Nanotechnology Science and Applications

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Lecture - 19

Impact of the Nanoscale on Optical Properties: Measurements

Hello, in this class we are going to continue our discussion on the Impact of Nanoscale on Optical Properties. In the last couple of classes leading up to this, we looked at; first of all, what are those optical properties? What is said that you can expect when you deal with different materials in terms of optical properties and what is the sort of the range that you can expect there.

We also looked at a fair number of details associated with the experimental approach that one might have to use; for carrying out this kind of a study. In particular, we use this opportunity to look at one type of technique to create samples for this study; which is the template-assisted study; template-assisted synthesis process. And as always with much of what we discuss in this course; these are all techniques that can be generalized and used for a variety of different systems.

We may be talking about it in the context of a system and that is the manner in which I would like to introduce it to you so that you see it in the context of its actual use rather than see it in isolation. And then you can use it as you see fit in some other system that you may be working on or you may be interested in working on.

So, in today’s class, we will look at some measurements that might come out of this kind of analysis and see what that conveys to us.

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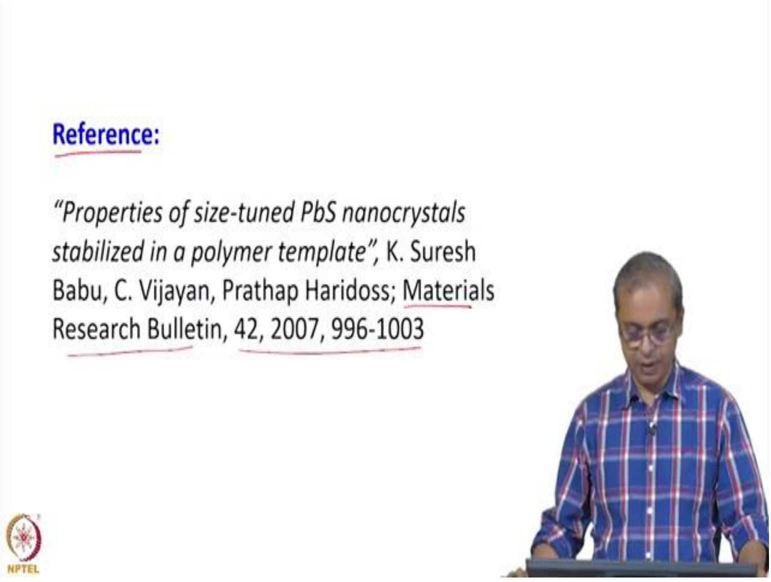

Reference:

"Properties of size-tuned PbS nanocrystals stabilized in a polymer template", K. Suresh Babu, C. Vijayan, Prathap Haridoss; Materials Research Bulletin, 42, 2007, 996-1003

Although, we are talking of a sort of a general system and we will try to generalize the results as much as possible. Here is one reference which you can use which is the properties of size tuned; lead sulfide nanocrystals stabilized in a polymer matrix and the reference is given here from a materials research bulletin publication. So, this is one reference that you can go and look up; there may be others and even, in fact, this itself will direct you to many other references in this area and you can see a similar such work.

So, we will, of course, keep it a general; we will discuss about general aspects of this kind of an approach.

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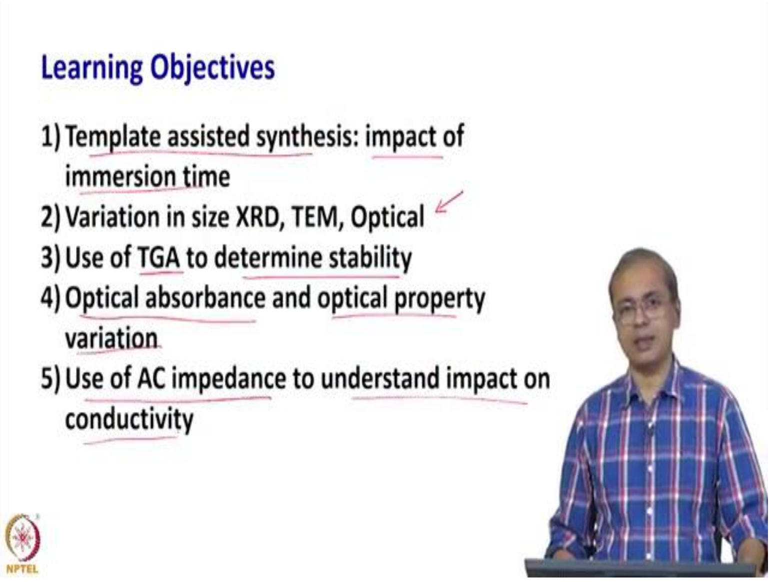

Learning Objectives

1) Template assisted synthesis: impact of immersion time
2) Variation in size XRD, TEM, Optical
3) Use of TGA to determine stability
4) Optical absorbance and optical property variation
5) Use of AC impedance to understand impact on conductivity

So, our learning objectives for this class is to look at the template-assisted synthesis process from the perspective of its impact of immersion time on the synthesis process; the impact of immersion time on the synthesis process. So, that is something that we will look at.

We will look at the variation in size as a function of this synthesis process parameters as obtained from XRD, from TEM and from some optical approaches. We will then look at a technique called TGA; Thermo Gravimetric Analysis which is used to determine something about the stability of various components present within the material; so that is something that we will look at. So, something associated with this stability of those components we will look at through this process.

We will then look at optical absorbance and therefore, look at the optical property variation from sample to sample and therefore, the size dependence of the optical properties; so that is something that we will look at. And finally, we will look at the use of a technique called AC impedance to understand the impact on conductivity due to the presence of these nanoparticles. So, that is sort of the range of different items that we will look at through this class.

Some of these techniques, I will touch upon briefly in the context of what we are discussing here. We may have a separate discussion which is more detailed on just our technique so to speak; so that we will see as we go on. So, today we will look at these objectives.

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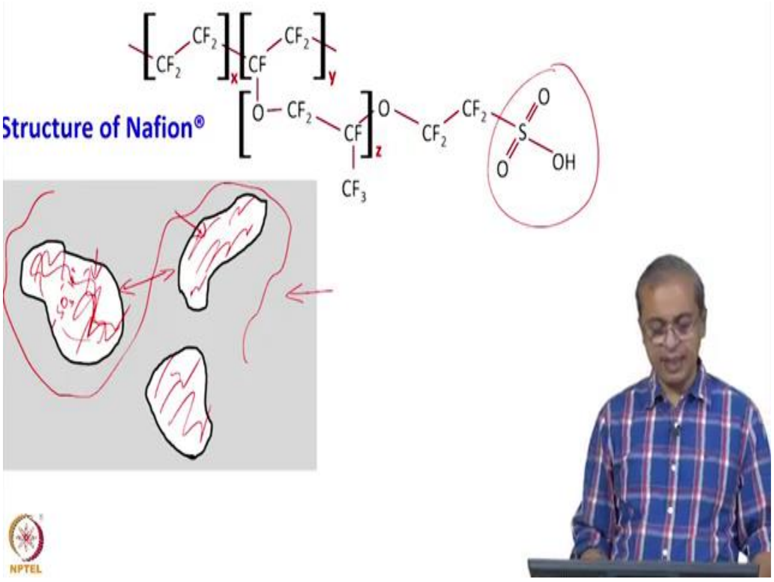

Structure of Nafion®

So, we saw already the structure of Nafion and as I told you that it is a tetrafluoroethylene that is being used and we create a polymer using that, there is a backbone chain and then there is a side chain. And finally, we have this SO_3H group which is the; sort of the active group in that system; the rest of it is a stable polymer and physically this is the structure.

