Advanced Ceramics for Strategic Applications
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Lecture - 15
Electrical Conduction in Ceramics (Contd.)

Having discussed the… Some of the very basic concepts of electrical conduction in solids.

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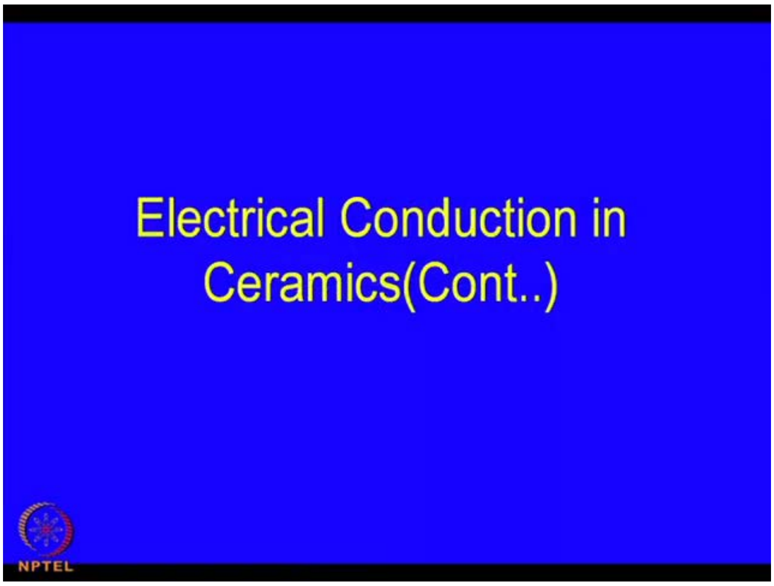

Electrical Conduction in Ceramics(Cont..)

Followed by the introduction of introduction of the band model.

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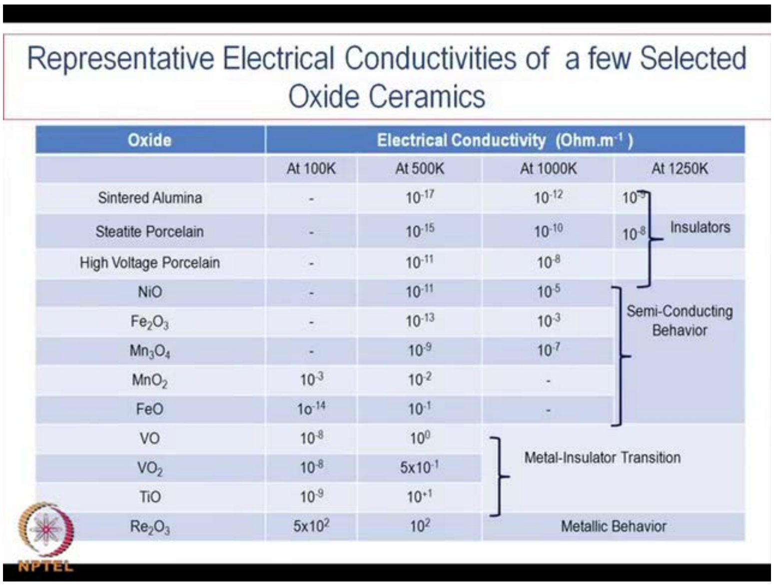

Representative Electrical Conductivities of a few Selected Oxide Ceramics

Oxide	Electrical Conductivity (Ohm.m^{-1})				
	At 100K	At 500K	At 1000K	At 1250K	
Sintered Alumina	-	10^{-17}	10^{-12}	10^{-9}	Insulators
Steatite Porcelain	-	10^{-15}	10^{-10}	10^{-8}	
High Voltage Porcelain	-	10^{-11}	10^{-8}		
NiO	-	10^{-11}	10^{-5}		Semi-Conducting Behavior
Fe_2O_3	-	10^{-13}	10^{-3}		
Mn_3O_4	-	10^{-9}	10^{-7}		
MnO_2	10^{-3}	10^{-2}	-		
FeO	$1o^{-14}$	10^{-1}	-		
VO	10^{-8}	10^{0}			Metal-Insulator Transition
VO_2	10^{-8}	$5x10^{-1}$			
TiO	10^{-9}	10^{+1}			
Re_2O_3	$5x10^{2}$	10^{2}			Metallic Behavior

And differentiating between metals, semiconductors and insulators. Let us try to look at actual ceramic materials how they behave in terms of the band structure, as well as the charge transport phenomena in real ceramic materials. Here is a list of electrical conductivities of a few selected oxide ceramics. We will see there is a very wide spectrum of electrical properties starting from the insulators over here. Then we have semiconductors there are some metals, some ceramics where there is a metal insulated.

Condition and the then we have some metallic behaviour in them. So, different kind of electrical properties are available in the host of ceramic materials. Some of which we have discussed briefly earlier. For example, sintered alumina aluminium oxide is a highly insulating material. So, also the complex compounds like steatite porcelain magnesium silicate, which is extensively used in industry as an insulator.

