that is needed is 232.

As a result, what you would see in the previous view graph, this is nothing but cadmium hydroxide and this is totally segregated out, as a result you would do and this is amorphous in nature. So, it will not show off in you x-ray as a impurity peak, there therefore, we need to take care, as to how the decomposition temperatures, can affect the final oxide formation. I will show in the next few slides, a another example of magnesium hydroxide doping in zinc oxide, in the next example.

(Refer Slide Time: 38:56)



Metal Hydroxide/oxide	Decomposition Temperature (°C)	Heat of Formation ΔH°_f (KJmol ⁻¹)
Zn(OH) ₂	125°	-641.9
ZnO	-	-350.5
Mg(OH) ₂	350°	-924.5
MgO	-	-601.6

Decomposition temperatures and heats of formation of Zn-, Mg-hydroxides and oxides

Manoharan et al, IIT Kanpur

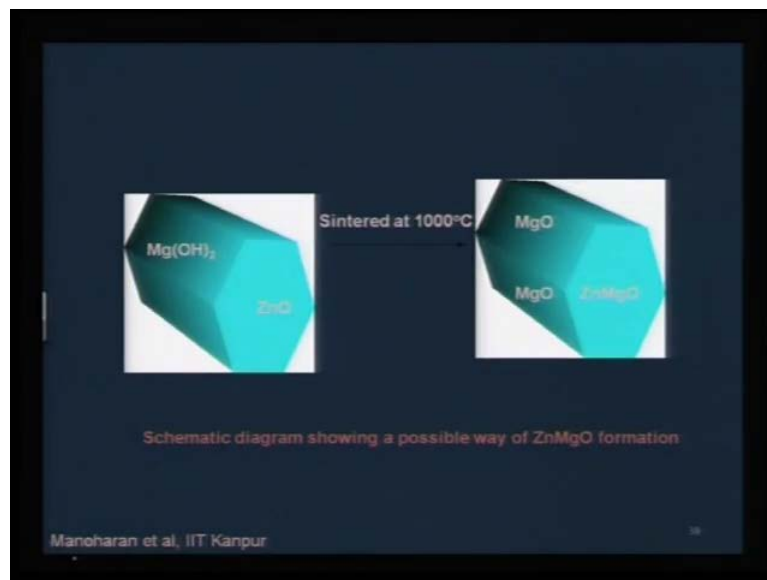
We can again look at another issue of magnesium doped into zinc oxide, zinc oxide is hexagonal in nature, therefore when you look at magnesium doping. Any segregation of magnesium oxide will come out, as a cubic phase then you can easily map, but what we see in reality is when you use polyol synthesis, you again see a very highly crystalline zinc oxide with no presence of magnesium hydroxide and if you look at the TEM.

(Refer Slide Time: 39:25)



It does not show any phase segregation. So, one can actually confuse, this to be a solid solution of magnesium oxide in zinc oxide.

(Refer Slide Time: 39:37)



But, what you see in effect is magnesium hydroxide is getting formed.

(Refer Slide Time: 39:44)

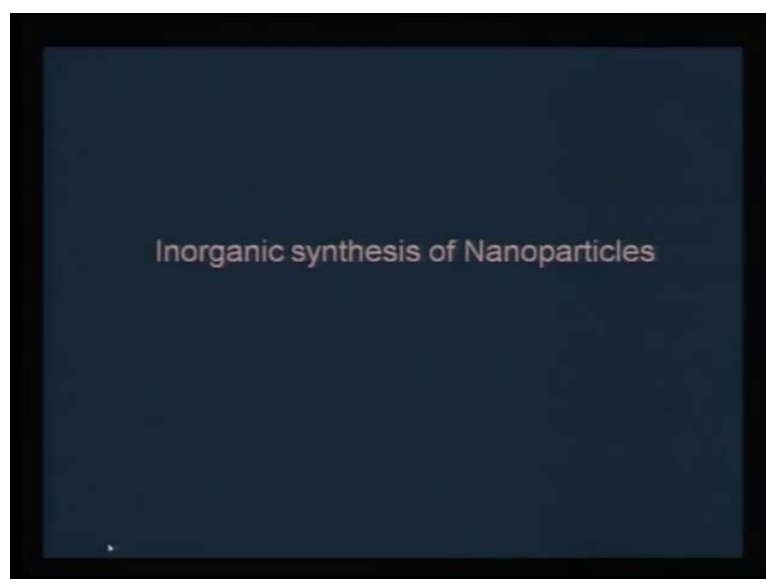
Metal Hydroxide/oxide	Decomposition Temperature (°C)	Heat of Formation ΔH_f° (KJmol ⁻¹)
Zn(OH) ₂	125°	-641.9
ZnO	-	-350.5
Mg(OH) ₂	350°	-924.5
MgO	-	-601.6