So, there is a sort of a region where the backbone is sitting and then you have the SO_3H groups; SO^{3-} H^+ groups here, which can then get replaced by PbS with the lead salt and then when you send a H to S you can get lead sulfide. So, this is the general way in which this template-assisted synthesis will operate and if you see the product that comes out of it; then you are looking at something that looks like this.

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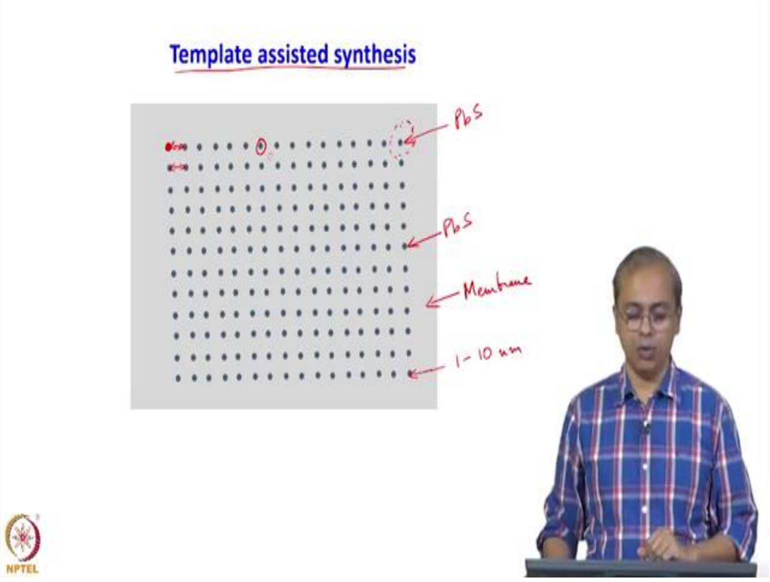
Template assisted synthesis

We discussed various aspects of how this might come together and this is just a schematic of how it might look once you are done. So, if you see here, we have like I said this these regions here; so, this is where you will have your PbS forming. So, all of these locations is where you will have the lead sulfide crystals forming. So, you are going to have individual locations of lead sulfide crystal separated by the backbone. So, that is essentially what you are going to have in your final product.

So, this is only a schematic I have I put hypothetically these are all lead sulfide particles. So, this is all lead sulfide and so on and you can see here that there is all around it; there is space which is the polymer backbone. Basically, this is a schematic and so although it looks like a regular array, it is not really you cannot assume that it is going to be a regular array. And this is also being shown to you in a two-dimensional sense because we are talking of a film, but in reality, even a film is going to have some finite thickness.

So, you should even consider this in a three-dimensional sense; so, for every particle that you see here, for example, there could be a particle below it. So, you could have a particle below it which is sort of like that in that region, but at a depth lower than this particle that you see here. And this array is simply to show you that these are going to be sitting there separated from each other; it does not mean that they are going to be sitting in a perfect square grid. This is in fact, even what I have drawn here is not a perfect square grid; it is an approximate grid, but it can be much more random you can have it much more randomly distributed.

But the points to remember are that they are individual particles and there is a space between the particles. And this is what as we mentioned in last class in great detail, this is what creates the stability for the particle. First of all, there is a space inside which it is growing; so, it cannot really grow much bigger than this space that you see here. And then on top of it, you have the space between those locations which is the space that is here.

And therefore, the particle that is here cannot talk to the particle that is here and therefore, they do not center and that is the; or (Refer Time: 07:08) centering is one way of looking at it, but they do not (Refer Time: 07:11) and they do not ripen; so to speak. So, they all sit separately from each other.

So, the sample that you get will look something like what you see on your screen and what you see is a membrane. And so physically the membrane could be exactly the size that you see on the screen, it could be something that you hold in your hand and that would be your membrane. If that is the scale, then these particles are too huge; we are talking of nanoparticles we are talking of 1 to 10 nanometer kind of size range or a few nanometers is what we are looking at.

So, in that scale in that sense, this is not drawn to scale if that membrane is something that you could actually hold in your hand. But that is typically what we are looking at you are looking at a membrane that you can hold in your hand in which there are particles which are finely dispersed which are separate from each other and stably held within that polymer matrix.

So, this is the template that is assisted synthesis and the kind of product that you will get from the synthesis process and it is going to be flexible because it is in a membrane, it has a host material. So, it has mechanical stability; you can hold it in your hand, you can do various things with it. And so it provides you nanocrystalline sample in a manner that you can work with the only kind of drawbacks being that you are going to have a relatively dilute presence of those nanoparticles because they are separated from each other and it is in the polymer matrix and you are going to have the polymer matrix.

So, whenever you put it to use; you have to in any technological application, you have to keep in mind that there is a polymer also present. So, which means even if those nanocrystalline particles can handle high temperatures; it is quite possible that the polymer cannot handle the same kind of high temperature plus there is also even in terms of optical properties; the polymer does not have 0 optical properties it is many of those polymers you can get in transparent form. So, from the perspective of visible radiation; they will be transparent, but it does not mean that they have absolutely no optical response.

So, under some circumstances, there will be a response from the matrix also. So, you have account for it; it is not that it makes it useless you have to account for it when you utilize it; so, this is the scheme of things. So, technologically you can put this to use somewhere; I mean you can create a surface on top of which you want to put this. I mean I do not know you want to use this for some application where high-intensity radiation is being absorbed. you want to protect something from a laser, then you could create the right kind of optical response at some nanoparticle put it in a polymer and keep it in between the laser and whatever is the item that you wish to protect.

So, these are all possibilities that you can do and, but you would need to do the appropriate background work to satisfy yourself that your system can actually accomplish it. So, that is something about the synthesis and how you would utilize that sample.

