Nanotechnology Science and Applications
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Lecture - 16
Nanosized Ferroelectrics

Hello, in this class we are going to look at the Ferroelectric Phenomenon and in the context of the Nanoscale. And as we have seen in all these classes, different material properties actually give you very interesting options, when you go to the Nanoscale. And therefore, you end up manipulating the material in different ways to help you accomplish some things I simply going to the Nanoscale.

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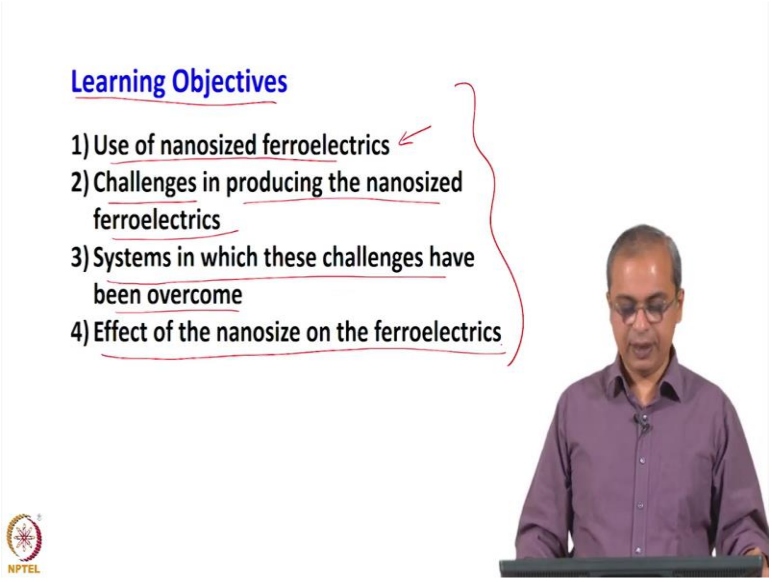

So, we will look at in this class the learning objectives for us or we will look at the use of Nanosized ferroelectrics. So, what is that sort of domain of application technology-wise and so on where there is some utility to having Nanosized ferroelectrics? We will also then look at what are the challenges in producing such Nanosized ferroelectrics. As you will see through the class it is not that easy, I mean there are many ways you can get Nano-sized particles; but if you go to the Nano-sized particles typically there is some difficulty in then accessing the ferroelectric effect at the Nanoscale and therefore, there are some challenges in that context.

Something about systems in which these challenges have been overcome and, in that context, what is that you know, how have they overcome it? I mean so, there is some system where they discover that you can actually do it better, very recently they have discovered this thing. And we would like to see how they have overcome it, what is the thought process behind which using which they have overcome it and they have been able to demonstrate.

And therefore, finally, the effect of Nanosize on the ferroelectrics which is part of the important information which was used to determine this overcoming this limitation of ferroelectrics in the Nanoscale; so, to overcome that they had to look at the effect of the Nanoscale on the ferroelectrics and therefore, figure out a way to overcome it.

So, these then are our learning objectives, we will as we go through the class, we will look at these objectives. As always, we will talk of the general concept involved, the thought process involved, the phenomena involved and towards the end of the class I will give you a couple of references; there are many such references. I will direct you to a couple of references which look at these details in you know, in more specifics and therefore, you can go and look that up if you have more interest.

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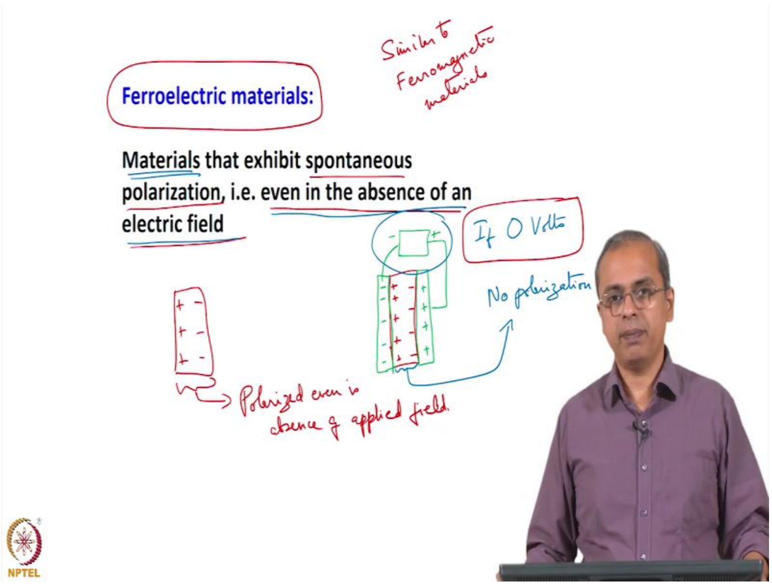

So, what is a ferroelectric material? So, let us start with that and then from there we will figure out what the Nano size does to it. So, the point is generally if you take any material. So, you take a block of iron, you take a piece of aluminium and so on and you keep it; it could even be a polymer material, it could be your ceramic cup that you have any of these materials. If you simply put take a voltmeter or multimeter and you put set some voltage, I mean we set it to read voltages, measure voltages and you put two electrodes on either side of the material, you are basically going to see zero. So, you will see zero voltage; that means the material does not have an inherent potential developed inside it. So, that is the significance of the fact that it is showing zero volts.

So, however, then there are some materials where it turns out that there is spontaneous polarization; that is even though there is an absence of an electric field, it is still showing you that it has got some charge developed. So, normally in other materials, in metals it is difficult if you put a field, if you try to put a potential difference it will start passing current and you will simply see the IR drop. But if you take any insulating material, you take whatever some zirconium oxide something like that and put two electrodes on either side of it.

So, it then behaves like a dielectric material, you put this material here and then on either side you put two electrodes. And you connect this to the negative of battery and then you connect that to the positive of that battery and you do something like that. So, you build positive charges here, on the electrode. So, this is the electrode and you build negative charges here. So, this material in the middle which is the dielectric material will build the opposite kind of charges to compensate for this buildup.