Decomposition temperatures and heats of formation of Zn-, Mg-hydroxides and oxides

Manoharan et al, IIT Kanpur

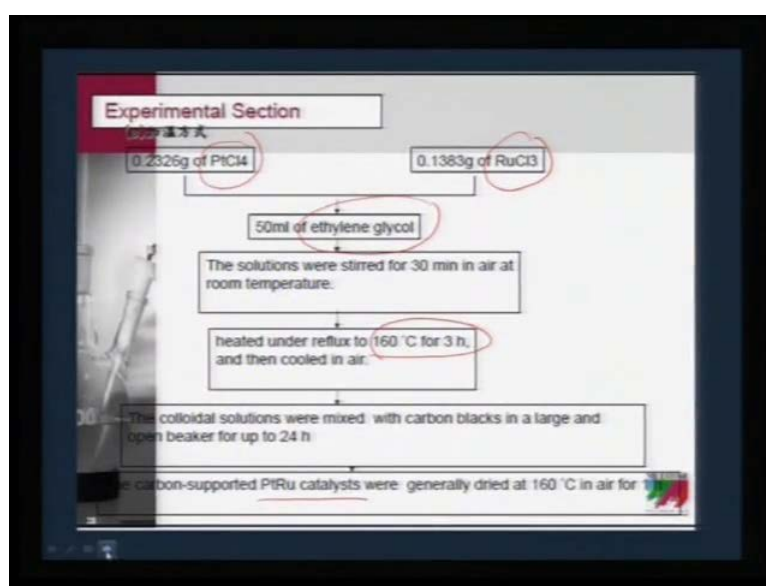
And because in as I showed in the earlier slide, magnesium hydroxide decomposition is only at 350 whereas, zinc hydroxide is forming at 125 degree C. Now, when you try to dope, any amount of magnesium hydroxide, this actually gets surface coated on the zinc oxide nano rods and therefore, because magnesium hydroxide is amorphous in nature, you would only see the zinc hydroxide sorry, zinc oxide nano rod pattern and you wouldn't see any presence of a phase separation.

(Refer Slide Time: 41:03)



Whereas, if you try to heat this, zinc oxide dots, which are coated with magnesium hydroxide, then at 100 1000 degree C, this gets converted into magnesium oxide. And then this magnesium oxide gets partially, doped into zinc oxide, which you can see from your P 1, slowly the bandage is actually going from 380 down to 240 or so with the blue shift in the absorbance. So, we need to have an idea about, the individual decomposition of this hydroxides, so as to map for, effective doping of these solid solutions. There are many examples from other groups, which I would like to quote, one is inorganic synthesis of nano particles.

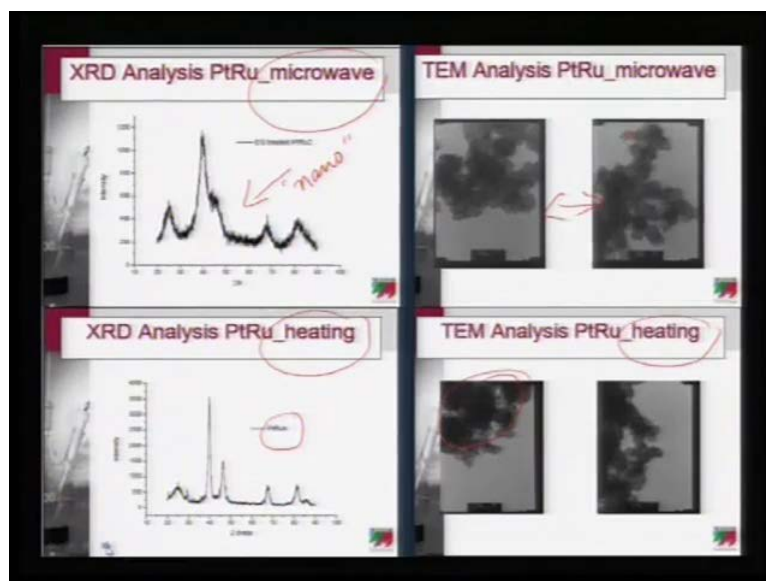
(Refer Slide Time: 41:12)



Let us take the example of platinum and ruthenium nano particles, these are used for a variety of purposes and again here ethylene glycol can be used. In a conventional heating procedure, this would require a reflux at 160 degree for 3 hours whereas, in microwave the whole reaction can be completed in just 15 minutes exposure. Therefore you can speed up this reaction, not only that these platinum ruthenium catalysts show a very different behavior, look at the x-ray analysis.