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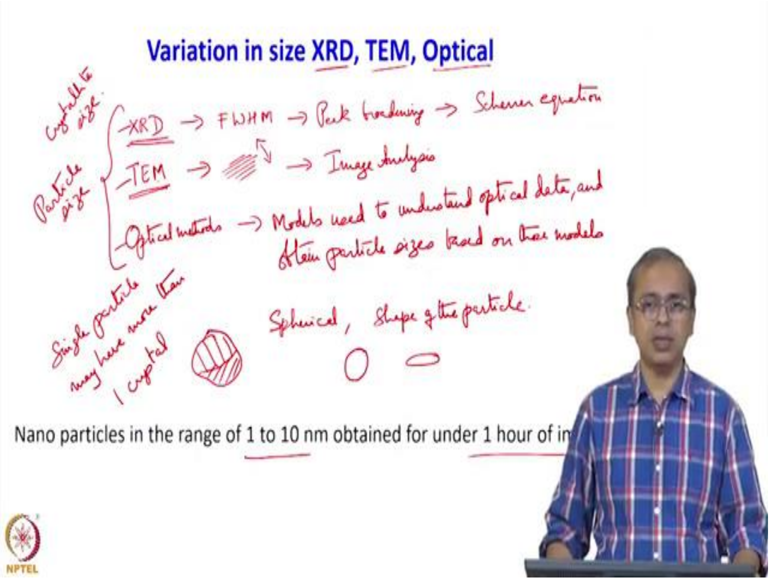

Variation in size XRD, TEM, Optical

Crystallite size

Particle size

XRD → FWHM → Peak broadening → Scherrer equation

TEM → → Image analysis

Optical methods → Models used to understand optical data, and obtain particle sizes based on those models

Single particle may have more than 1 crystal

Spherical, Shape of the particle

Nano particles in the range of 1 to 10 nm obtained for under 1 hour of in

So, now it is interesting to see that you can actually obtain size using XRD. We spoke about the broadening of the X-ray diffraction peak and how that is used as a way of gauging the fact that you have now got a nanocrystalline particle. And that you can actually use that to use the full width at half maximum to get yourself the crystallite size.

So, there is an XRD approach to do this using Full Width at Half Maximum, peak broadening and the use of the Scherer equation. You could also get this from transmission electron microscopy, you could do imaging bright field, dark field kind of imaging. And then based on the kind of imaging that you do, you will actually see those crystals and depending on the microscope that you are using, the type of microscope using the resolution of the microscope you are using you can actually see crystal planes. So, you will actually see some crystal planes that look like that.

So, you would be able to see that in your microscope and therefore, you can just looking at the microscope and the scale of the image; you can actually figure out what your crystal sizes are. And in this case, you are doing some kind of image analysis and image analysis is quite a powerful process. If you use it correctly, please remember this is true for any experimental technique; many experimental techniques are extremely powerful techniques if you use the right kind of instrument and choose the appropriate kind of sample and test it on the right under the right conditions.

And most importantly if you do the analysis in the most appropriate manner; it is easy to over-analyze data; it is easy to make generalizations that are not true about that particular form of analysis. So, you have to be careful; if you do it carefully you can get very defendable answers you can get answers that you can confidently defend in a presentation and that is what you would have to do.

So, image analysis is often used and then there are also optical methods where there are some models that are used; to understand optical data and obtain particle sizes based on those models. So, this is in all these cases there is a fair bit of as I said analysis. You have to be careful on what are the assumptions behind those analyses and satisfy yourself that the sample that you are running and the conditions under which you are testing those samples are consistent with those assumptions.

So, that is something that you have to satisfy yourself with and to the extent that you can do that; your analysis becomes better and better and better. So, I mean what I mean by those assumptions are sometimes in the analysis there will be an assumption that the particles are spherical or there will be a way in which you can integrate into these into that analysis or introduce into the analysis the shape of the particle. So, if it is spherical there will be some constant that you will have to use; if it is sort of ellipsoidal, you might have to use some other constant so on.

So, there will be some constant there which you can vary and then pick an appropriate constant that is correct for the aspect ratio of your particles and then utilize that in the analysis, and if you do that then you get answers that you can sort of defend. So, now in generally, you can all use all of these techniques for coming up with particle sizes for the sample, but it is also true that what will happen is when you do this, you are getting nanoparticles in the range of 1 to 10 nanometers.

So, like we are saying this is some kind of template at assisted synthesis where you are immersing the matrix, the polymer into the solution that has the salt for varying degree of varying durations of time. So, you could have from several minutes to 1 hour of immersion and then correspondingly a different amount of salt enters the system and corresponding to that the crystal that grows when you in expose it to H to S; is of different sizes.

Now, even though you get nanoparticles in the range of 1 to 10 nanometers, what you will see is that between these three techniques, you may find some variation and answers. Generally, what happens in all these cases is often the trend is the same. So, if you see small particle sizes in one case and after say longer duration of immersion; between 15 minutes of immersion and say 45 minutes of emotion. So, three times the duration you are giving you will see a distinct increase in the crystal size, but the actual value that you get for 15 minutes and the exact value that you get for 45 minutes; based on the technique that you use this one or the or the three different techniques that you use, you may get values that are different.

So, we have to make a judgment call on what is of the three techniques which is the technique that is giving us the most believable answer and then use that value. And for this you can take the assistance of literature also, you may have similar such studies carried out in the literature by a variety of different researchers internationally. And you can see why they are preferring one technique over another, what conditions are relevant in which helped them make that decision that this is the technique that we are more comfortable with for our decision on crystal size. So, we will go with that technique.

So, you look at that and then you make a decision on your system; whether this is the right way to do it or your argument has to be is different because the sample is different and therefore, you are preferring some other size. So, now that what you have to understand is that for example, the X-ray diffraction data gives us crystallite size. And often what you are seeing from micrographs in TEM and if you do image analysis on the TEM; you are seeing particle size using the TEM.

So, the reason one of the reasons why they may not match is that a single particle may have more than one crystal. So, this is quite possible you may have a single particle that has more than one crystal. So, in the TEM you see a particle that looks like that, but actually, it consists of two; two crystals here. And based on how that particle is oriented you may or may not completely capture this information and also you have to understand the field of view of different experimental techniques.

When you look at an electron microscope image; you are looking at an extremely small area of that sample. You are looking at a location in the sample which is only 100 nanometers across. And you have taken one such sample from a bigger sample which is say 5 centimeters by 5 centimeters; something some such thing, you are taking a 5 centimeter by 5-centimeter sample which is that film that you made. And in that you are looking at a region which is say 100 nanometers by 100 nanometers or 500 nanometers by 500 nanometers you assume even 1000 nanometers. So, 1000 nanometers is one micron you are looking at a 1 micron by 1-micron region of a sample that is several centimeters by several centimeters.