So, you will see positive charges built here and negatives charges built here and this will be in proportion. So, what is coming from that material will be in proportion to what you are applying using those electrodes and that is how the overall charge neutrality gets maintained? So, this is what you see in most materials.

So, now when this what you are applying drops to 0 when this drops to 0; if it is 0 volts, then you do not see any polarization. So, for most materials this is the case; if you put 0 volts, you will see no polarization. Now what we are saying is, this polarization is this idea that you have these charges separated; you have positive charges sitting one side negative charges sitting the other side. So, what I have shown you here is polarization, that material that is in the middle got polarized, you have got+ and- charges separated out. So, this happened in this particular case because you applied a voltage, externally applied voltage you put on electrodes touching that material and then the polarization of that material happened.

When that externally applied voltage dropped to 0, the polarization also drops to 0. So, there were no further separation of positive and negative charges. That separation of positive and negative charges is polarization voltage drops to 0 the separation also drops to 0 and then you have, so a net neutral material. So, generally, that material is a net neutral material, any time you pick it up it is neutral that is the way it is.

But some materials are having this situation, where even if you have not applying an electric field. So, even if it is 0 volts, even if the applied electric field is 0 volts. So, you have not applying any external electric field, even if you apply no electric field it will show you polarization. So, it will show you this polarized behavior, I am just I mean for schematically I am just showing it to you.

So, in the absence of any applied electric field, it will sit in this manner, it will sit polarized, even in absence of applied field. So, this type of material is called a ferroelectric material. It is very analogous to a ferromagnetic material where also you have magnetism in the absence of any other applied magnetic field ok; so, ferromagnetic, so similar to our analogous to ferromagnetic material.

So, there also you see magnetism in the absence of an applied magnetic field. Whereas, in paramagnetic materials, diamagnetic materials you see their magnetic response only when you are applying a field, applying a magnetic field on them. So, in response to the applied magnetic field, the material responds in some way; you drop the field to 0 the materials response also drops to 0. But in ferromagnetic materials, you apply the magnetic field it responds to the magnetic field, but the moment you drop the magnetic field, it continues to stay magnetized. So, that is the idea.

Similarly, for ferroelectric materials, you for some of them you may have to apply an initial field to get them to get polarized; once you have done that you drop the field it will remain polarized. So, that is the idea here and so, that is the ferroelectric material. So, why does a material show Ferroelectricity? So, what is that phenomenon that is happening inside that material that helps that material demonstrate Ferroelectricity to us?

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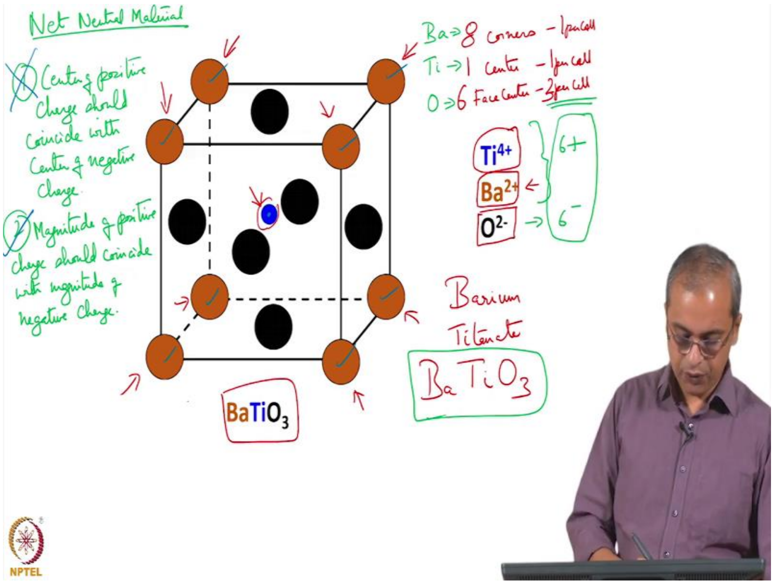

So, for that let us look at a typical material that is often used to highlight this phenomenon, which is Barium Titanate. So, Barium Titanate is what we are looking at, barium titanate.

So, it has this formula $BaTiO_3$. So, you can think of it. So, structure-wise what I am showing you on the image here is, the structure that you can think of associated with this barium titanate. So, for example, you can think of it as an fcc structure in which you are putting specific atoms at specific locations and that is how that crystal I mean happens to be.

So, for example, if you take barium here which is a 2+ oxidation state, this 2+ oxidation state it sits at all the corners. So, there are 8 corners and each of these corners is shared by 8 other you know, I mean 7 other unit cells. So, totally 8-unit cells share each corner. So, if the cubes if you arrange the cubes that is how it comes. So, therefore, 1 per cell you have only one atom and that is why you get Ba; Ti has an oxidation state of 4+ that sits in the middle.

So, that is one Ti sitting in the middle. So, that Ti completely belongs to this unit cell. So, 1 center, 1 per cell. So, again you get 1 and 1. And then finally, the oxygen which is in the oxidation state of 2-, 2- oxidation state they occupy all the face-centred locations. So, you have here 1 2 3 4 5 6; 6 face centers, each is shared by 2 cells and therefore, 2 adjacent cells and therefore, you have 2 per cell on average 6/2 I am sorry, 3 per cell 6/2 is 3 per cell. So, this is what you get; and excuse me, that is how you get barium titanate.

So, you get barium from this then you get titanium from this and oxygen from this. So, that is how you get your $BaTiO_3$. So, excuse me, now you have positive charges in this cell, unit cell and you have negative charges; now there are a wide range of materials most of the ionic crystals are all like this, you have cations and anions and they are all present in the crystal; however, they are all neutral.

So, overall neutrality is maintained in most of the materials, despite the fact that you have positive charges and negative charges and there is a wide range of such materials, I mean there is a huge number of ionic solids where there are positive positively charged ions negatively charged ions, but the whole material is neutral.

