fNanotechnology Science and Applications
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Lecture - 17
Impact of the Nanoscale on Optical Properties

Hello, in this class we are going to look at the Optical Properties and the Impact of Nanoscale on Optical Properties through this course that is the underlying theme that we are investigating; which is to look at what does the nanoscale do to specific properties. And then in that context see, if there is some interesting product that you can create out of it, interesting technology that you can create out of it and in that process utilize this interesting phenomenon that you are seeing at the nanoscale.

So, in this class we will look at the optical properties; particularly in this class, we will keep the intention would be to get an overview of what these optical properties are. In particular to understand what is that phenomenon that is happening at a material level that reflects in the form of an optical property that we observe. And then, therefore, when you see a variation in that phenomenon you can understand that naturally there is going to be variation in the optical property. So, that is the idea that we will explore through this class.

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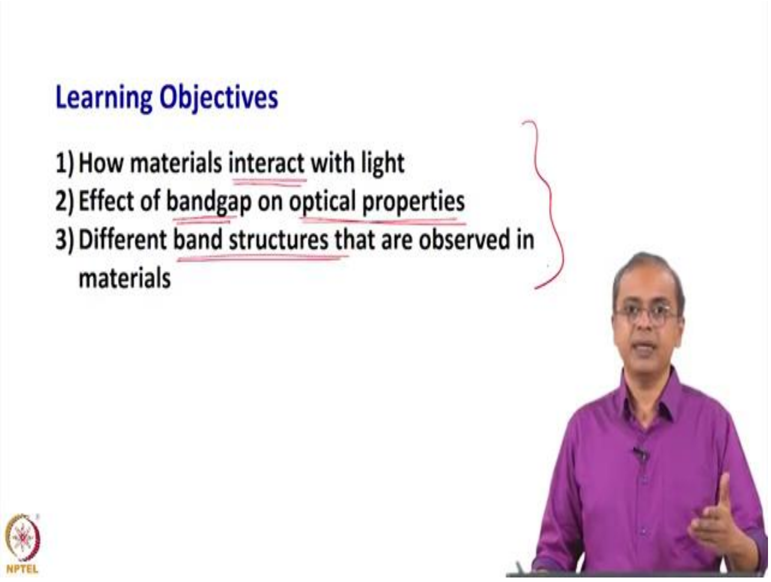

Learning Objectives

1) How materials interact with light
2) Effect of bandgap on optical properties
3) Different band structures that are observed in materials

So, a learning objective are, we will first look at how materials interact with light. So, this is I think a very important thing for us to understand, what is it that is happening when light interacts with matter and to some degree, we may already be aware of it; but for sake of completeness, we will look at it to see how materials interact with light. In particular we will look at the bandgap; we normally think of bandgap from the perspective of electrical properties. So, here we will look at the bandgap from the perspective of optical properties and see what is the effect of the bandgap on the optical properties and so, that is the aspect that we would like to focus on.

And also, we will try to understand, that the bandgap gives you one part of the story. So, even if you have a material with a certain bandgap and therefore, you expect a certain type of optical property; is it possible that with the same material, with that same bandgap you can get actually properties that look somewhat different. So, that is also an idea that we need to explore and understand. So, we get a sense of how we can manipulate the materials to suit our applications.

We will finally, also look at different band structures that are observed in materials and therefore in that context get a sense of what is possible with various materials. So, those are our learning objectives it will give us some idea of the phenomena of the interaction of light with matter and some idea of the internal working of the material and how that impacts the optical property that we are observing.

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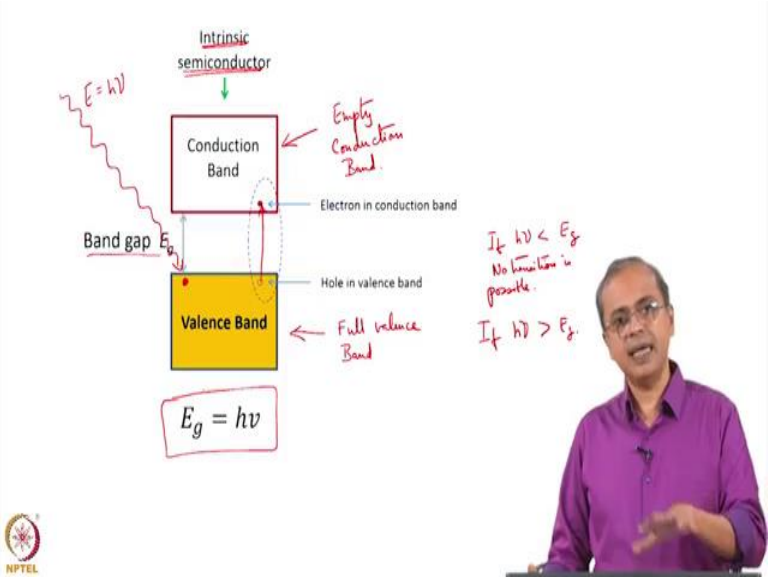

So, we will begin by looking at this idea that material may have a band structure that looks something like what you are seeing here; that there is a conduction band which is vacant and you have a full valence band. So, we are looking at a material which does not have an impurity level in it and so, it is an intrinsic semiconductor. So, by definition this means the charge carriers present in this conductor, the number of charge carriers that you have this material or the density of charge carriers that you have in this material will be a direct function of the temperature and nothing else. So, because there is no other impurity level, you raise the temperature, then you have more of these transitions from the valence band to the conduction band and you have, therefore, got more charge carriers; these electrons in the conduction band and holes in the valence band will carry out the conduction process for you.

So, related to this is the bandgap. So, the material has a bandgap Eg and if you take this material and it interacts with light. So, we will say that there is a photon of light that comes in and then that photon has some energy E and if it has a frequency υ; that it is energy is E = hυ this is the equation from Planck. And so, you have this energy E = hυ that comes in and then it transfers that energy to some electron. So, that is actually a probabilistic process. So, when you so, if there is an electron sitting here. So, when light interacts with matter, it may or may not interact with an electron because it has to sort of reach the same point as an electron. And so, there is some probability associated with it. So, you may have some photons of light that arrive at a material that o not interact with any electron, even though they have some energy that they could transfer to an electron. So, there is a probabilistic aspect here. So, in any case within the scope of that probability, we will assume that this photon interacts with this electron and it tries to transfer the energy hυ to that electron.

Now if that energy hυ is less than this bandgap, this if it is less than if E; if hυ is less than the bandgap, then you are not able to get this electron to make a transition. It is the bandgap is a set of energy levels that are forbidden for the electrons in that material and therefore, this electron cannot go to that location in the bandgap and therefore, it actually does not interact with that photon. So, it is unable to pick up that energy from the photon and then the photon just passes on without interaction.