So, you are looking at a spot that is four orders of magnitude smaller than the sample. So, 10^{-2} is the size scale of that in; 10^{-2} meters is the size scale of that sample and you are looking at a region which is 10^{-6} size scale. So, always when you take such a small region and then you try to generalize for the full sample; you are prone to a greater amount of error because you are going to assume that the rest of the sample is actually exactly like that.

You can actually do that sampling in four or five places, you can do image analysis correctly you would have to take at least four or five spots in that sample, but still, nevertheless, you are looking at an extremely small region in the sample and making some generalization about the entire sample.

So, this risk exists every time you use an electron microscope; whether you are using scanning electron microscope or transmission electron microscope; this risk is always there you are looking at an extremely small region and how representative it is of the whole sample is always something that you should question yourself. XRD on the other hand actually in this context is actually a very comfortable technique to use. Because you are actually looking at a region that is significantly larger then what the electron microscope is looking at.

So, there is a much greater chance that what you are. So, it maybe says 1 centimeter across by 1 millimetre across by 1-millimeter depth. So, you are looking at a sample size which is actually very close that, that is the sample size that is getting irradiated by the X-rays. So, the X-rays are penetrating that region and then they are coming out of the sample from that region and that is what you are measuring in your detector.

So, maybe not 1-millimeter depth maybe few microns depth, but nevertheless, you are getting a fairly significant; several orders of magnitude higher sample volume is being examined by an X-ray diffractometer relative to what an electron microscope is examining or probing. So, to that degree the data that you get from the XRD is more likely to be representative of what the whole sample is. And therefore, data that you get from the XRD is usually more believable from that perspective.

At the same time the sensitivity if you take the sensitivity into account; you may be able to reach some very fine detail using the electron microscope which you will not be able to reach using the XRD. So, there is a tradeoff there; so, it is a tradeoff that you have to pick and choose from in terms of what you are trying to accomplish. But here for example, if you are looking at crystallite size across the sample; then XRD is probably giving a more believable and more representative answer.

In any case, so this is something that we keep in the back of our mind and then we decide what which of these data we want to use. But it is good to have multiple techniques if the crystallite size is a very important aspect of your study. And in this case, it is because you are looking at the trend of some property with respect to trend in crystallite size.

So, therefore knowing your crystallite size accurately and in a defendable manner is a very important aspect of your study. And therefore, it is nice to have multiple techniques even if they do not completely agree with each other; it is nice to have multiple techniques to confirm that at least the techniques are all predicting in the same order of magnitude. So, if all of them are predicting less than 10 nanometers that is great news; that means, they are all agreeing with each other based on the data that they are producing.

And then if they also agree on the trend; if you see samples which are growing in size; are appearing to grow in size in all the three techniques then that is great news for you; that means, between the three techniques you have consistency on at least two things that the order of magnitude is right and the trend is right. And with that you pick one of the techniques which gives you the most I mean; I know the widest range of data for various samples and is also no defendable from this perspective that it is taking a larger volume fraction of that sample into account.

So, XRD is that we have a very nice way to do it. So, this is the idea with respect to crystallite sizes and sample sizes in nano material related study. And some techniques we have looked at here based on any other technique you use; you should also put in a similar amount of care.

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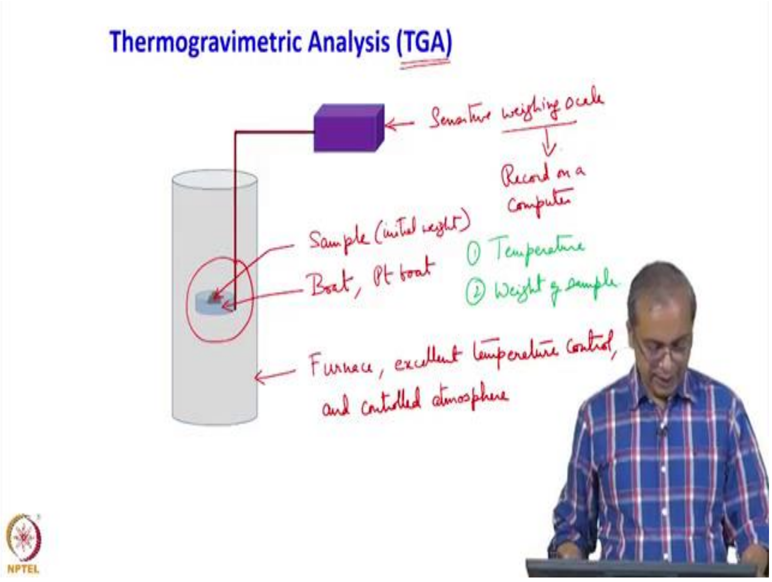

Thermogravimetric Analysis (TGA)

So, the next thing we can do is having found out this information; there is another analysis called Thermo Gravimetric Analysis or TGA, which is used often to study what kind of stability we have in the sample. And the technique I mean experimentally the technique is actually conceptually very simple. So, what we do is there is a furnace; so, this is a furnace, where we have say excellent temperature control and we also have a controlled atmosphere.

So, controlled atmosphere if we choose to you can keep this one as air or you can have say nitrogen flowing through it or argon flowing through it and so on. So, you can select the atmosphere that you wish to have in this furnace and at least the design should enable you to do that. Then inside this furnace we have a boat this is called a boat; this could be using some stable material, some material that is stable even at high temperatures. So, for example, a platinum boat; it is just called a boat because it has that shape; it simply has it is simply a container in which you can keep some sample and then you have the sample.

The sample sets on that boat; so that is what we have; this boat is basically floating. So, this is actually floating; so, it is not sitting on anything, so this boat is actually floating it is just suspended like this. So, this line that you see here is the manner in which this boat is suspended. So, it is floating in the air so to speak I mean, but suspended by this line that is holding it up there. And then from there that is connected to some sensitive weighing balance weighing scale.

So, some sensitive weighing scale is there which is very accurate and precise and so on and that is presented. So, in principle, this is what TGA is and if you just look at the parts here; you can actually make one in your lab by yourself. Because it is just a tube furnace of some sort in which you can have this boat and you just buy a few parts you can make it. You have commercially available systems where this is done in a much more sort of well-defined way, but they have looked at the relative accuracy of various things and so on.

Now, the data from this scale weighing scale you should be able to record on a computer; on a computer for or in some other form. Today everything is recorded no computer, but basically, we need to be able to get data out of it; so, data we should be able to record in some form. So, all we do is the data that gets recorded is twofold. So, you are recording basically temperature and weight. So, those are the two things that we are recording from in this experiment and as I said you can control the atmosphere.