Why is the whole material neutral? The reason it is the overall material is neutral is that; the center, the geometric center of all the positive charges put together is the same as the geometric center of all the negative charges put together. So, you take a weighted average of all the positive charges and see what is the center corresponding to all the positive charges that exist in that system; and then take the weighted average of all the negative charges and see what is the center of that negative charge. You will find that the two of them the positive charge and the negative charge have the same center and the value of the positive charge and the value of the negative charge is also equal. So, if the two centers match and the value of the two charges matches, then you have a net neutral material.

So, center of positive charge should coincide with center of negative charge. So, this is for a net neutral material, which is what like I said most materials are net neutral. So, center of positive charge should coincide with the center of negative charge; and magnitude of positive charge should coincide with a magnitude of negative charge. So, if both these conditions are met, magnitude of positive charge is equal to magnitude of negative charge; and center of positive charge is equal to center of negative charge, then the material is charge neutral I mean and it is not polarized also.

So, if you look at the system that, we have here we have barium which is positively charged, you have titanium which is positively charged and you have oxygen which is negatively charged; you have 1 barium per unit cell, you have 1 titanium per unit cell.

So, if you combine these two you have 2+ 4+ you have 6+. So, a positive charge per unit cell is 6+ we have 3 oxygen is per unit cell each of them are 2-. So, if you take this into account this is 6-. Therefore, this is the total magnitude of positive charge and the total magnitude of negative charge is the same; therefore, on average this material is charged neutral. So, that is the first point we need to note. So, therefore, it meets that criteria, it meets these criteria of charge neutrality. So, these criteria is met.

However, it turns out that this material has a ferroelectric behavior, it means even when the absence of an applied field you see a net polarization of charges. That is because you have this condition not being met; the center of positive charge is not coinciding with the center of negative charge in this material. So, the center of the positive charge if it were perfect you know if the lattice points were typical of an FCC lattice point; then the center corresponding to the phase centers would be right in the middle of this lattice.

Center corresponding to the, corners these 8 corners that you have that would also be at the same location. So, if you and the center corresponding to this central atom would also be at the same location. So, therefore, you would have all of the 6 negative charges on average sitting at the center of the lattice; and all of the 6 positive charges also sitting at the center of the lattice. Then you would find that there is no net polarization. In this material it turns out, that is not true in barium titanate, turns out that the center of the negative charge is not at the same location as a center of the positive charge.

To understand this better, we will look at this image here. So, what happens here, is that if you look at the structure carefully, you find that the positive charges. So, if you take barium. So, it is sitting at the corners and then if, but if you look at the titanium and versus the oxygen; you find that the titanium is slightly displaced with respect to the oxygen. So, the titanium is in the body center, please remember it is at the body center, it is right in the middle here. So, titanium is sitting here and oxygens are the face center. So, you are looking at it from the front. So, you are sort of looking at it from this direction in this next image.

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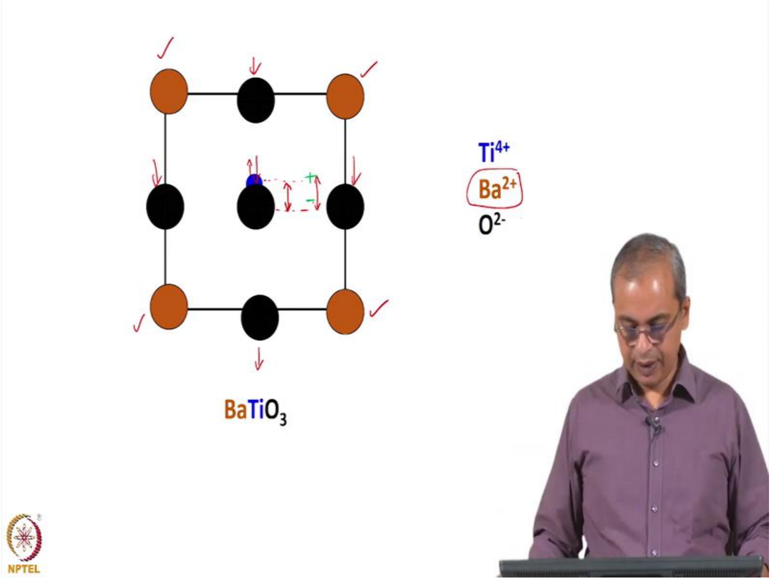

So, if you are looking at it from the front, you find that the oxygen ions all have all moved down a little bit, relative to the center of that lattice; whereas, the titanium ion has moved up a little bit with respect to the center of that of the lattice. Therefore, the net there is a net positive charge, the center of all the positive charges put together is a little bit displaced and the center of all the negative charges is a little bit displaced. So, you see some difference here, which is I mean schematically I am showing you this difference here. So, the positive and negative charges are slightly displaced.

So, you sort of think you can think of it that way. So, it is kind of displaced. So, therefore, this polarization exists. So, this is a ferroelectric material and this is the way in which it happens to be.

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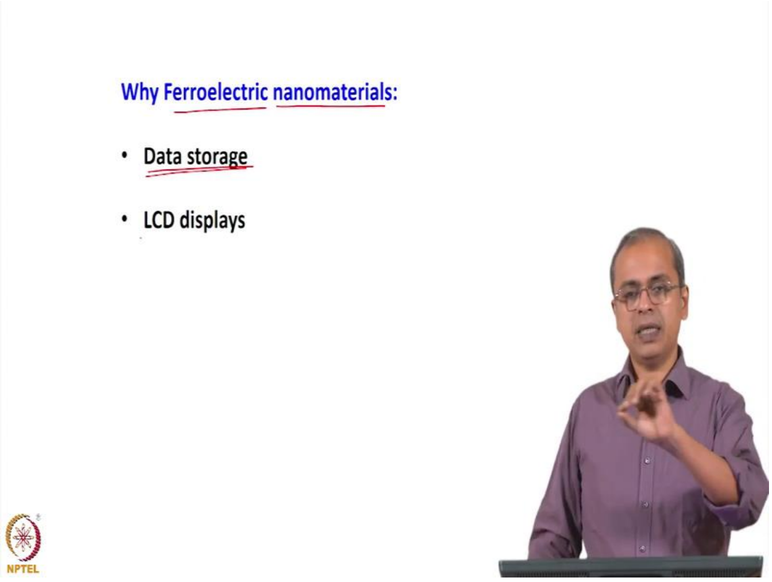

So, now where can we use these materials and what is so important about a ferroelectric Nanomaterial? So, that is something that we need to look at. So, there are at least a couple of applications, if you look at literature you may find more possibilities, but at least couple of applications which are very technologically significant; which we in today's usage of technology, we interact within a very significant manner. The first is data storage and the second one is LCD displays.