So, if hυ is less than E_g, no transition is possible; and so, the photon goes through without interaction. If on the other hand hυ > Eg so, E of that energy of that photon which is hυ is greater than that of the bandgap, then the transition occurs from the valence band to the conduction band. And of course, so, therefore, the threshold value is this Eg = hυ. So, that is the threshold value with once you cross the threshold value, the transitions begin to occur, and therefore, the light is able to now enable transitions from the valence band to the conduction band.

So, interestingly this I mean; so, it means that you need to have this kind of frequency to enable this transition and if you do not have this frequency you will not enable this transition. So, this is a general case of an intrinsic semiconductor we can now look at a range of possibilities of materials with different kinds of band structure and using the same idea try to understand what it is that you are likely to observe.

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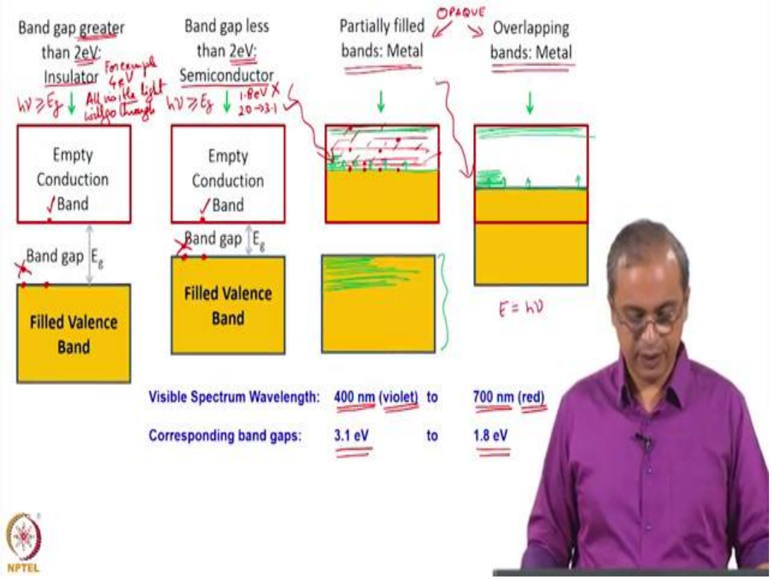

Band gap greater than 2eV: Insulator

Band gap less than 2eV: Semiconductor

Partially filled bands: Metal

Overlapping bands: Metal

Empty Conduction Band

Band gap E_g

Filled Valence Band

Empty Conduction Band

Band gap E_g

Filled Valence Band

Visible Spectrum Wavelength: 400 nm (violet) to 700 nm (red)

Corresponding band gaps: 3.1 eV to 1.8 eV

So, if you see here you have four possibilities here the first two, we are calling as metallic systems. So, in a metallic system, the band structure is such that either you have two bands that are overlapping; in other words the valence band and the conduction band are overlapping; or you have a partially filled band, in which case you have within the same band you have all these empty levels out here. So, this consists of energy levels that are all available in empty.

So, now in either case what happens is, if you take the highest occupied energy level which is here, take the highest occupied energy level here and the highest occupied energy level that is here. Then immediately above it right above it, so at a right above it are all energy levels that are vacant and available. So, even here there are energy levels that are vacant and available. So, and these energy levels are extremely closely spaced. So, we are looking at energy levels are really closely spaced.

So, actually even though we say it is a bandit is not a continuous band in that sense, it is a discrete set of energy levels, but those discrete set of energy levels are extremely closely spaced, to the extent that for our application purposes they appear continuous. So, that is why we draw it as a band. So, even this band that we see here is, actually a series of discrete states which are very close to each other, going all the way across ok, so that is basically the idea that we have.

So, now, when you take a metallic system and any light falls on it, this idea of E equals so, there is no bandgap here. So, there is no it is sitting in a situation where available energy levels are continuously available above the highest occupied energy level. So, therefore, any energy that is available in a photon, photon coming with any energy. So, E equals hυ, any value of υ, any value of the frequency the energy is sufficient to do a transition from this location to some location above it; so, from here to here or from here to here or from here to here, etcetera.

So, you have a continuous set of energy levels to which these electrons can move and those continuous set of energy levels begin almost directly above the energy level at which the electron is currently situated. And therefore, there is no real restriction on the frequency that the incoming radiation needs to have to enable a transition. So, this is what we will have with respect to metallic systems.

Then we also have semiconductor systems that we just saw, you can have typically a semiconductor would be one where bandgap is less than about 2 electron volts; and there, of course, we have this threshold of hυ should be greater than or equal to Eg for the transition to occur. So, if you have an electron here, it cannot transition to a location here this is not allowed; on the other hand it can transition from this location to this location, so this is allowed, So, that is why you have a certain range of frequencies that will not interact with that semiconductor and the interaction here would result in a transition and since a transition is not possible that range of frequencies will not be able to interact with that material. And only if you cross a threshold frequency of hυ greater than or equal to Eg the transitions will begin to occur.

Now the same thing is true with an insulator, where the bandgap is greater than 2 electron volts. So, the same hυ greater than or equal to Eg is a requirement here. So, similarly something here cannot transition to a location here, whereas, something here, an electron here can transition to a location here. So, that is the idea that we have and so, correspondingly when light arrives at this material only if you have energy greater than the bandgap you have a transition.

Now, given this general picture, we need to compare this with what we typically consider as visible light to understand, what is it that we can expect with respect to visible light when it interacts with this range of materials. So, if you take visible spectrum, the wavelength of the visible spectrum is from about 400 nanometers at the shorter end of the wavelength to about 700 nanometers or 0.7 microns on the larger end of the wavelength spectrum. And the longer wavelengths appear to our eye as red color and the shorter wavelengths appear to our eye as violet color and that is how you get the range of colors. So, about 0.4 microns to about 0.7 microns is what the ranges.

So, the corresponding bandgaps are, if you do E equals hυ you will get for the violet end of the spectrum about 3.1 electron volts and for the red end of the spectrum 1.8 electron volts ok; so, this is typically what we see. So, if you take, now if you given this range of energy levels between 1.8 and 3.1 electron volts for visible light; if you now take that radiation and look at it is interaction with the possible band structures that we have here.