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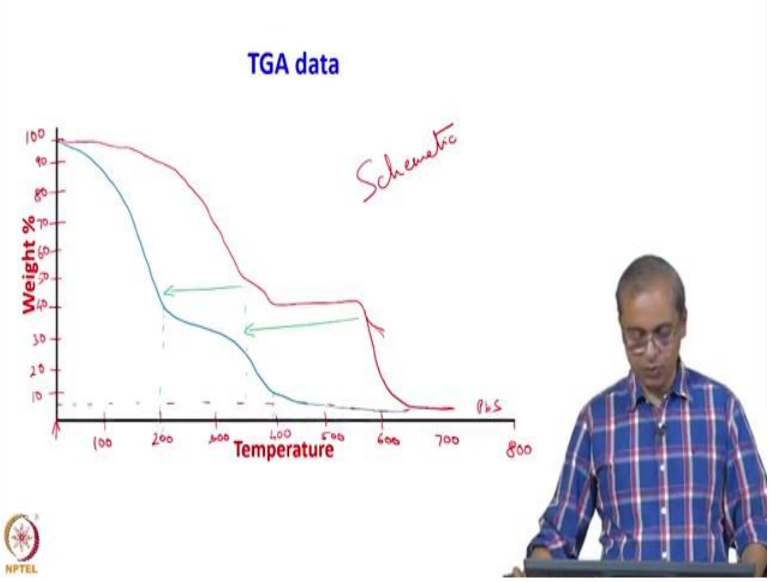
TGA data

So, what is done is; so basically, you put some weight of sample inside there. So, some sample you put; so, you measure its initial weight and you have that some initial weight. So, and the system will record it and so that you already have and so that initial weight is set at 100%; so that is 100% of the sample, so that is 100%. So, on your y-axis you have weight percentage; so, we will just call this 100%.

So, let us just split this up here, so this is halfway mark. So, let us just say ok; so, we have 10, 20, 30, 40, 50, 60, 70 yeah; so, this is what we have 10, 20, 30. So, this is the percentage on the y-axis and then temperature. So, whatever this is this is room temperature out here and then whatever temperature we are going to let us say; we are going up to say 700º C or 800º C; this let me call this 800º C. So, halfway mark is about 400º here; so, we will have 100, 200, 300, 400, 500, 600, 700 something like that.

So, all we are going to do is we are going to raise the temperature of the sample in some atmosphere of our choice could be air could be argon and so on. And then based on what we are trying to study; if you are trying to study oxidation processes, it will be in air. If you are looking at some other stability it could be in some argon atmosphere etcetera and then you will track the weight of the sample as a fraction of the original weight.

So, usually what happens is that as you start raising the temperature; there will be different phenomena that will happen at different points in time.

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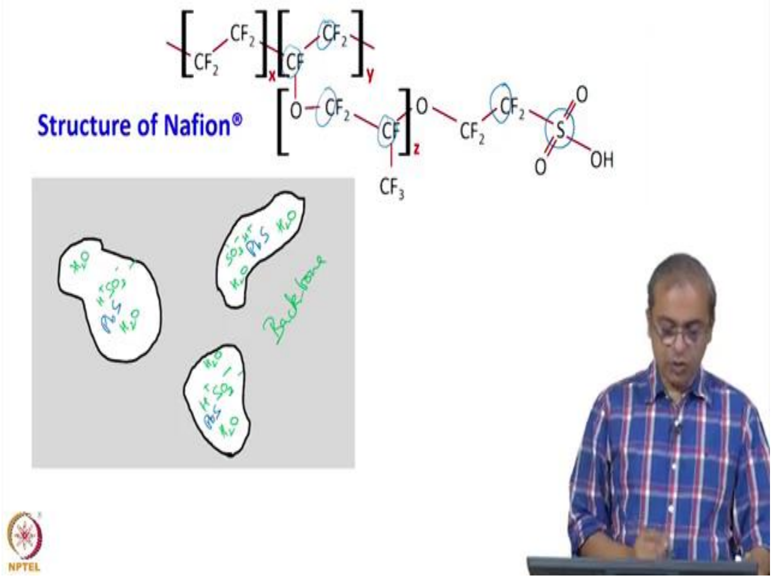

So, for example, if you look at the nafion structure as is mentioned here you have these SO^{3-} H^{+} groups plus you also have water. So, you have water, you have SO^{3-} H^{+} groups and then you have this backbone here; the backbone of this polymer.

So, each of these has some stability; stability in the sense the there is a certain amount of energy required to remove one of these constituents from the system. So, for example, usually, water is something that is going to evaporate very fast and boil away if you cross say about 100ºC. So, that is going to happen and then based on the strength of these various bonds as you go to higher and higher temperature; one of these bonds will break down. And then it will that part of this polymer degrade and go away; you go to even higher temperature then whichever is the strongest bond so that has the highest bond strength and therefore, it means you need more energy to break that particular bond.

So, if you go to high enough energy you will break that bond and then that component will also go away. So, this is the process that you will see that is happening and then gradually you will see different differing levels of weight that is going away.

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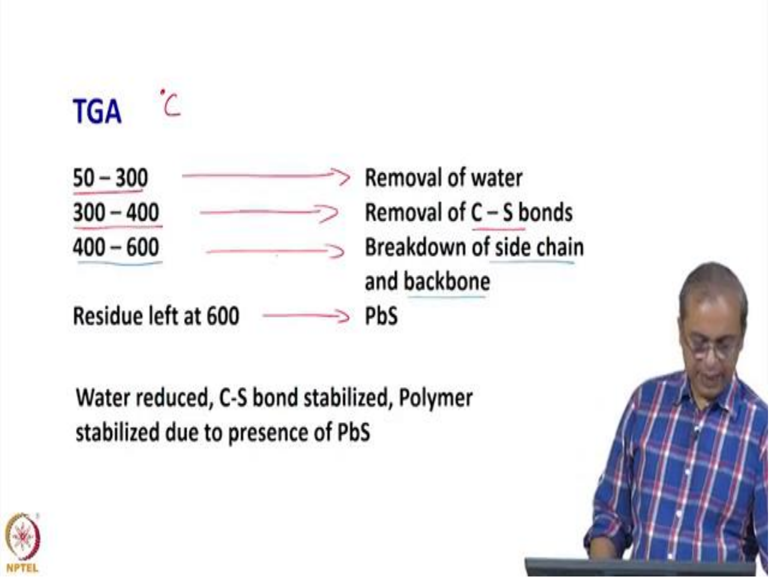

TGA °C

50 – 300 → Removal of water
300 – 400 → Removal of C – S bonds
400 – 600 → Breakdown of side chain and backbone
Residue left at 600 → PbS

Water reduced, C-S bond stabilized, Polymer stabilized due to presence of PbS

So, for example, you can see here between 50 and 300ºC; we have. So, this is all ºC; so, between 50 and 300ºC, we typically have removal of water.