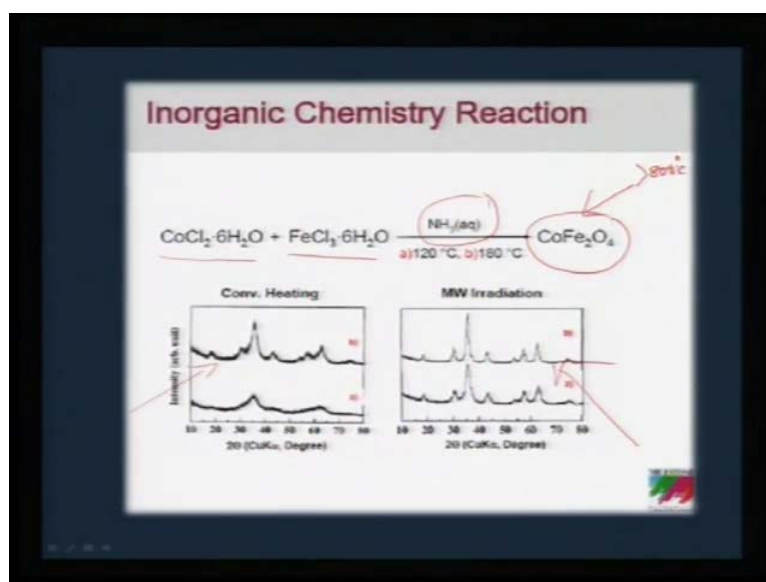
So, x-ray analysis of platinum ruthenium, which is exposed to microwave clearly shows a very different x-ray pattern compared to the conventional heating procedure where here, you see PtRu₄ type of an x-ray pattern, which is highly crystalline whereas, in this case you see a broad or x-ray broadening in these peaks, which is indicative of nano size. So, whenever there is x-ray broadening, you talk about a nano size regime and that is the reason why it is not highly crystalline.

(Refer Slide Time: 41:43)



So, if you look carefully at the t e m pictures, both the pictures here enlarged versions, there is more agglomeration in the case of, conventional heating method where, there you see very dark patches whereas, the particles are much thinner and finer. And nearly separated in the case of microwave centred samples therefore, making nano materials microwave can still perform a better job compared to conventional heating.

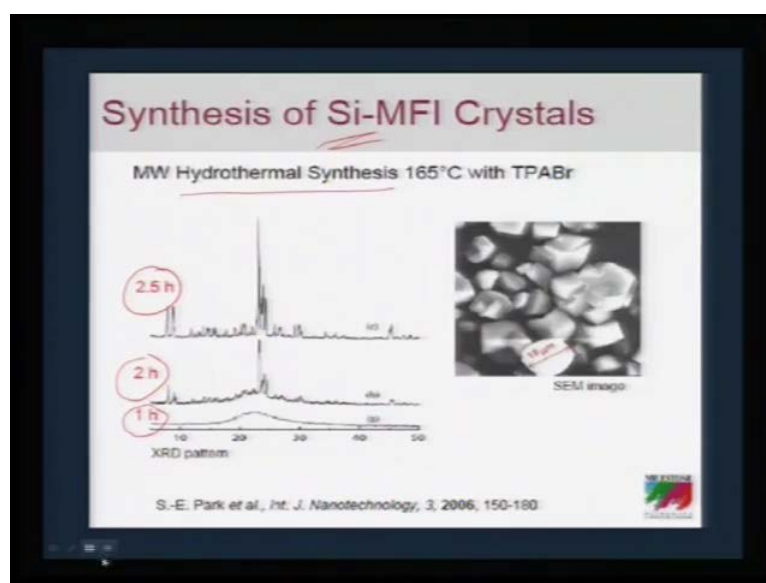
(Refer Slide Time: 42:55)



And if you want to make cobalt ferrite for example, take cobalt chloride and iron chloride and if you can expose this to microwave by reducing it with ammonia, then you

can see, that difference between conventional heating and microwave heating. So, if you going to employ convention heating, you can see that it is poorly mapping whereas, in the case of microwave heated reactions, it is faster and then you get the single phase without any problem. So, you can make spinel compounds using simple reduction technique and then you can isolate the final product with much ease, you should also realise making such a spinel phase materials in solid state, actually requires temperature more than 800 degree C where, you can speed it up in no time.

(Refer Slide Time: 43:53)