If you consider metal, so if you look at metal, in this case either with overlapping bands or with partially filled bands, both at 1.8 electron volts as well as 3.1 electron volts; we have the, I mean some available energy level is present within this material, somewhere up there. So, there are some available energy levels there, there are some available energy levels here. So, it does not matter whether you have 1.8 electron volts or you have 3.1 electron volts or any value in between 1.8 and 3.1. You will always have some energy level which can accept an electron, which is kept recently seated at the highest possible energy level when you are give it this difference. So, you take this electron here and you give it 1.8 it will probably end up here, if you give it 3.1 it will probably end up here, some such thing.

So, the entire spectrum of visible radiation that arrives at a metallic surface can be absorbed by that surface ok, because there are a continuous set of energy levels. This is the reason why metallic surfaces are typically blackish in color, I mean or of that nature they absorb all light, they are not transparent at least, they are opaque because all the light that falls on it gets absorbed. It is also true of any other system where you would have a continuous set of energy levels. So, for example, graphite is also black for a similar reason it is opaque for the same reason, that there are continuous set of energy levels available in it and that is able to absorb the radiation. So, that is the reason why metallic systems are opaque.

So, now given that idea, now if you look at semiconductors and insulators, let us assume that we have a semiconductor of about 2 electron volts bandgap; if you look at this then a photon arriving at 1.8 electron volts. So, we will say it is a 2-electron volt. So, if you take a 1.8 electron volt photon, it cannot interact with this material; because at 1.8, it does not have sufficient energy to get it past the 2-electron volt bandgap. So, this will not interact whereas; once you cross 2 to 3.1 all of these will interact. So, this material will absorb radiation from 2 electron volts to about 3.1 electron volts. So, all of that radiation it will absorb, it will not absorb radiation which is between 1.8 electron volts and 2 electron volts.

So, what will happen is wavelengths which are between 1.8 and 2 electron volts will actually go through this material, will not interact with this material it will go through this material, other wavelengths will get absorbed by this material. So, now, if you look at this material in sort of a transmission mode. So, this light on the other side you keep the sample in front of you and then you see the light coming through, you only see wavelengths which are in the 1.8 to 2 electron volt region coming through to you. So, that if you see is closer to the red end of the spectrum. So, this material will look somewhat you know, somewhat closer to red in color. So, somewhere between orange, red some such color you will see with this material.

On the other hand, if you take an insulator, we say it is bandgap is greater than 2 electron volts. Let us assume that we have an insulator, for example, 4 electron volts. Let us assume that we have an insulator where the bandgap is 4 electron volts. If you take an insulator which has a bandgap of 4 electron volts and you now look at the visible spectrum interaction with it; then the entire visible spectrum from 3.1 electron volt to 1.8 electron volt, the entire visible spectrum will not interact with this sample. So, if you take an insulator with this kind of a bandgap and you keep it in front of you and then you have light shining from the other side which is trying to go through the sample and then reach you, all of the visible light will go through the sample. So, all of visible light will go through.

Therefore, if you take a sample with a bandgap of 4 electron volts that sample is now going to be transparent to the visible spectrum. So, insulators which usually have large bandgaps are typically transparent to visible radiation. And so, therefore, you can see that based on the band structure; you can have an opaque material; you can have a transparent material which is having some color based on what frequencies are going through, what frequencies are not going through. And then you can have another material which is basically completely transparent and so, it looks like clear glass. So, that is essentially what we can possibly have.

Interestingly I think there is one important point that we must pay attention to here. And that is normally, we will we have this intuitive feel that when something with certain energy comes and hits a surface then if the energy is not sufficient it does not go through that surface; if the energy crosses some threshold it just about breaks through that surface; and then if the energy is high it will go right through that surface. So, that is our intuitive feel for how some material with some energy interacts with another material on which it is incident.

So, our intuition is that more energy means it will go through, less energy means it will not go through. So, you sort of that is our idea of how it will interact so, notionally we may think that higher energy photons will go through a material, lower energy photons will get absorbed by the material that would be our intuitive feel. But in this case that intuitive feel is not correct; you will see here that if the bandgap is a certain value when photons with less energy come to that material they actually go through because they are unable to do that transition. So, they are not interacting with that material. So, whatever energy they give they get back and they continue. So, they do not really go through, I mean interact and enable any transition.

Whereas photons with higher energy actually enable transition and therefore, actually get absorbed. So, this is sort of counterintuitive in that sense, higher energy photons are getting absorbed, lower energy photons are going through the material as so, the material is transparent to them. So, that is I think a very important point to absorb because it is very counterintuitive to our, thinking process.

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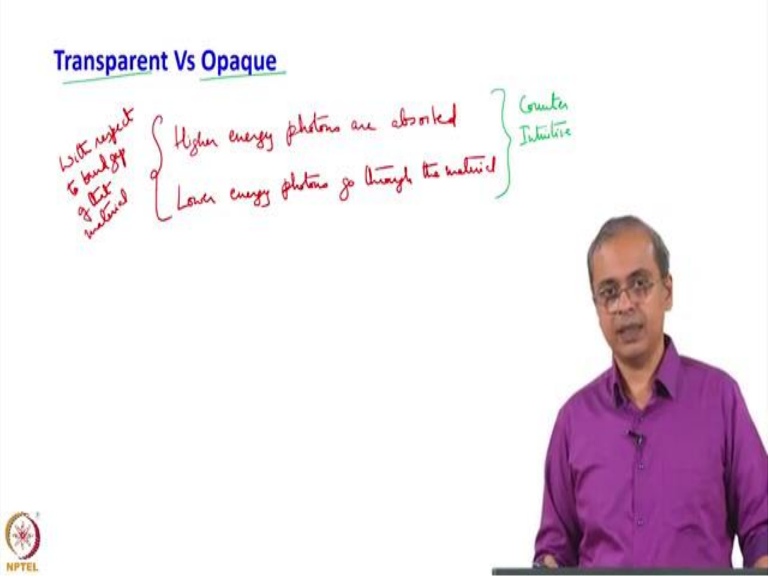

Transparent Vs Opaque

With respect to bandgap of that material

Higher energy photons are absorbed

Lower energy photons go through the material

Counter Intuitive

So, that is this idea of transparent versus opaque, higher energy so, this is with respect to the bandgap of that material. So, that is what decides whether something is transparent or opaque and most importantly this is very counterintuitive. So, it is very counterintuitive, normally you would not think this to be the case. So, this is this idea of when something is transparent versus when something is opaque.

Now, let us look at something more interesting again, we have now sort of got an idea of what is happening when light interacts with matter, but this is not the whole picture. It turns out that we can consider possibilities this is scientifically what is supposed to happen in the material. But in reality, you may actually have a situation where it seems like something should happen, but you are actually seeing something else happen. So, we need to understand what is happening. In particular if you look at something that is transparent, where the expectation is that the material is supposed to be transparent, you can actually create situations where that material is not transparent.