So, you will ask the question of why up to 300ºC, why not at 100ºC? All water should leave at 100ºC. So, this is true if the water is right at the surface right. So, if you take a cloth and you have water just sitting in the top surface of the cloth; then yes it will disappear at 100ºC. But if you have some polymeric system where the water is trapped inside that polymer; then it does not necessarily leave at 100ºC, it may that there may be some type of bonding inside which holds the water in.

So, it may associate for example, with that SO^{3+}; I mean a SO^{3-} H^+ group and that H^+ will become H_3O^+ along with water. And so, you may need to provide more energy to get that water out of that polymer and away from the clutches of that rest of the groups that are there and then get it out of the system.

So, that is why you actually end up having a little wider range of temperatures around 100ºC; a wider range of temperatures over which eventually the water leaves and it does not leave at one unique temperature in this type of sample. Some other sample it may leave at that exact 100ºC you may have all the loss associated with water.

Then between 300 and 400ºC, you have breakdown or removal of these CS bonds; which is what you see here; so, this bond between the S here between the S that is here and the C that is here. So, this bond begins to break down around this larger higher temperature range between 300 and 400ºC. And then if you go to even higher temperatures 400 to 600, you start seeing breakdown of the side chain and backbone.

So, many of the CC bonds that you see here; all these kinds of bonds here and here and here, for example, they all start breaking down if you go to temperatures closer to 600ºC. And then since this is in, we are taking a sample where you have created lead sulfide nanoparticles; so, these PbS nanoparticles are sitting here. So, this PbS nanoparticle is what will remain once you cross about 700ºC. So, once you cross 600ºC where you basically lost all of the polymer parts of it; what you have remaining is this the residue that you have remaining is all lead sulfide.

So, this breakdown occurs here and then break down occurs there; so, you finally, have some lead sulfide that is left. So, just in terms of a schematic, you are looking at something that starts at 100%. And then as you approach it is beginning to drop here around 300 and drop some more and then you may have some format you may have some features etcetera. And eventually you will see some based on what is present there you will see around 600º C; nothing will be left or rather you will have a very small percentage left.

And so, you will see you know; it is something that comes down and then just goes off like that and then that is your what is the residual. So, whatever is residual this is all PbS; this is just a schematic you should get actual data. So, this is just a schematic here; you should look at actual data to see what is happening. But this is the basic idea that you start seeing some weight loss at various temperature regimes and then you can correlate that with various things that are happening in the sample and then you will have something that is left behind which is your lead sulfide.

So, you can get a sense based on the amount of lead sulfide that you have; you can look at this data and you can see if it is impacting any of these transitions in any significant way. So, if you put a nanoparticle into a polymer matrix; you can see the interaction of that nanoparticle with that polymer matrix by just following the same plot for differing amounts of nanoparticles. So, let us just say that for example, at some other condition you see like this let us just say that you see like this; under some other condition. Then what does this mean? It means that in each temperature range right; you are having more weight loss so to speak.

And also, this what was occurring; what took till about 350° C to happen is now happening by the time it is 200° C itself. So, what; so, this is this got shifted backwards right. So, these things got shifted backwards; so, some transitions got shifted backwards under some other operating condition.

So, you can say that by adding some by do to that presence of those nanoparticles something became less stable. So, it more it is able to exit the system sooner; so, something like that. So, this is the way in which you look at TGA data in the presence of some nanoparticle and then try to make some assessment as to what has happened to that polymer due to the presence of these nanoparticles. So, this is how we use TGA data in this context and understand the various relationships that are there in the system and what is happened to the various bonds that are present in the system due to the presence of the nanoparticles.

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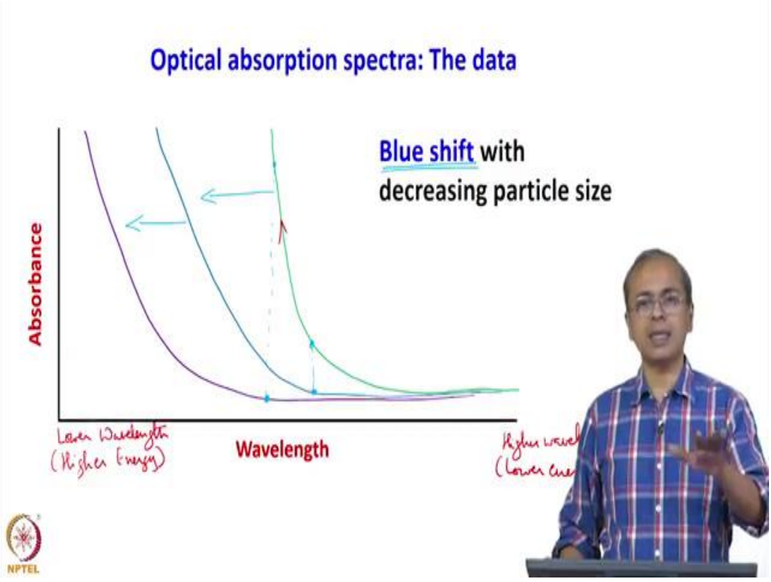

Optical absorption spectra: The data

Blue shift with decreasing particle size

So, optical absorption spectra is the other data that we use quite a bit and as I pointed out generally the; what is observed is the fact that when you look at this data for the bulk particle. So, you will see some data that looks like that. So, nothing is getting absorbed; so, this is wavelength. So, this is a higher wavelength means lower energy and this is lower wavelength means higher energy.

So, what this means is that when the wavelength is high; basically, the material is not absorbing anything because no transitions are happening. And then as you keep on decreasing the wavelength at some point you cross the threshold corresponding to that bandgap of that material and then suddenly this absorption begins to go up in a very significant way; the material is absorbing in a very large manner. What is seen with a variety of nanomaterial systems is that the; this absorption spectrum which is so directly related to the bandgap of that system actually changes dramatically when you go to the nanometer size scale.

So, what you see is that as you go to nanometer-sized scale; you will start seeing essentially data that looks like this and you go to more and more smaller sizes then you see data that looks like that and so on. So, we just put in different color there. So, you can see the differences and so on. So, this idea that first of all that the data is changing in is itself something that is very interesting. Because normally as I said if you go and look at the bandgap of any material silicon, germanium whatever it is you will see only one value in any literature that you go and look for it and that is because they are typically talking only of bulk bandgap; they are not talking of anything else.

So, here the fact that you see the shift implies that the bandgap is changing. Because it is able to actually not respond to even your now come up to this point and here up to this point and it is still not showing any absorption so; that means, the bandgap has changed. Because if it were absorbing already you would have seen this level of absorption could have absorbed this much and here you have absorbed completely look at that you would have absorbed that much right.