So, both of these are technologies that we interact with a lot. So, in data storage as that you are storing data in typically these days it is magnetic storage. So, that is a place where you can store data and may be ferroelectric materials can be used with respect to that; and similarly LCD displays are displays that we use I mean are one of the types of displays that we use for various you know, say computer applications or even entertainment applications and so on.

Of course, there are different types of displays this is one kind of a display. So, in both cases, let us see briefly what is the possibility of using a Nanomaterial and then later see what is the challenge involved in it.

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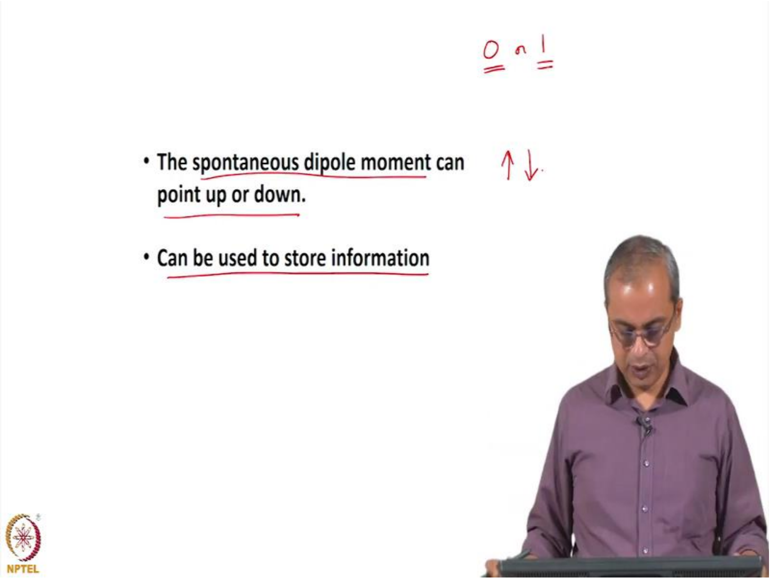

So, if you look at a ferroelectric material as I said, you have a spontaneous dipole moment that can point up or down. So, you have a spontaneous dipole moment that can point upwards or it can point downwards. So, therefore, this can be used to store information, see ultimately in computer storage you are storing everything as a 0 or 1. So, you have a 0 position or 1 position.

So, you claim that 1 is switched on or switched off something like that we will have. So, that is the way in which you put this information together, you convert all things that you type is as numbers and whatever it is that you are trying to do you convert that to internally it converts everything to zeros and ones. So, the storage basically has zeros and ones. So, and then you have some logic by which you read that storage and then do with it.

So, you have to have a system by which you can identify a location and claim that it is 0; and then something should be different about the adjacent location or some other location and you can claim that, because it is different I am reading that as a 1 and this you do throughout the device. So, wherever you see the first kind of condition, you call it a 0, you wherever you find the second kind of condition you call it 1.

So, this is generally been done with ferromagnetic materials. So, you can magnetize it upwards or magnetize it downwards and then you can claim that down is 0 and up is 1;

and then you can on that basis you can think of some concept like that, based on which you can do this.

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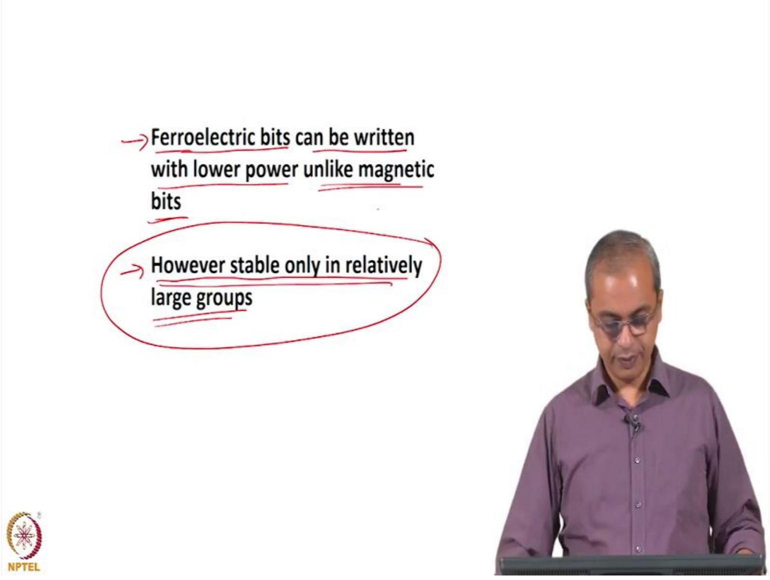

So, the same concept we can think of for using ferroelectric materials because it has that spontaneous dipole moment, spontaneous polarization that can exist in it; you can polarize it upwards or you can polarize it downwards. So, therefore, you can think of the concept of a ferroelectric bit; a bit is basically where you are holding the 0 or 1. So, you can think of it as a ferroelectric bit, which you can switch to as a condition that you can keep calling as 0 and another condition that you can keep calling as 1.

And so, this can typically be written with lower power, unlike magnetic bits. So, the common storage that we are using which is magnetic and which is working just fine, we are using a lot of it I mean extensively. But if you see the whole field of computer science and engineering from the material perspective, they want to reduce the amount of power or amount of electricity required to do each activity.

This is very important in pushing the frontiers of computer science and engineering, particularly computer engineering to push the frontiers of computer engineering. Because for more and more calculations to be done more and more operations to be done, lot of communication is going on internally. So, current goes somewhere, does something, comes back, does something else lot of stuff is going on. So, everywhere there is an IR drop and therefore, heat is generated.