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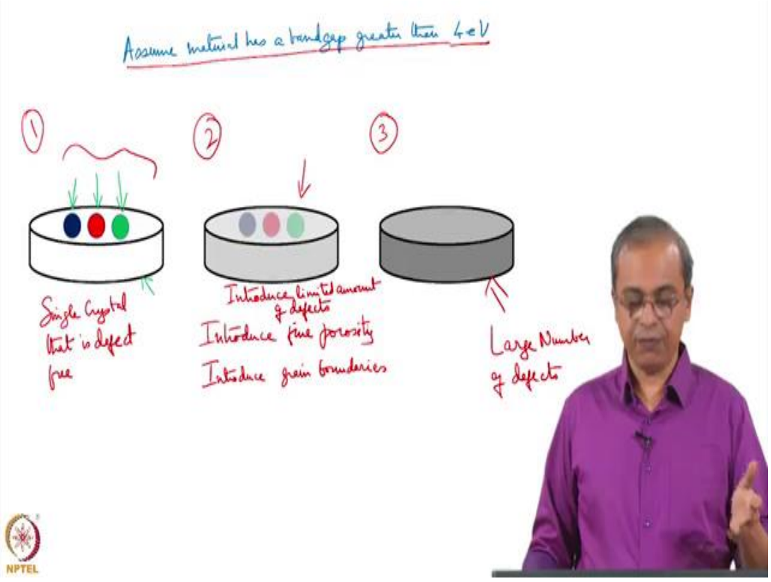

So, just to give you some I mean idea here, let us assume that we have a solid material here, sort of like what you see here and let there are 3 dots, 3 colored dots that are present. That is present on one side of that, you keep this disc in front of those 3 solid dots. we are using some, some insulating material which is basically having a large bandgap; assume material has a bandgap greater than 4 electron volts.

So, let us just assume that this is the case, that we have a material that is a bandgap that is greater than 4 electron volts. So, as I said since the visible spectrum is between 1.8 and 3.1 electron volts, in principle, this material should be transparent. Therefore, when you have this situation here where you have these three colored dots and you keep this disc in front of those three colored dots you should actually see those dots, you should be able to see through that material and see those dots. So, that is what our expectation is and indeed this is what you can get, you can easily get the situation with this kind of material.

At the same time, I can assert that it is possible for me to take the exact same material and do something to it which enables me to create a situation wherein fact, the material is translucent. So, in the first case it is opaque, I mean sorry in first case it is transparent and so, here case 1 it is transparent; in case 2, I have it as translucent; and I can do something more to that material which makes it opaque, in case 3 It makes it opaque. And when I say do something more, I am not changing the composition in any way; so, composition, chemical composition, crystal structure all of that are exactly the same. So, I am not changing anything to the composition, I am not changing anything with respect to the crystal structure and so on and you can get this.

And this is actually true, I mean in fact, you can get, for example, samples of zirconia; zirconia you can get in which is actually used sort of like an artificial diamond so to speak. You can get that in transparent conditions, you can also get that in opaque conditions where the light will not go through and in fact, therefore, it is used for bio applications as we saw in one of our earlier classes. So, you can actually get this range of materials. And how do we reconcile that as given the fact that scientifically we are saying the bandgap is 4 electron volts and therefore, it should be transparent. And as I said in these three cases, I not change the bandgap, I have not changed the chemical composition and I have not changed the crystal structure. So, the way we accomplish this and the way it is actually happening in the system, it has got to do with what defects are present in the system.

So, if I introduce fine porosity or you introduce grain boundaries; if you introduce fine porosity or you introduce grain boundaries, then you will move from something that is completely transparent to something that is translucent and then eventually it becomes opaque. The more boundaries that you introduce, the more interfaces that you introduce; a boundary is an interface, similarly, porosity also is an interface because it is interfaced between the material and air for example. And so, porosity also introduces interfaces, grain boundaries also introduce interfaces. So, a single crystal that is a defect-free; defect-free meaning it does not have porosity. For example, a single crystal that is defect-free will be transparent. If you take a single crystal and introduce porosity in it or you take the same material and make it a polycrystalline sample with some limited number of grain boundaries in it, you can make the material translucent. So, some defects here, some number of defects. So, in this case we have introduced some level of defects. So, if you introduce a limited amount of defects, you make it translucent; if you have large number of defects then the material which was transparent and then later became translucent can now become opaque.

So, this is the way in which we can manipulate the optical properties, you can change the band structure itself or you can introduce the defects without changing the band structure. So, all of these processes will help you change the optical property of the material. So, you can using these techniques you can make something go from transparent to opaque and as you will see there are ways in which we can manipulate the band structure and therefore, you can even change the color of the material if you desire. So, this is the idea behind the optical properties.

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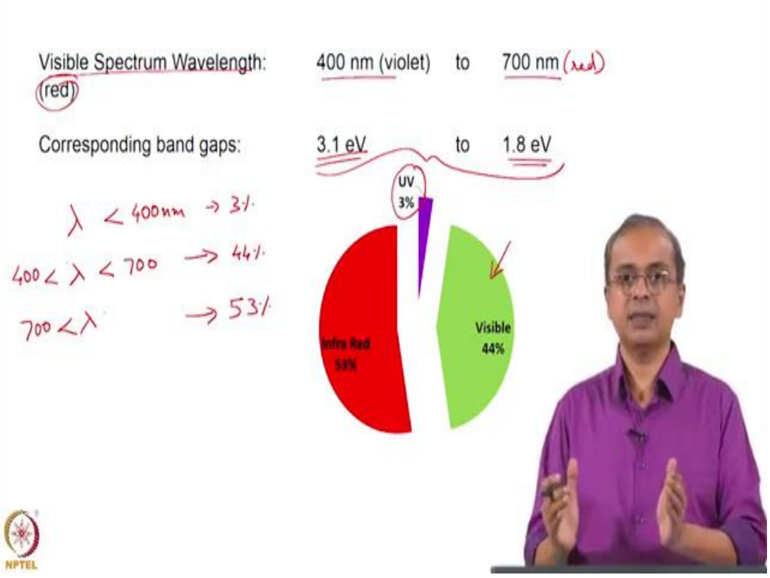

Visible Spectrum Wavelength: 400 nm (violet) to 700 nm (red)
(red)

Corresponding band gaps: 3.1 eV to 1.8 eV

$\lambda < 400nm \rightarrow 3\%$
$400 < \lambda < 700 \rightarrow 44\%$
$700 < \lambda \rightarrow 53\%$

Incidentally, it is also useful to know what is our visible spectrum? So, the visible spectrum, as we just discussed is between 400 nanometers to 700 nanometers which is, which goes from the violet end of the spectrum to the red end of the spectrum. And so, this is the red end of the spectrum, it should appear this is red and this is the range of bandgaps 1.8 to 3.1 electron volts. If you see the distribution of energy across the spectrum, the intensity across the spectrum, then you will find that if you look at light that arrives on the surface of the earth 44% of it is in the visible spectrum. So, 44% of it falls in this range 1.8 to 3.1 electron volts.