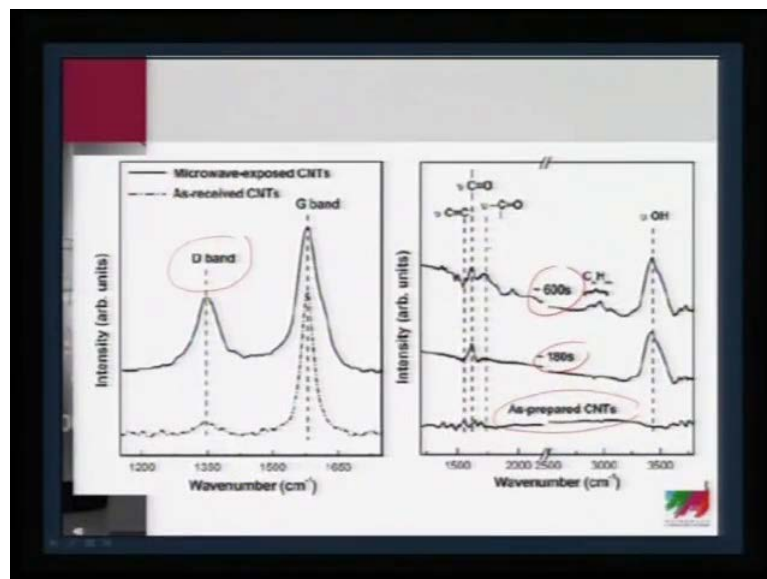
So, microwave can be used for such reactions and also microwave for thermal hydrothermal synthesis, microwave can be used as a heating source, than a furnace for making silicon crystals and as you would see here exposure to microwave, you can crystallise these particles in a much more clearer way. Another good application, which actually can prove very cost effective is functionalizing carbon nano tubes.

And carbon nano tubes as you see here, this is the G band and D band of the carbon nano tubes and as received and a microwave expose. So, the microwave expose are showing a very clearer D band, which is due to, the influence of microwave and also compared to the as prepared carbon nano tubes, those which are exposed to different exposure levels of microwave, clearly show that the carbon nano tubes, can be functionalized with ease.

(Refer Slide Time: 44:16)



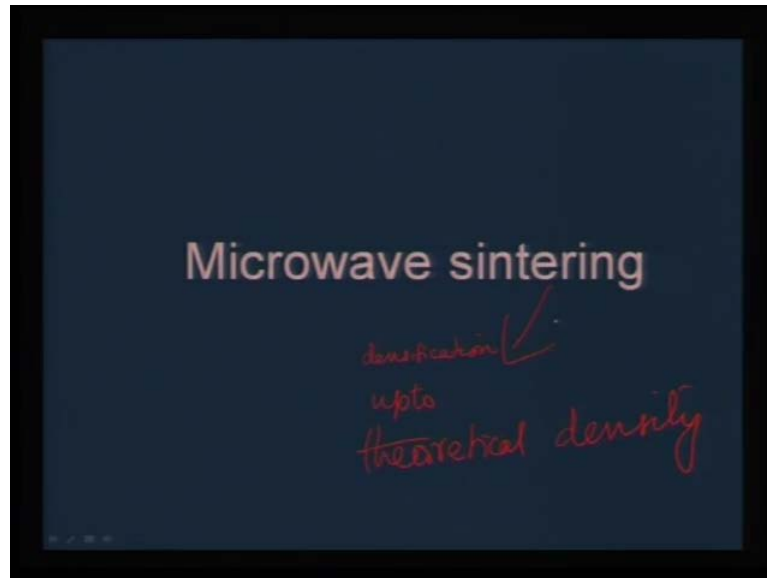
(Refer Slide Time: 44:25)



Otherwise the conventional heating technique, usually involves boiling it with nitric acid for a very long time. But, digestion in microwave appears to be a very economic and a very facile route, to functionalize the carbon nano tubes. Therefore this can be extended for functionalizing carbon and nano tubes, apart from synthesis, we can also use microwave for sintering purpose. As you know sintering is a very long phenomena and it takes days sometimes several hours, for sinter sintering any compound, when I mean

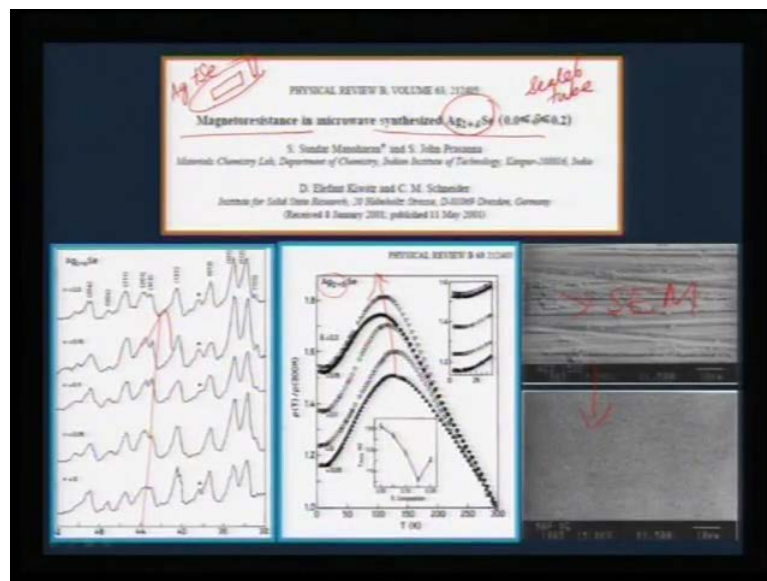
sintering, we are making powder compacts and that can be sintered or that can be densified to theoretical density.