So, if you take supercomputers; one of the greatest challenges in the commercialization of supercomputers is the fact that there is a tremendous amount of heat being generated. So, surprisingly most you know, high-end computing manufacturing companies, for them air conditioning is a very important challenge.

You have to air-condition the place with the correct flow of air, it is not simply having air conditioner at one corner of the room, you should have a flow of air, cool air which is or some other coolant which goes to all those locations where heat is being generated. So, heat management is a very important thing in computer engineering when you get to like really top-end computers that are pushing the frontiers of what is being accomplished.

So, it helps in a tremendous way if you can accomplish the same thing inside the computer using a lot less electricity; that means, your burden on the cooling decreases dramatically, and therefore, you can increase the or with the same amount of cooling you can now increase the amount of computation you can do. Which is huge, I mean even if you like half the heat burden you can double the computing power. So, that is dramatic. So, that is very important.

So, people focus on finding ways to reduce the amount of current required. So, it turns out, when once they discover that you can do a change in ferroelectric states from 0 to 1, whatever you call to define a 0 to whatever you define as 1; if you can do that change with less electricity, then you can do for a magnetic storage going from 0 to 1; then clearly that is a great winner, I mean you have a great thing that you can use in the realm of computer engineering.

So, therefore, from the perspective of data storage, a ferroelectric bit is more desirable than a ferromagnetic bit as of today. So, therefore, there is interest, that is definitely there. So, what is the challenge there? The challenge is this, it turns out that the stability of that ferroelectric group, for it to stay consistently as 1 or for it to stay consistently as 0, it turns out that this stability happens to occur only if you have slightly larger groups, larger groups of atoms. So, that is when it happens. And the reason is in all these cases, there is thermal energy which is fighting this you know, any other internal phenomena that is there it will do even ferromagnetic behavior, etcetera can be disrupted, if you have put enough thermal energy into it. So, there is always some thermal energy that is there; there is interaction between adjacent polarized locations, etcetera.

So, you even though you are trying to set zeros and ones you have conflicting forces which are trying to randomize the whole process. So, you need stability in that what you set a 0 should stay stable at 0; what is set as 1 should stay stable as 1. So, this is very important it turns out that in ferroelectric systems, you need to have a little larger collection of atoms for the stability to be maintained, for as a 0; another larger collection of atoms and therefore, unit cells for the stability to be maintained as 1.

So, even though it is using less power, if you need a larger collection of atoms to enable you to set 0 or 1, then your density of information stored decreases. If the density of information stored decreases, now for the same 1 GB hard disk, you will need let us say; if you can only store you need twice as many atoms to enable you to do this storage with using ferroelectric systems. Then instead of when a 1 GB hard disk has a certain size, the same 1 GB hard disk if you were made you have to make with ferroelectric material it will have twice the size.

So, a factor of 2 is very significant it is not a small change I am just giving a factor of 2 as an example. But the point is in computing that is the other challenge; one is to reduce the amount of electricity that is involved, the other is to reduce the size that is there. Because the size also impacts the distance that the electricity has to travel to do some activity and again you have the IR drop. So, if you have reduced the amount of electricity required, but you have doubled the distance, you are not really saved anything. So, therefore, this is a challenge, if you want to use ferroelectric phenomena for doing data storage then this is a challenge.

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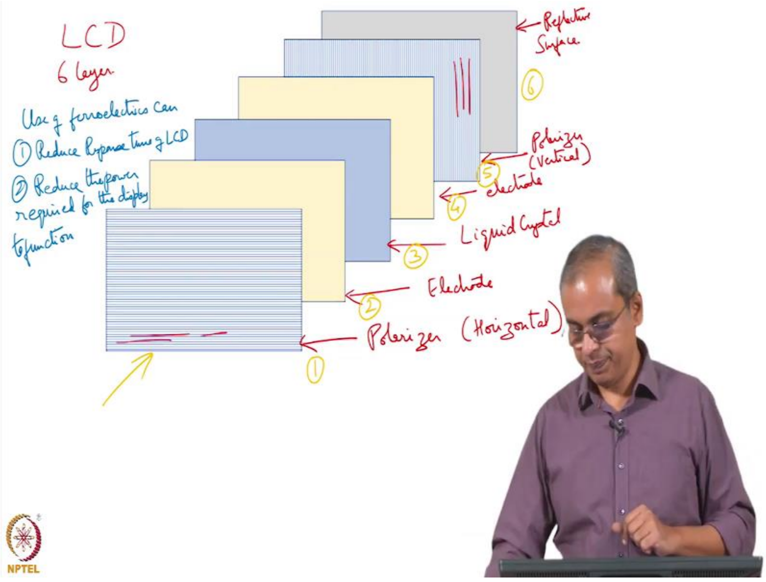

Now, so that is with respect to ferroelectric with respect to data storage. So, now, let us see also with respect to LCD displays. LCD displays where does the concept of a ferroelectric material enter into the picture and what are some possibilities that we have? Generally, in LCD displays, you have let us see here 1 2 3 4 5 6 layers you have. So, usually what will happen is, this is the typical kind of layout, these 6 layers are in a very thin region. So, some few maybe under 10-micron kind of region you have in which you have the 6 layers and that together is your LCD display.

So, the central part of the display is this layer which has the liquid crystal. Now the liquid crystal consists of molecules which can orient themselves in different ways and then based on an electric field. So, they have some oriented, layout, but they flow like liquids. I mean, so they have behavior that is similar to liquids, they also have this organized behavior similar to crystals and that is why you get this named liquid crystal for this kind of material. And they are also, you can find a liquid crystal system which are also a responsive to electric field.

So, you apply the electric field it will that crystal will orient in some direction, all of them may be little randomly oriented once you apply a field, they will all orient in a certain way. And if there are liquid crystals which will then, which have a twist in then and therefore, if there is light going through them, it will twist the light. So, it will try to twist the light. So, this is the kind of concept that is involved. So, what happens here the central part is this liquid crystal and there are two electrodes; then on the front-most layer is a polarizer.