You have about 3% which is ultraviolet. So, about 3%, so this is 44%. So, 3.1 so, if you have frequency or energy, let us go to frequency; frequency which is or wavelength in this case, because wavelength is what I have given you lambda which is less than 400 nanometers then that is 3%. Lambda between 400 and 700 that is your 44% and lambda that is longer than 700 nanometers, so that is your 53%.

So, 53% of the radiation comes in the infrared, 3% in the ultraviolet and 44% in the visible spectrum. So, that is your full spectrum. So, in fact, when we talk of optical properties and maybe we are thinking about say using it for a solar cell application or something like that. Many times, in our mind it is a visible spectrum that sticks in our mind we keep thinking of the visible light that is falling on us what and it is very important thing to be aware of and to use the visible spectrum. But we should also be aware of the fact that less than half the energy that is coming in, as radiation from the sun which is what we are receiving on earth less than half then that energies are coming in the visible spectrum. So, if you take the more than that is coming in the infrared, more than what you see in the visible spectrum and there is a tiny amount sitting in the ultraviolet range of this spectrum.

Therefore, it is interesting to see, if you can manipulate if you can take a material and change it is band structure. So, that it absorbs more and more of this complete spectrum and therefore, you can get more and more energy absorbed from the incoming radiation. And in fact, it is in this context that people look at the nanoscale materials from the perspective of optical properties. They would like to use the kind of flexibility that nanoscale materials give with respect to optical properties to try and capture more and more of this spectrum in the more complete sense and therefore, capture as much of the energy as possible.

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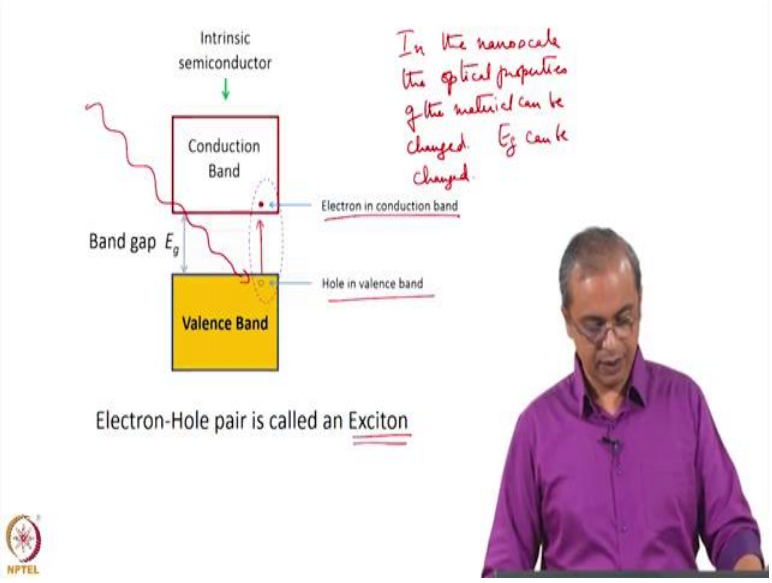

In the nanoscale the optical properties of the material can be changed. E_g can be changed.

Electron-Hole pair is called an Exciton

So, how does this happen? So, I mentioned that if you go to the nanoscale, the optical properties can be changed. Basically, we are saying that the bandgap can be changed. This is a very important thing to concept to remember, see when we look for a bandgap of any material, if you look at literature and you look for a bandgap of any material you only see one value listed for it, you do not see a range of values. Typically, you look for no silicon or germanium or something you will see one value for the bandgap that is listed there. And the reason you see only one value listed there is that the general assumption is that you are looking for what is referred to as the bulk bandgap, because for most applications that is what we use; we use what is called the bulk bandgap and therefore you see only one value.

But through a lot of scientific study people have recognized that fact that, if you actually go towards the nanoscale, from if you start from bulk macrocrystalline material and you move towards micro crystalline nanocrystalline materials of the same substance then it turns out that the bandgap can actually change. And therefore, you will have a different bandgap for the same material; in other words, you will have the material I showing you a completely different optical property by going to the nanoscale and that is the whole idea of this nanoscale with respect to optical properties.

So, what actually happens is that you have when you do this transition when you have this incoming radiation. And you do this transition from variance band to conduction band, this combination of an electron in the conduction band and a hole in the valence band, this combination acts as a pair and it is called an Exciton. And many times, the exciton is what sort of helps us, I mean see something as an optical property that is it impacts what we perceive as the bandgap of that material. This exciton actually behaves somewhat like a hydrogen atom because you now have one positive charge and one negative charge.

Of course, you do not have a proton here, you do not have the mass of a proton here, you only have a positive charge and a negative charge, and it behaves it has some similarities to a hydrogen atom. And so, just like you can have Bohr radius for a hydrogen atom, there is a Bohr radius for the exciton. So, it is called the exciton Bohr radius. And this can actually be a relatively large value, relative to the size of a typical atom that we are looking at. And this exciton Bohr radius has basically means that the exciton needs that much space or it is in a position to move around in that much space. And if you make the particles smaller than that then the exciton is getting constrained. And this leads to a change in the, what is perceived as the band structure of that material and it is called confinement; this idea is called confinement and changes the band structure.