(Refer Slide Time: 45:45)



So, that is densification up to theoretical and that is the use of sintering powder compacts. So, I will show the facile nature of microwave process, how we can achieve all this in a faster rate.

(Refer Slide Time: 46:15)



This is one of our groups work way back, this is published in physical review b where we have tried to synthesize a variety of silver selenide compounds, using microwave.

Silver and selenium, they coupled with microwave very easily, but this compound cannot be made in open vessel therefore, this is a sealed tube experiment, that you can try to do and with different concentration of silver, we can try to look at the magneto resistance ratios.

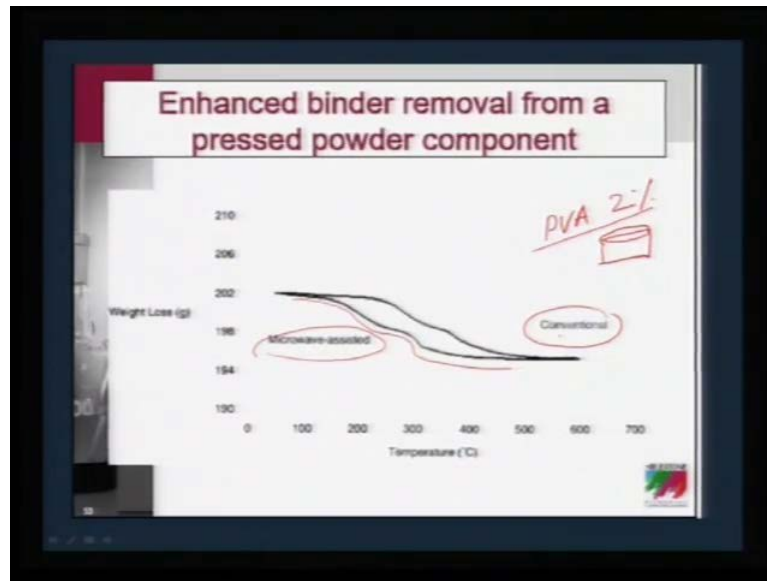
As you would see here all the compounds with silver variation can be achieved and a systematic change in the resistance versus temperature is also noted with a very clear dependency on silver composition. There is a systematic variation as you would see, the insulator to metal transition is noted in silver selenide compounds and one important point is when, we take silver and selenium and mix it and make this sort of cylindrical compacts.

And then put this in a sealed tube and we try to expose it, there will be very bright flashes coming, in this vessel, which will not only yield silver selenide formation, but it will also densify the compact. Densify the compact to such an extent, this is the S E M image of the silver selenide, that you would see there is no porosity, absolutely more than 99 percent theoretical density can be achieved simultaneously.

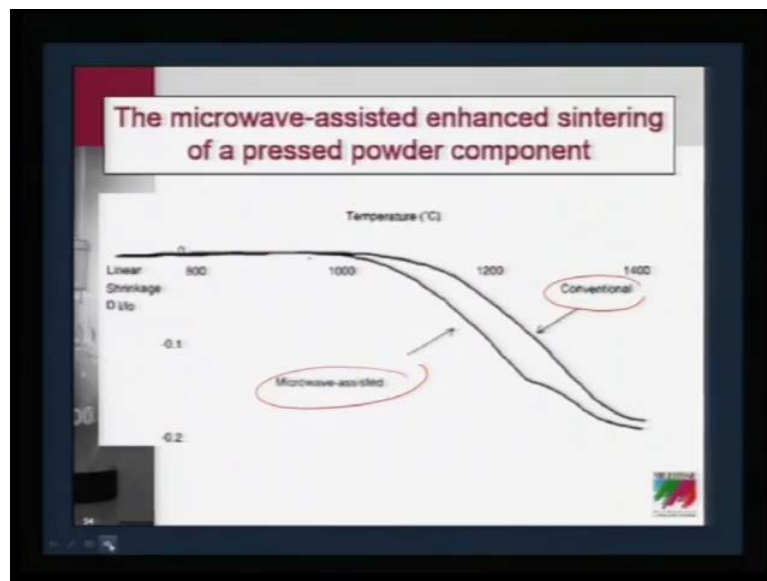
So, this is one of a classic example of using microwave sintering, not only you can prepare, but simultaneously sinter the compound, to the final product. So, this is an example and as you would see, if you take a E P M A electron probed microanalysis of this to map only selenium distribution, just to see whether selenium has segregated or it is uniformly distributed, all these minute spots, that you would see here. This is due to selenium mapping, which means selenium is equally distributed in the short period. So, silver selenide formation is a very classic example of doing both the synthesis and sintering together at the same time, which is a very versatile route to synthesize products.