In this case, I have got the lines horizontal. So, let me just call it horizontal and this layer here is also a polarizer, but here I have got the lines vertical. So, I will put vertical. And finally, right at the back we have a reflective surface. So, this is the sort of the set of layers that are involved. Now what happens is if light comes in. So, you have light coming in here, some light that is coming in. So, this polarizer that is in front, the horizontal polarizer makes the light only the light that is polarized in the horizontal direction goes through this first layer; all the other light is prevented from going through the layer. So, some light goes through, all of which is plane-polarized in the horizontal direction that goes through.

So, then that goes through, there is a transparent electrode it continues past the electrode, it goes through this liquid crystal layer. So, it goes past the. So, first goes through this layer, then it goes through this transparent electrode, then goes through the liquid crystal layer. In the liquid crystal layer, based on the orientation of the molecules the light is twisted. So, now, by the time. So, between this second electrode and the fourth electrode if you apply the correct kind of potential; then you will find that light that was that started off horizontal, you can orient it to vertical condition as it comes off the fourth electrode, as it comes through the liquid crystal layer and enters the fourth electrode.

So now, after it crosses the fourth electrode, it will come to the polarizer which is the fifth layer here, it arrives at the fifth layer here, which is a polarizer which is polarized in the vertical direction. But you have started with a light which was polarized in the horizontal direction, you twisted it to a light which is now polarized in the vertical direction. So, when it comes to the vertical polarizer, it is able to go through because the that vertical allows light to pass through which is vertically polarized.

So, it goes through, it hits this sixth layer which is this reflective surface; and then comes right back. So, it does the exact reverse in the back. So, it is coming back vertical. So, it comes through the polarizer; then it gets twisted to the horizontal condition due to the potential between the 2 electrodes on either side of the liquid crystal display. Then comes to the front, which is the polarized horizontal direction it is also in the horizontal direction it comes right out. So, when you set up this situation, when you look at the display you see the display is bright. So, light goes in and comes back and so, you see a bright display.

So now, if you apply the potential in some regions such that this twist, in that in those regions the molecule will not twist the light from horizontal to vertical. So, let us say, it does some random twist, it is not going from horizontal to vertical. So, then when that light goes to the second polarizer it is not polarized in the vertical direction. So, it does not go through the polarizer, it does not go through the second polarizer, it does not reach that mirror or the reflective surface, it does not bounce back; as a result, you do not see light in that region.

So, wherever the polarization of the twist of the molecule is not correct, you will not see the light coming back; where it is correctly twisted you will see the light coming back. So, this is how you figure out; you can force some regions to say stay dark, some regions to stay light and that is how you get the display. So, you write something in black and white you get it in black and white and then you can do this. So, then again, we can add some color to it and then you start seeing; once you add 3 pixels to it you start seeing the color, but in general, this is the process.

So, here also, if you want the system to respond faster it is interesting if you can add ferroelectric nanomaterials to those liquid crystals; and then that will help them respond faster, it will help them respond to even minor changes in potential. So, both again from the perspective of reducing energy, so use of ferroelectrics can potentially, I mean reduce response time of LCD, it will also reduce the amount of energy power required; it reduce the power required for the display to function. So, both of these things will do. So, or at least there is a possibility that it will do both these things and based on the system you can see, whether it make which of them is greater phenomenon; but at certainly it will help reduce the power required to do this process.

So, there is interest in developing ferroelectric materials which are in the nanoscale; again, you the smaller the scale more effective the display is. Because again for just like for data storage; for display also as you were aware pixel size is very important, smaller the pixel size the finer is the display. And therefore, the display looks continuous to us rather than big squares which are pixelated and then you do not like the image that you see, you want very fine pixels so that the image looks smooth and nice.

So, then if it is a nanometer-sized ferroelectric material that is certainly very useful. So, we have seen both with respect to magnetic storage and with respect to LCD displays; both of which are like technologies that we work with, that we utilize quite extensively; the availability of a ferroelectric material in the nanoscale is very useful to us.

We also saw that I mean the concept of ferroelectric phenomena in itself we saw; and we also made note of the fact that due to various disruptive forces that may exist, usually when you go down to the nanoscale you are not able to see the ferroelectric behavior in many systems. It is not showing you, sustained polarization in the absence of an applied field. So, that is a challenge that needs to be overcome.

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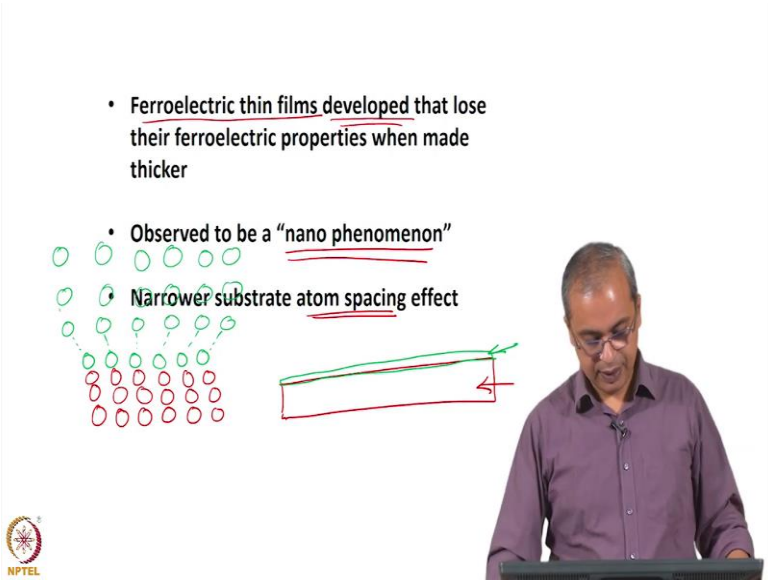

So, what people have done? In fact, and I will draw your attention to some references at the end of the class. So, there were some reports that which said that in for example, in a hafnium oxide-based system; they found that at an extremely small nanometer-sized scale they were able to see ferroelectric behavior. And at the same time when they went to slightly larger particle sizes, they actually lost the ferroelectric behavior. So, this was counterintuitive and in fact, the opposite of what they had seen in many other systems; they found that in the system. And initially there was some feeling that maybe it was some artefact of the way the experiments had been done or of the sample's etcetera. But so, there was some more thought was necessary to understand why this was happening in nanoparticles of this hafnium oxide-based system. And it is also I mean, just getting the particles is one thing because you can do that with let say ball milling and so on; but to do a controlled study to understand what is going on, another group has actually basically looked at ferroelectric thin films.