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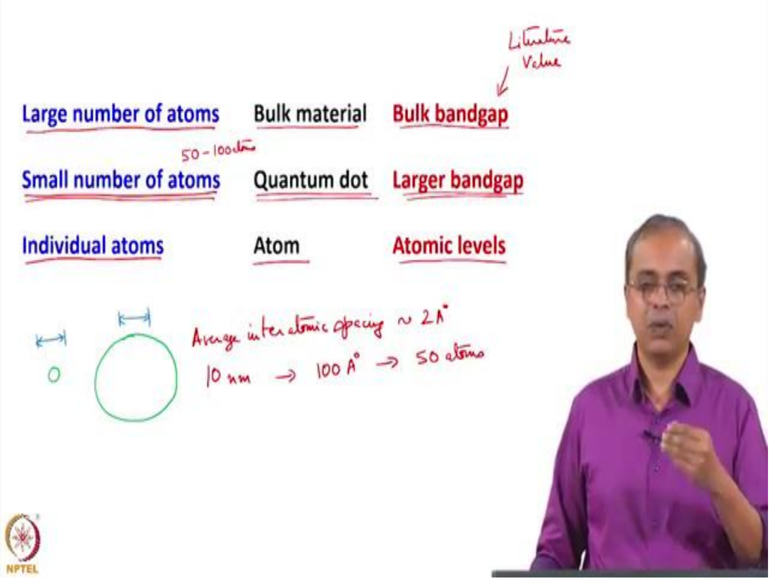

Literature Value

Large number of atoms	Bulk material	Bulk bandgap
Small number of atoms	Quantum dot	Larger bandgap
Individual atoms	Atom	Atomic levels

50 - 100 atoms

Average interatomic spacing ~ 2 Å

10 nm → 100 Å → 50 atoms

So, what we actually see is that as I said you can have a large number of atoms and in that case what in a sort of a grain structure or crystal structure; and that would be something that we would refer to as the bulk material. In that kind of material, you will see the bulk bandgap, which is what you will see typically in the literature. So, this is the typical literature value. So, you go searching for a bandgap this is the value that you will get.

If you go to the other extreme, you have individual atoms. So, that is an atom I mean by a definition that is a single atom. So, there you do not have a bandgap per say, but you have atomic levels. So, you have specific atomic levels which you can then you can access, even when you do X-ray diffraction; when you generate an X-ray that is what you are doing you are knocking off an inertial electron and an outer shell electron from a discrete value falls into the inertial location. And therefore, you have a very specific frequency of radiation being released by that atom, which is in the frequency range of the X-ray spectrum.

So, that is the other end of the spectrum; so, you have X-rays at that end of the spectrum, you have the bulk bandgap material behaving in the bulk showing you the bulk bandgap of that material if you have a bulk material. Between these two, if you have a small number of atoms which is typically what you will see in a nanomaterial; like I said in a nanomaterial if you are looking at distance with average distance between atoms is about average interatomic spacing is approximately 2 angstroms in most materials.

So, if you have a 10-nanometer particle size, which is very likely in many nanocrystalline samples that you see the particle size could easily be 10 nanometers. So, 10 nanometers are 100 angstroms and; that means, this is about 50 atoms across. So, 50 atoms across is that dimension. So, I mean, of course, you can make a spherical particle. So, then you assume say the radius is 50, radius is 25 atoms and then you can figure out how many atoms are there; so, that is what we will assume for a typical nanomaterial.

So, if you are talking of a small number of atoms, so off the order of 50 atoms, 100 atoms, 50 to 100 atoms something like that; then you are actually in a regime that is between single atoms and the bulk. And what we see, what it is then referred to is that it is referred to as a quantum dot. And how this quantum dot interacts with this electron-hole pair, is what decides what is going to happen with the bandgap of the material. So, in particular if you have, you have two particles; one small one and one large one. And your exciton Bohr radius is this much. So, this exciton Bohr radius clearly is smaller than the large particle and therefore, in the large particle you see the bandgap of the bulk. On the other hand, here, it is larger than the particle and therefore, the exciton is now getting confined within this particle and therefore, you see behavior which is different from that of the bulk. And that is what ends up creating a shift in the bandgap.

Usually, it is a blue shift which means it is moving towards higher frequencies or lower wavelengths and so, this is what happens. And this is called creating a quantum dot and with this you can change the optical property of that material and therefore, you can get the same material with a different bandgap. And this is very important technical accomplishment for us because you can now get a range of materials which have a wide range of band gaps, but the chemical composition is exactly the same. And that is a very useful thing for us to have because many times in technological situations if you have dissimilar materials then you have a situation where you can have corrosion between the materials, you can have mismatch in thermal expansion coefficients and so on.

So, if you are trying to make a solar cell out of it and you have dissimilar materials present there, then each material may expand in a different way, the cell may crack and then you will eventually not have something that is working. But if you want to absorb the entire spectrum; you would not absorb the infrared part of the spectrum, the visible part of the spectrum as well as the ultraviolet part of the spectrum, then you do need a range of bandgaps, so that, you can capture this entire spectrum effectively.

If you have only one bandgap, although technically you can capture most of the energy in this process, you actually end up losing a lot of it; you get very ineffective capture of energy if you have only a single bandgap. You are able to capture more of the energy only if you have a range of band gaps and therefore, it is necessary to have a range of band gaps. And it is particularly useful if you can have the same chemical composition and same crystal structure giving you this range of band gaps, and so that for this nanocrystalline approach to manipulating the bandgap or I know designing the bandgap, so to speak is very effective and useful for us.

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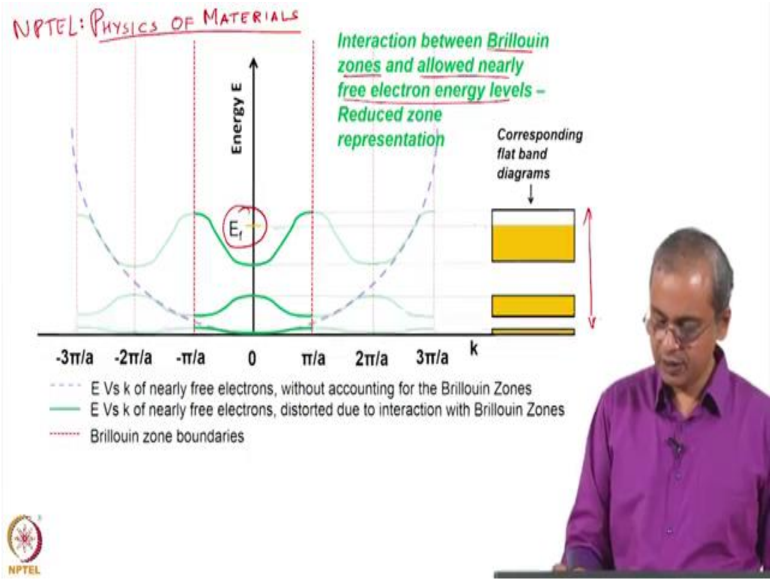

NPTEL: PHYSICS OF MATERIALS

Interaction between Brillouin zones and allowed nearly free electron energy levels – Reduced zone representation

Corresponding flat band diagrams

- - - - E Vs k of nearly free electrons, without accounting for the Brillouin Zones

—— E Vs k of nearly free electrons, distorted due to interaction with Brillouin Zones

······· Brillouin zone boundaries

So, without going into much detail here, I just wanted to show you the fact that actually, the bandgap comes due to an interaction between the Brillouin zones and the allowed energy levels of the free electrons. Actually this part of the discussion is explained in considerable detail in another course; in another NPTEL course if you are interested, you can if you are interested in understanding this in greater detail on the background of how this diagram comes about, what are all the factors that are taken into account to create this diagram and so on; then you please look up this course on Physics of Materials.