In sintering one of ceramics for example, one of the important problem that, we encounter is taking over the binder out of the matrix and then densifying it. As you would see here conventional synthesis, the binder usually it is P V A, that is used polyvinyl alcohol say 2 percent of polyvinyl alcohol is actually taken to a ceramic pellet like this and it is actually heated, so to densify. So, this P V A has to be first removed, before it goes through a size reduction and as you would see, microwave assisted synthesis, actually takes out the polymer binder in a much more facile way compared to conventional route.

(Refer Slide Time: 48:55)

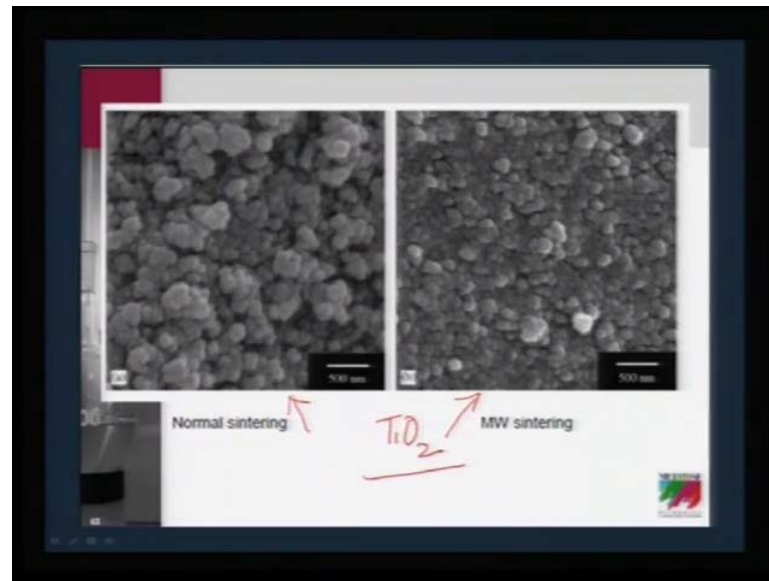


(Refer Slide Time: 49:44)



And also the linear shrinkage mapping that is the densification can be easily achieved using microwave reaction, compared to conventional process.

(Refer Slide Time: 49:54)



And this is another example of titania nano particles, which are sintered using microwave approach, compared to normal sintering, as you could see here, these mono sized grains are intact. And they are more uniform and better densification is achieved compared to normal sintering.

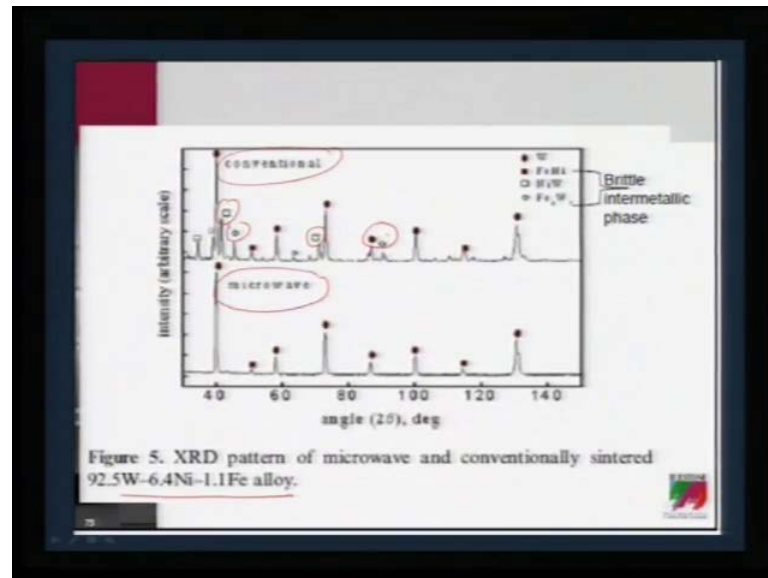
(Refer Slide Time: 50:21)



So, microwave sintering is comparably much more effective and also if you look at sintering of alloys of multi component alloys. The sintering using microwave is much more uniform and with smaller grains compared to conventional stuff, because grain

boundary and grain size can largely affect, the properties of the final product, Therefore, you seem to get a controlled grain size growth in microwave, which can be exploited for device purposes.