So, you are not seeing that instead it is actually sitting very close to it is almost acting like it is not absorbing. And; that means, its bandgap has changed and that is something that is very fundamental to the material may be some fundamental property or changed of that material simply by going to the nanoscale. So, many nanomaterials when you look at their optical properties if their semiconducting materials and you are looking at their optical properties; you see this tendency that their absorption moves to lower and lower wavelengths or higher and higher energies. And since lower wavelength is moving in from the perspective of the visible range; it is moving from the red end of the spectrum towards the blue end of the spectrum; this is called blue shifting.

So, you will see in the literature that you read to say the data was blue-shifted basically it means that the data move towards lower wavelengths of absorption and so this is what you will see as a very useful technique from this you can extract the bandgap by using appropriate equations and extra. So, basically you would extrapolate these lines see where they hit the x-axis and then from that you have to do a little bit more calculation; it does not directly give you the bandgap a little bit more work is required. But this is the data that gets you the bandgap and it sort of conveys that you directly in this plot.

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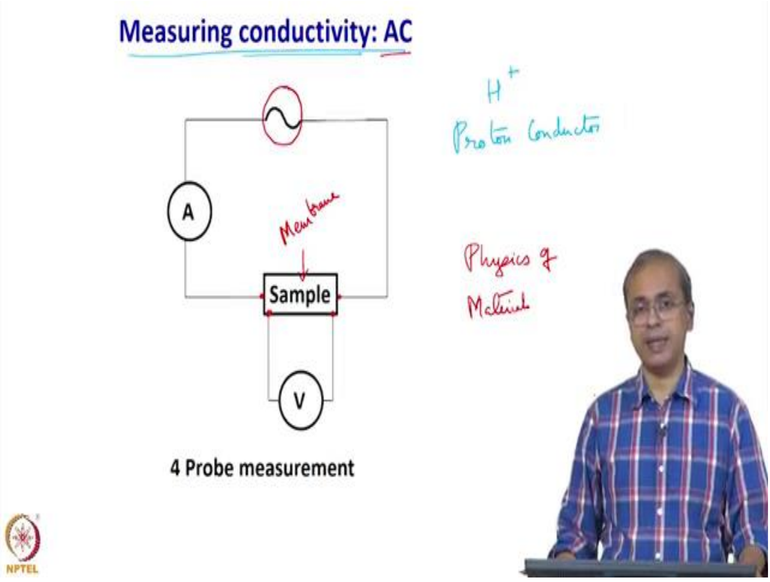

Measuring conductivity: AC

Finally, we also look at what is happening to the membrane itself. So, to understand what is happening to the membrane; one of the properties of the membrane is its conductivity. So, the membrane originally had H+ ions; so, it is typically a proton conductor. And so, it has a conductivity proton conductivity, not electronic conductivity, but proton conductivity which is ionic conductivity associated with it and so if this is your membrane. So, that is your membrane sample and you can get its conductivity using a four-probe approach. So, you have the current sources touching contacting it at two places and then the voltage leads contacting it a little bit more at towards the interior.

And you can put an AC signal because it is not electronic conductor; you cannot just put a DC signal on it if you put a DC signal it will simply charge up like a capacitor and stop. And that does not help us I mean you can actually get conductivity measurement even from that; if you do the if you capture data in this even during their charging process right. So, if you capture data during the charging process from that you can calculate out the conductivity if you wish. But generally speaking, it is very easier and more effective and useful for us if you use the AC conductivity technique; AC impedance technique to help us get ourselves values for the conductivity of this sample.

This technique is actually explained in great detail in another course in the NPTEL course on Physics of Materials. So, I refer to this course earlier also, but you can see this technique there; there is a thing that is one class there where this is explained in considerable detail. So, I will not get into the detail of this technique, but suffice that you can get conductivity values of a sample using this technique; particularly you can get ionic conductivity out very well measured through this process.

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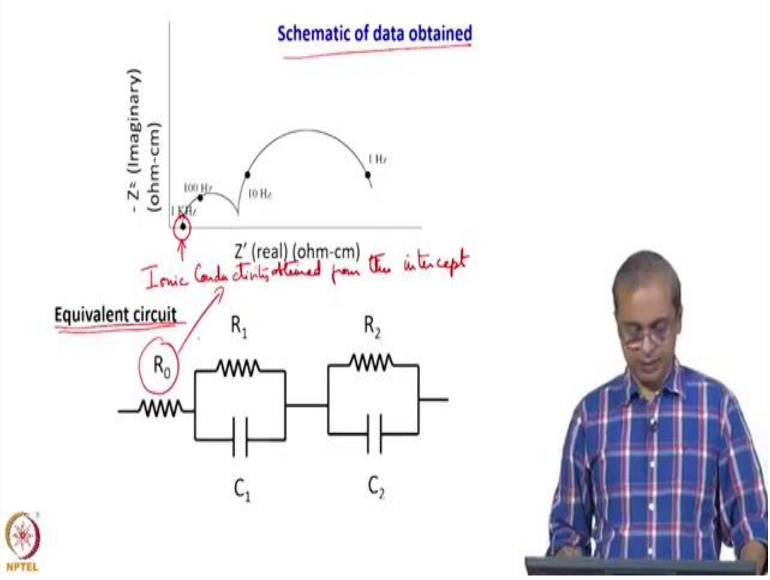

Schematic of data obtained

Ionic Conductivity obtained from the intercept

Equivalent circuit

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And it turns out that to do this; you will actually have to get some data out of it which will a schematic of the data is shown here. And this data we would have to fit an equivalent circuit and some equivalent circuit you have to select. So, there is some process the data analysis process involved in this; you do not directly just fix a value to it, but particularly you will get one intercept here that intercept is your ionic conductivity is obtained from this intercept. There are other factors like electronic conductivity also which are impact that intercepts, but still you can; from this you can get your ionic conductivity value.

So, there is an equivalent circuit and this R_0 is what will help us get this I mean this is resistance here or so from this you ought to get be resistivity and then the conductivity, but that is the process that we will see.

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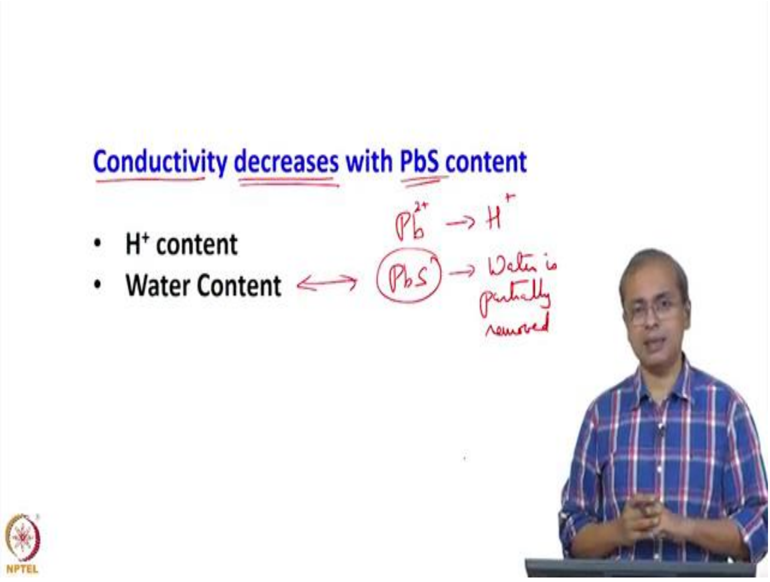

Conductivity decreases with PbS content

- H^+ content
- Water Content ⟷ (PbS) → Water is partially removed

$Pb^{2+} \rightarrow H^+$

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And generally, what is observed in this kind of a system is that when you increase; if you take nafion as the host material and in that you put the lead sulfide nanocrystals, what we see is that it impacts the membrane in two different ways.