It is an NPTEL course and there are few classes specifically focused on band gaps and Brillouin zones and what is a Brillouin zone, what is this E versus k diagram that is shown here, and how you can know draw this diagram and how these band structures are drawn. So, that is a much more detailed discussion there. So, I will not redo the discussion here, we will simply use this final diagram that comes from there. Just to understand the fact that there is an E versus k diagram and in that diagram, there are features and those features get reflected in the band structure that we tend to draw. So, this band structure that we tend to draw is a direct result of where the Fermi energy level is which is this E f and how this diagram ends up being. And this is something that is very useful to know. So, you please look up this information, if it is of interest to you.

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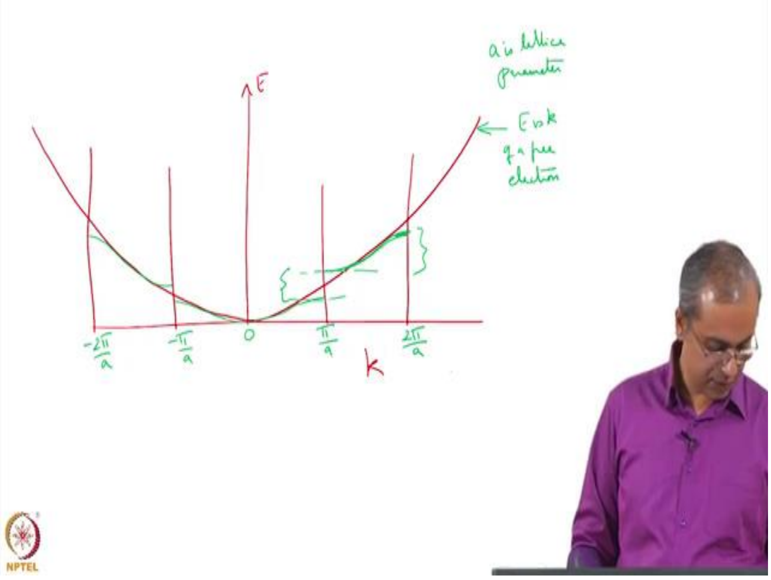

For our discussion, we simply take this diagram and we will keep in mind the fact that this has come because of an E versus k parabola, that is possible and how that parabola interacts with Brillouin zones. So, you have these Brillouin zones that. So, these Brillouin zones are coming from the crystal structure of that material and at the boundaries of those Brillouin zones these parabolas distort and that is how this diagram has come about.

So, that is a distortion and these are all the Brillouin zone boundaries that you can see. So, those boundaries occur at if called a 0 -π/2 by a this is π/a and 2π/a, where a is the lattice parameter. So, this is just a quick look at how that diagram comes about. This parabola is the free electron parabola ok so, this is all I am going to point out here, there is a free electron parabola, how it interacts with Brillouin zones gives you these distortions of this free electron energy levels; and that distortion is what creates forbidden energy level here, and an allowed energy level, forbidden this is forbidden and this part is allowed. And that is why if you see here you get an allowed energy level in this range, this is allowed and this is forbidden. So, that is how you get these bands and band structure. So, that is information that you can look up in this Physics of Materials course.

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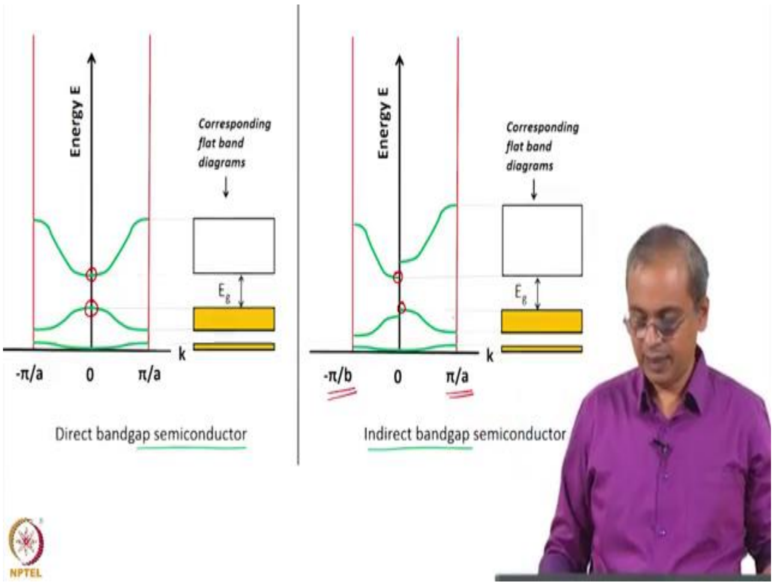

For our discussion again with respect to the optical properties, it is also of interest to know that there is something called an indirect bandgap semiconductor; and there is something called a direct bandgap semiconductor. So, direct bandgap semiconductor is there and indirect bandgap semiconductor is there. The primary idea here is that, because again we are looking at this from the perspective of optical properties, it is valuable to know whether it is direct or indirect and the primary difference between them is the location of these positions, which so, this position here.

So, for example, here this is the highest position of electron energy levels in the valence band. This is the position of the next available energy level which is the lowest energy level in the conduction band. And in this diagram on your left here, so this the diagram that I have marked on, those two locations are in the same region in k space. Whereas, here you have the highest occupied energy level at one location and the lowest unoccupied energy level in another location; in another direction in the b direction. So, you have π/b and π/a.

And so, these are two different crystallographic directions. And I mean, because it is a compact diagram you are seeing it like this, but what it basically means that is that you will have a π/a position coming in one direction and the π/b position appearing in another direction; maybe orthogonal direction you will have the π/b kind of direction appearing. And therefore, when you do a transition in an indirect bandgap semiconductor you cannot just go up in energy to get the electron to the here next available energy state.