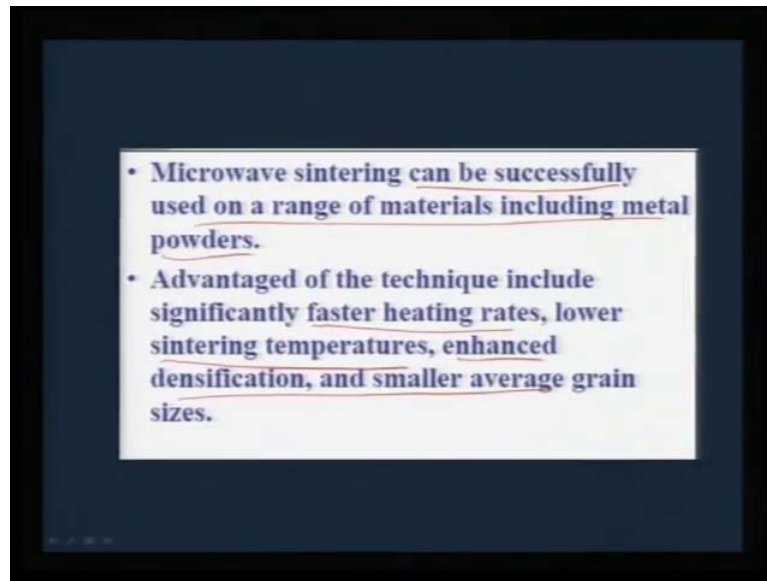
(Refer Slide Time: 50:55)



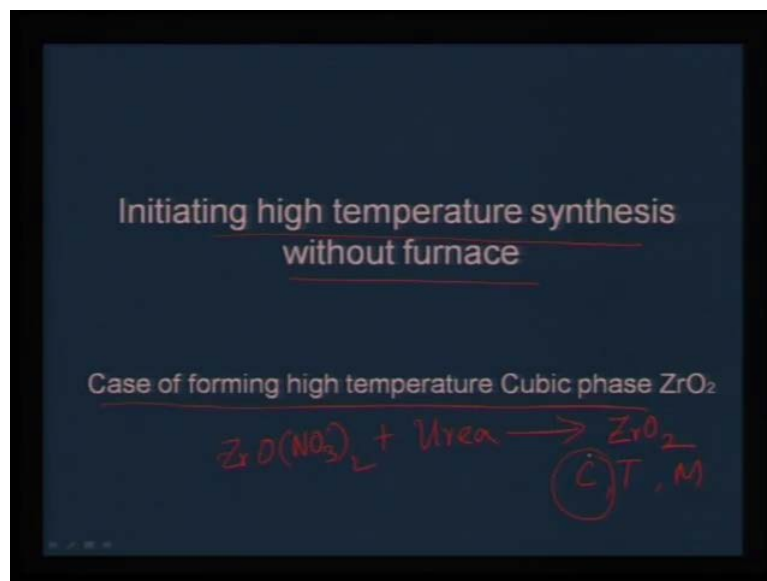
And there is another example of how microwave and conventionally sintered alloys can work out, as you would see in the microwave case, there is not much phase separation, only one particular phase is promoted during sintering whereas, in the conventional case you see various phases are emerging out. This is because of inhomogeneous heating or there is no volumetric heating, therefore this phase separations occur, as you are taking the temperature from low temperature to very high temperatures.

So, a conclusion on microwave sintering is it can be successfully used, for a range of materials including metal powders. Advantage of the technique include significantly faster heating rates, lower sintering temperatures and enhanced classification and controlled grain growth, therefore microwave one of the main application in inorganic materials is to do with sintering.

(Refer Slide Time: 51:33)

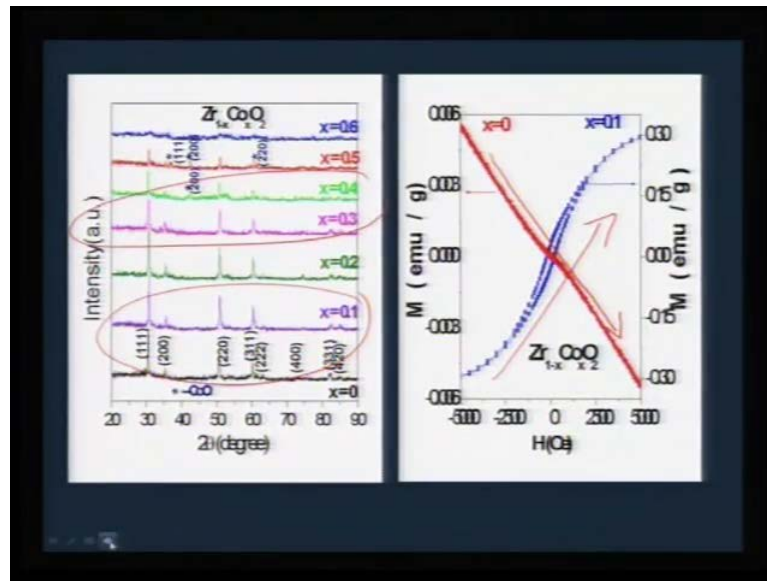


(Refer Slide Time: 52:04)