So, they looked at ferroelectric thin films, to see if they can get their ferroelectric property or lose their fellow electric property based on the thickness of the film. So, this way you have some control on the size and to see what is happening. And so, some substrate is taken, on which this film is deposited and then they studied the ferroelectric behavior. So, they found that this happened this was true, that actually at very small sizes, they were able to see ferroelectric behavior.

But once they cross some about 10 nanometers or so in size; once they started crossing thicker to thicker films, the ferroelectric behavior disappeared. So, they were able to confirm that there is some kind of a nano phenomenon that is happening, which is what is enabling; so, there is something unique to the nanoscale. So, there's something happening which you can call as a nano phenomenon and that is helping a certain system show you ferroelectric behavior at nano sizes, but not which is disappearing actually in the larger sizes.

And when they studied, they found one of the critical parameters was that the substrate on which they were making the film. So, you have usually this kind of a substrate, I mean some solid material which is strong and on top of that you deposit the film, right and then that is how we study the film. So, they found that the spacing of atoms in the substrate. So, atom spacing interatomic spacing in this area was less than the interatomic spacing in the film, based on the original crystal structure that was there for those two materials.

So, this means, usually what happens is if you look at atoms that are there in any system. So, you will have atoms these are the atoms corresponding to the substrate and you have many of those atoms. So, you have a large number of those atoms, on top of this you are putting the layer of the film.

Generally, what happens is the atoms tend to line up because that is when they have the least amount of energy, relative to other locations that they may have. So, the crystalline structure tries to sustain the same crystalline structure on either side that is when the overall system has less energy. So, they try to line up.

So, now, if your original material actually had larger spacing, let me just exaggerate it here. So, that as a separate material it had spacing like that; you are taking a material that is widely spaced and you are trying to force it down right. So, by doing, so you are actually applying compressive stress on that material and it is strained in a compressive direction. So, therefore, they found that this strain seems to be having an impact on the ability of that material to show you, the ferroelectric behavior indeed in under some conditions.

And basically, as you add more and more atoms, you keep adding more and more atoms on top then it goes back to having the original spacing of that material. So, that is how the material behaves. So, the thinner the layer the greater is the impact of the substrate on the layer; the thicker the layer less is the impact of the substrate on the layer. So, because the layer starts having it is own behavior as you move away from that interface, it is very critical to be close to that interface.

So, they were able to see that the when you apply strain this seems to be happening. So, first of all, that this phenomenon is true it is happening and it is happening in the nanoscale; and that it is happening due to the presence of compressive stresses.

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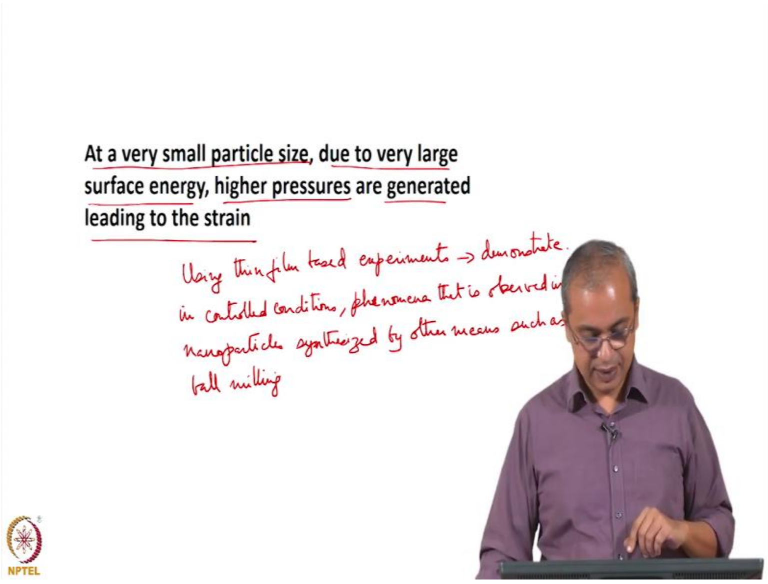

So, then they investigated the nanomaterial itself in some greater detail. And they reach the conclusion that basically at very small particle sizes due to the very large surface energy of all those bands that are still unsaturated, they were trying to reach out to each other to saturate themselves; they are sort of effective effectively compressing that particles.

They are compressing the particle; in that system it turns out that you can think of it as a high pressure that is being generated on the surface of the particle trying very hard to saturate those bonds; that sort of competitive thing that is happening there, leads to a strain that is being generated in the system. So, there is some strain that is being generated in the system, as a direct result of this process that it is where there is all these bonds that are trying to compete and compress each other.

So, therefore, using thin film-based experiments some groups have been able to show demonstrate in control conditions, phenomena that is seen in nanoparticle synthesized by other means such as ball milling. So, this is also nice to know, see how they were trying to investigate nano-sized phenomena and that I mean so, there is different people have tried different things. So, the synthesis technique is important when you are doing science related to nanomaterials; because the synthesis technique brings with its certain peculiarities, which you should be conscious of and therefore, you can very intelligently take advantage of and that is the or at least be alert to.

So, you see some phenomena and you are trying to understand, then you start thinking about all these things, this strain that is there and then so on and then try to reach a conclusion based on it. So, ball milling gives a different kind of conditions to the particles, they are being hammered, they are broken down, but maybe it could introduce impurities. You are already talking of a nanoscale material, in that even if you have a few atoms of impurities then that is a significant percentage of impurities. And you may have variation in sizes, you may not have enough control to say that you have got only this particular size. So, you have those peculiarities associated with it.