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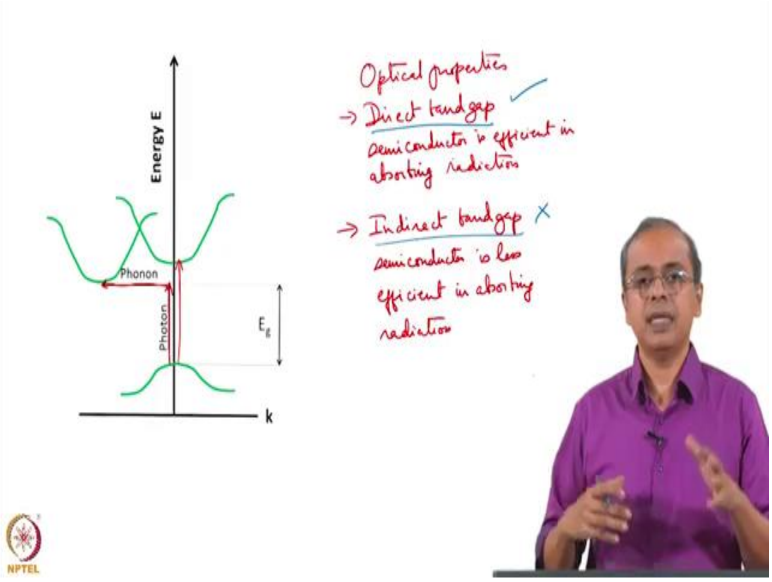

Optical properties
→ Direct bandgap ✓
semiconductor is efficient in absorbing radiation
→ Indirect bandgap ×
semiconductor is less efficient in absorbing radiation

So, what you normally have is, if it were a direct bandgap semiconductor your electron would go straight from here to here; if you put energy here into it. But in an indirect bandgap semiconductor, you actually have to raise the energy level of the electron and then you have to also move it to another location in the crystal structure for it to get actually absorbed into the conduction band. And so, from the perspective of optical properties; the direct bandgap semiconductor it is much more effective in absorbing the radiation, incoming radiation, efficient; the indirect bandgap semiconductor is inefficient is less efficient.

So, this is useful to know, because it helps us narrow down the systems, the material systems that we would like to focus our efforts on. So, if the material system we pick is an indirect bandgap semiconductor, ahead of time we know that it is not going to be very efficient in gathering photons. Because the photons have to raise the energy of the electrons and do and one more process has to happen before the electron goes to the correct location where it can get absorbed. On the other hand, if you take a direct bandgap semiconductor, if the photon has enough energy to just raise it to the available location where the next available energy level is, then that is all is required it will get absorbed.

So, therefore, the systems that we pick, we would prefer to pick something that is a direct bandgap semiconductor. This is what we would prefer to pick, this, on the other hand, we would not prefer to pick; unless there is some other commercial reason why we would need to pick that. So, for example, silicon is actually used quite a bit for solar cell applications, but in fact, if you look at it is an indirect bandgap semiconductor; it is not a very appropriate material to use. But simply because it is available commercially in large quantities and in a sense relatively cheaper, it is not that cheap, it is relatively cheaper and therefore people end up working with that.

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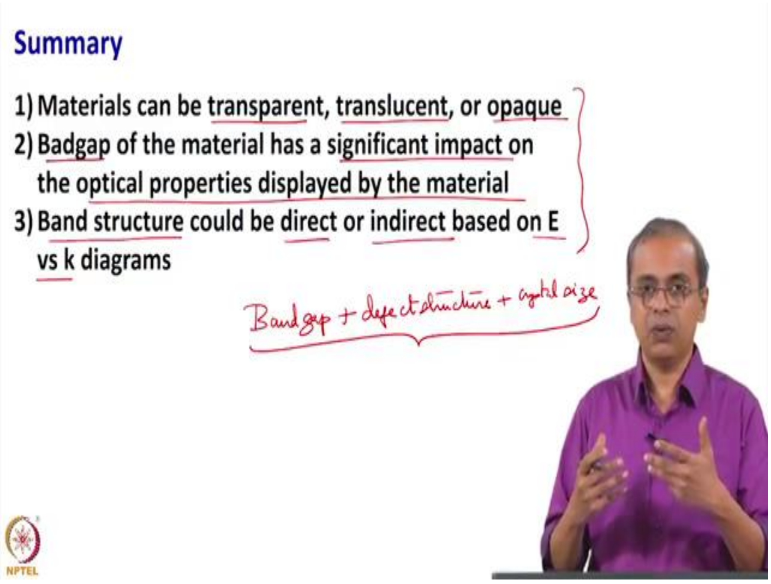

Summary

1) Materials can be transparent, translucent, or opaque
2) Badgap of the material has a significant impact on the optical properties displayed by the material
3) Band structure could be direct or indirect based on E vs k diagrams

Bandgap + defect structure + crystal size

So, the summary for off what we have discussed today is that materials, of course, have optical properties; we are very familiar with materials with the optical properties that materials display. In particular we understand that materials can be transparent, they can be translucent or they can be opaque. So, all these possibilities are there. The bandgap of the material has a very significant impact on the optical properties displayed by the material.

So, bandgap has a very significant impact on the optical properties that the material is displaying, but that is not the whole story as I said the bandgap plus the defect structure. So, bandgap plus defect structure is, so you have to add bandgap plus defect structure. So, together they impact the optical properties quite a bit and the band structures can further be manipulated whether you are in macro size or in nano size and based on that size you would have a size-related impact on the bandgap of the material and therefore, on the optical properties.

So, in reality, the full picture is the bandgap plus the defect structure plus the crystal size, all three of these together will get us the overall picture that we are interested in of the optical property of that material. And therefore, if you take this full combination, you can take one single material system and create a wide range of materials out of it, which show a wide range of different optical properties. In terms of the color of that is being displayed, in terms of whether it is transparent translucent or opaque.

So, a pretty complex range of optical properties or a significant range of optical properties can be displayed by the same material, if you simply manipulate these things; and we have seen some ways in which this can be done. We also noted that the band structure itself could be direct or indirect based on the E versus k diagram and as I said there is another course which deals with these diagrams are much greater detail; you can look that up if that is something that is valuable to you.

So, the band structure would be direct or indirect and that again impacts how effectively we see the optical properties. So, the optical property you can make a prediction that it is going to do certain things optically. This, whether it is direct or indirect, tells us how efficiently it will do that; display that property will it be very efficiently doing it or it be relatively inefficiently doing it. So, these three are major conclusions here that they can have different properties, the bandgap can have an impact and band structure including whether it is direct indirect and any other defect structure that is present gives us the overall picture of the optical properties.

So, with this background, we will look at more the nanoscale in terms of how you can create nanoscale materials for optical studies and what kind of properties you might get from them, what kind of technique you would need to use to you know, probe those properties and examine the result that you get. So, those we will do in our subsequent classes this is our background for those classes.

Thank you.