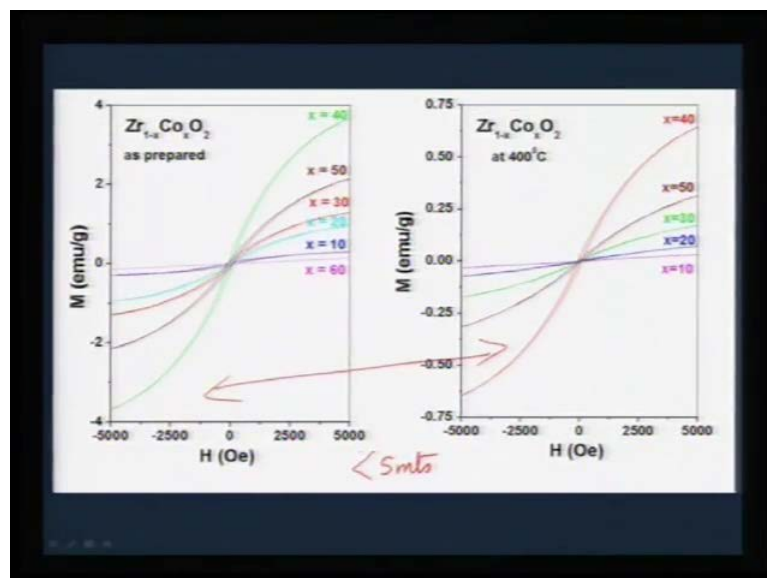
We can also initiate high temperature reactions without a furnace and I have discussed this in other modules also, but let me quote one example, before I make some conclusion. Case of forming high temperature cubic phase of zirconia, we can try to achieve using a microwave, how do we do that we take a zirconyl nitrate and we can use urea or carbo hydrazide or any of the fuels and this would actually give us zirconia nano particles. And these zirconia nano particles can either be cubic or tetragonal or monoclinic, either of this, as you would see from this microwave initiated reactions, you always get the high temperature phase.

(Refer Slide Time: 52:59)



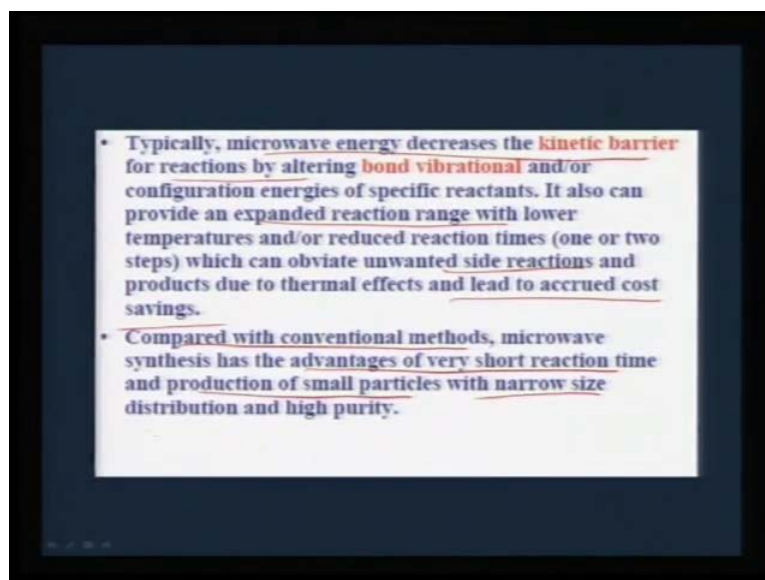
So, therefore, you microwave can be used to completely avoid a furnace heating and as you would see here very clearly, that cubic zirconia phase is formed and you can even dope cobalt, in this case up to 30, 40 percent with convenience without any impurity phase. And this is the typical magnetic curve for ZrO_2 , which shows a diamagnetic signal whereas, 10 percent cobalt doped one shows a very clear hysteresis, so you can achieve a high temperature phases in no time using combustion.

(Refer Slide Time: 53:32)



And these are other view graphs, which tells us, that such magnetic phases can be very conveniently prepared and all this can be done in less than 5 minutes time, because it undergoes a high temperature combustion reaction.

(Refer Slide Time: 53:50)



So, to conclude let me bring out few things, typically microwave energy decreases the kinetic energy barrier for reaction, by altering bond vibration energies, of specific reactants. It also provides an expanded reaction range with lower temperatures and reaction times, which can obviously, avoid side reactions and this can lead to lot of cost savings. So, this is one of the main advantage and compared with conventional methods microwave synthesis has advantage of very short reaction time, production of small particles with narrow size distribution and high purity.

For those of the hearers, I am just confining or limiting the use of microwave only to inorganic materials, but the it is a big ocean, because more than 10000 papers are recorded on microwave synthesis alone where, variety of organic synthesis has been achieved. And in organic synthesis usually, it is the selectivity and the yield, which is very important and this has been enhanced using microwave synthesis. So, for those who are interested in organic synthesis, you can go to many of the websites and the published papers, which will give you, a classic outlook about, how microwaves can be used for organic reactions also.