The thin film, on the other hand, you can measure the thickness of the thin film, usually thin films are made under high vacuum conditions and very clean conditions. So, you have much greater possibility that you are getting a much purer product; and therefore, with greater confidence you can say that the property I am seeing is the property of that particular oxide layer rather than something else. So, you get that kind of control, but it is not a particle.

So, you are then trying to extrapolate some result from that thin film to another synthesis process which is the ball milling kind of process. And then trying to understand why there is a phenomenon that is showing up in both cases, you have understood that there is some stress, in this case, could be something else in another experiment you are doing. You understood that you have to see what is happening in the particle morphology which is sort of mimicking this in the thin film or no film.

So, like this lot of interesting work is there and this is an example of where this has been done. So, we see that there is a path to get to Nanomaterials which have a ferroelectric behavior. And in fact, not just that we find materials which very uniquely give you this ferroelectric behavior only in the Nanoscale and that is again very interesting to see.

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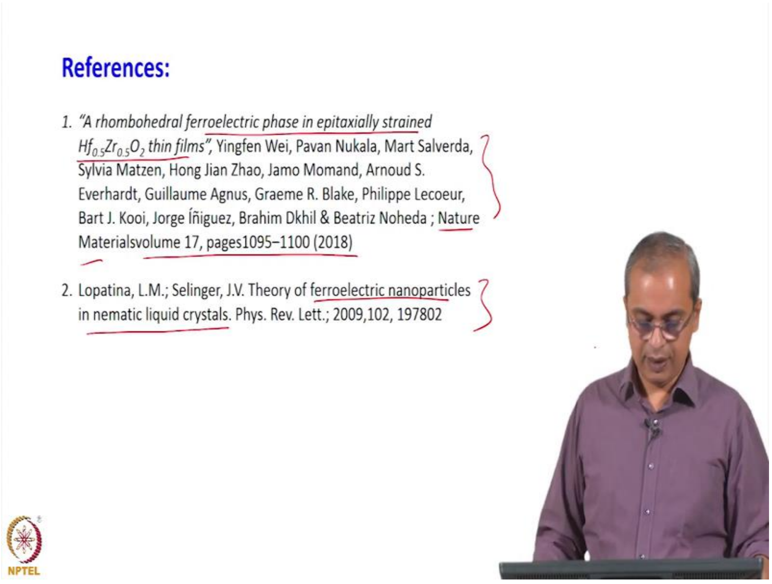

So, here are a couple of references which you can go and lookup. So, this is a pretty recent reference in nature materials you can see this is the volume and so on. This is a 2018 publication you can look at it, talks of rhombohedral ferroelectric phase in epitaxially strained hafnium zirconium oxide thin films and this is the group that has done it.

So, you can go and take a look at it with to see much greater details of this specific system, what they did with respect to the specific system, how they made those measurements and how they were able to come up with a theory that helped them link things up. There are quite a few dis references on ferroelectric, use of ferroelectric

Nanomaterials in nematic liquid crystals. So, this is just one example of it that I am showing you here, if you go and look at references you will find several such references you can certainly look at them, looking at that exact idea that we were discussing a little while earlier in the class.

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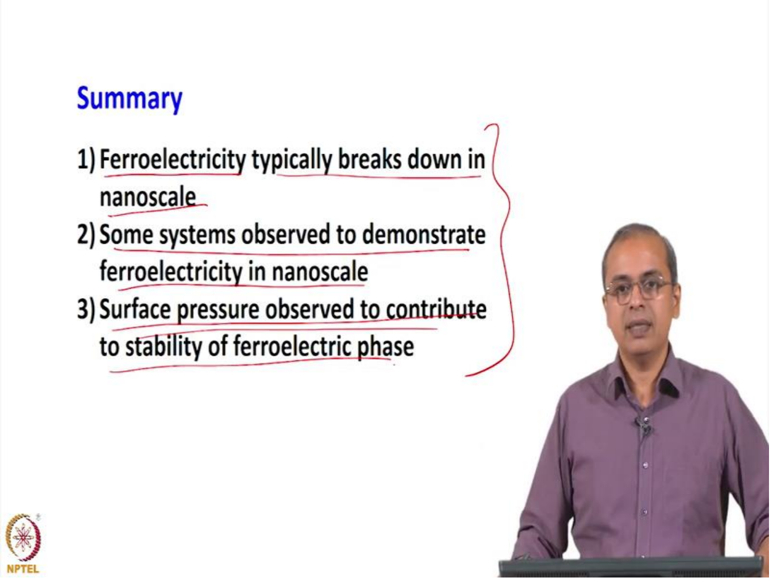

So, in summary generally, it has been seen that Ferroelectricity or ferroelectric behavior typically seems to break down in Nanoscale. At the same time, studies have shown that in some systems interestingly the ferroelectric behavior seems to be visible.

In fact, particularly in the Nanoscale as opposed to the micro-scale. And there are ways to we found that there is a lot of application to this Ferroelectricity in the Nanoscale both with respect to I mean, at least with respect to two major technologies that we would be interested in data storage and displays both of which I mean, extensively use in modern world today. Both these cases you would see that there is some need for these Nanomaterials which show Ferroelectricity. And therefore, to, first of all, make them is interesting, to understand how they behave and why they behave so is another interesting thing.

So, we could see that there are studies which seem to show that surface pressure, which may be significant in the case of Nanomaterials because of their curved surface and so on; that surface pressure because of the high surface area that is there, the large number of unsaturated bonds that are there. Sort of effectively contributes to a compressive force on that particle and that seems to create because of the pressure you are moving from one face that is stable in as per the phase diagram at room temperature and atmospheric pressure to another phase which is at room temperature and, but at a much higher pressure.

Even though you are not applying, physically you do not seem to be applying any pressure; you are not putting some pressure, you are not compressing it in a cylinder or any such thing. So, we are not applying any such pressure, but still there seems to be pressure being developed by the system itself and that helps it to move from one phase to another phase because the phase diagram say and as dictated by the phase diagram of that system; and this combination of events helps us have a ferroelectric material in the Nanoscale.

So, that is our summary for the class, very interesting use of Ferroelectric Materials in the Nanoscale and the phenomenon and the science behind it.

Thank you.