First of all because lead is coming in; it is replacing it is removing the H^+. So, this H^+ ion is being replaced by the lead ions that are coming in and therefore, you are losing some protons from the system. Additionally, due to the presence of PbS which occupies some space water is also being removed; it is partially removed. So, now both the H^+ ion as well as the water are both necessary for us to actually have good conductivity values that the membrane should display.

So, if the membrane display is good conductivity value; it means there is a fair amount of protons present in the content in that membrane and also there is a fair amount of water. So, that is as a combination is what gives the membrane good conductivity in this kind of a system this kind of a; (Refer Time: 45:30) system.

The combination of the presence of water as liquid water I mean or the what state of water is usually something that has to be discussed in greater detail; presence of water molecules and the H^+ ions is what gives it good conductivity. So, normally as you had lead sulfide into this system it affects both, it affects the presence of H^+, it reduces the amount of H^+ ions that are present and it also reduces the amount of water present that is present.

Therefore, the conductivity of this material decreases with the presence of lead sulfide. So, you can sort of again see I mean this is a; this data is not directly relevant for us from the perspective of optical applications. But you can see the impact of having grown this nanocrystal inside that material on the property of that material itself and that is something that is you should be aware of. So, the reason is that every finally, when you put it to some technological application; you are you may not be putting it there for just one property of that material. It may be that you need more than one property of the material for that material to be useful in that technological application; in that end-use.

So, you should be cautious in understanding what is happening to the properties of that material; as you load it up some other material like in this case say lead sulfide; as a nanocrystal inside that host matrix. So, that you understand both the impact on conductivity and you also understand the impact on the optical property and both those properties may be relevant in some particular application.

So, you have to be aware of impact on both of them and then and if it is still useful you can go ead and use it or you can pick that optimum point where the impact on conductivity is still acceptable; at the same the presence of the nanocrystal is sufficient that it is meeting some application requirements.

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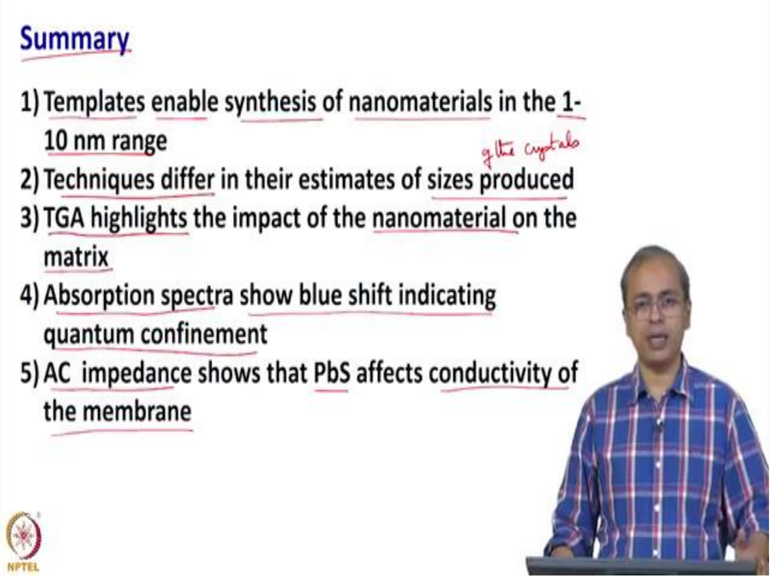

Summary

1) Templates enable synthesis of nanomaterials in the 1-10 nm range
2) Techniques differ in their estimates of sizes of the crystals produced
3) TGA highlights the impact of the nanomaterial on the matrix
4) Absorption spectra show blue shift indicating quantum confinement
5) AC impedance shows that PbS affects conductivity of the membrane

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So, to summarize the template-assisted synthesis; templates enable synthesis of nanomaterials in the 1 to 10-nanometer range. And I will say that this is a kind of value which is very generically presented here. It really depends on the polymers structure whether you get sizes of a particular range or a higher range or a lower range.

But it is possible and it has been shown that it is quite possible for you to get in this range and if this range is desirable to you; you can use it as it is or you can select another polymer where the size ranges that you desire are becoming possible or you can manipulate the polymer to get the size ranges that you want.

Different techniques can be used to estimate the sizes of the crystals produced of the crystals. So, different techniques can be used and we spoke about XRD, we spoke of which is X-ray diffraction TEM which is transmission electron microscopy and also optical methods. So, these are all different techniques you can use to select to figure out what is the size of the crystals that you have created. And then they may not exactly match we discussed that they may not exactly match you have to make a judgment call on which is the most appropriate technique for you. And based on that what appears to be the appropriate technique; we can put our faith more on the technique. So, that is something that you have to be alert to.

TGA which is Thermo Gravimetric Analysis highlights the impact of nanomaterial on the matrix; particularly on the stability of the matrix in if some you see some dough some feature appearing at lower temperatures; it means you have weakened something if the same feature now appears at a higher temperature it means you have strengthened it. So, this is the way in which you use TGA to understand the impact of one constituent on another constituent.

Absorption spectra show a blue shift in the data indicating this idea of quantum confinement. And the idea that the creation of nanocrystalline structures actually changes the bandgap of the material from the bulk bandgap values. And finally, AC impedance shows that lead sulfide or for whatever is material that you are growing there can affect the properties of the membrane such as the conductivity; due to various impacts that it may have one constituent of the membrane.

So, for example, the protons that are present or the water that is present. So, both of them can be impacted and therefore, the conductivity can be impacted. So, this is a sort of a composite set of analysis that you can do with respect to nanocrystals in a polymer where the primary purpose of this kind of activity is from the perspective of optical properties.

And the fact that you can manipulate band gaps and presumably use this material for some say solar cell application where you are interested in bandgap because that decides what part of the solar radiation it will absorb. And in that process a more complete analysis of what all has happened as put these nanoparticles in this matrix. So, this is our discussion on the optical properties and we will look at other details as we go forward.

Thank you.