Then of course, the high voltage so called high voltage porcelain which is used in transmission lines all of them are highly insulating materials. There are some data you can see 500K and 1000K, and you will find in the insulation property or the conductivity increases as we increase the temperature. That is the normal behaviour of an insulator as well as a semi-conducted c r.

Only difference is the conductivity of semiconductors are at a higher level than the insulators. So, these are the transition metal oxides and because of the particular defect structure and the concentration of point defects and resulting non-stoichiometry. We do get a semiconducting behaviour in the oxides. Then there are some relatively uncommon oxides like V O V O 2. And etcetera you will find the conductivity there is a huge gap, or a huge change of conductivity from a low temperature to a high temperature.

A sudden change a sudden jump unfortunately the curves are not here, but once you refer it to curve we will find that there is eight orders of change magnitude. Change from 100K to 500K change. So, which means there is a basically a transition is happening from an insulator to almost like a conductor. Same is the case with here you will also find huge change between 100 degree and 500 degrees. And there is a sudden sharp change in the conduction mechanism and also there is a phase transition.

Compared to all of them here is material rhenium oxide Re 2 O 3. We will find if you look at these values here, you will find the conductivity actually decreases the conductivity slightly decreases, when the temperature is increased. So, it is basically a metallic behaviour kind of situation. So, among all the ceramics different kind of ceramic oxides. We find different properties and obviously they are related to the structure, their defect structure and also the basic conduction mechanism, which is a valid for them.

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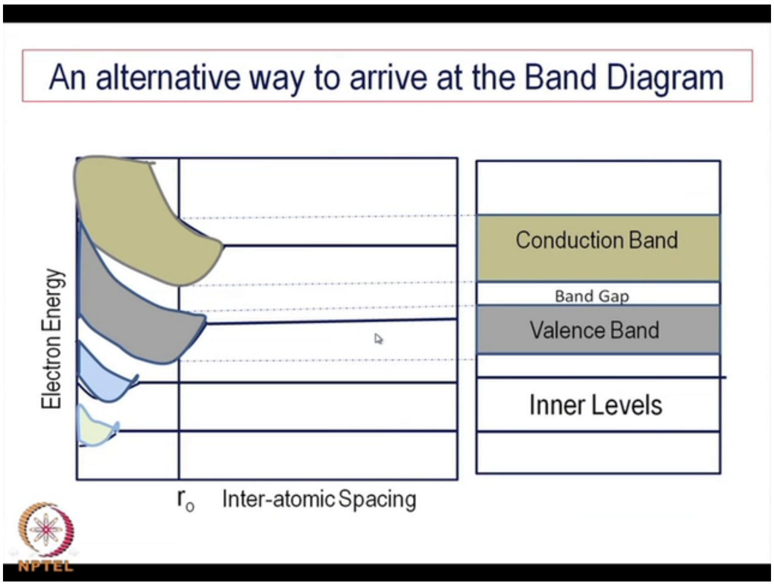
An alternative way to arrive at the Band Diagram

But this particular diagram we have discussed deeply in an earlier class. We have seen the origin of a band model or the conduction or the band gap. The valence band and the conduction band how it comes across, how it comes up with the introduction of the variable potential of the electrons in the solid. Here is a different approach we can visualize a band gap from a slightly different angle. Here these are the orbitals, these are the orbitals of different atoms, which are normally there.

And these are the inner orbitals or inner levels and this is the outermost orbital, the outermost orbital the diameter is larger, whereas these are smaller. So, if you are bringing two different individual atoms isolated atoms from a distance, then the outermost electron will come or interact with each other of the two different atoms first and then the others will interact. So, normally there would be a equilibrium distance of separation depending on the particular structure of the element and the prescribed structure in which it crystallizes. So, there will be always inter-atomic spacing and that also determines the lattice parameter and so on.

Here initially when the distance of separation is much larger than the inter-atomic spacing or the equilibrium inter-atomic distance of preparation. There is no interaction between the orbitals of the two atoms. So they have discrete energy levels a single energy levels, whereas when they come to each other they interact they overlap the electron cloud overlap with each other particularly from the first outer orbitals. And then there is a degeneration the energy gets splitting and we have a band of energy here. Both wherever there is a overlap there will be a band of energy.

So first this gets splitted up and the degenerated at the highest level that forms the highest level. Whereas, the next one is, the next inner level and that also gets splitted up, and you have a band of energy here. Whereas, the inner cores the inner levels do not interact still at the inter-atomic spacing or the equilibrium distance of separation there are still not interaction between them, so they remain unchanged.

So they are actually discrete levels, inner levels remains as discrete levels, but the outer levels gets degenerated into bands. So, there is a quasi continuous bands or quasi continuous energy levels available at the outer orbital’s, whereas they do not have they have a discrete energy there the bands unchanged. So these two will have the first the highest bands can be often considered, as the valence bands and the conduction band whereas, the gap between them is called the band gap. So, this is also another approach, which we can take while considering, or while visualizing the band energy of a system. This becomes quite useful particularly when we are talking about ionic solids like the ceramics and the oxides.

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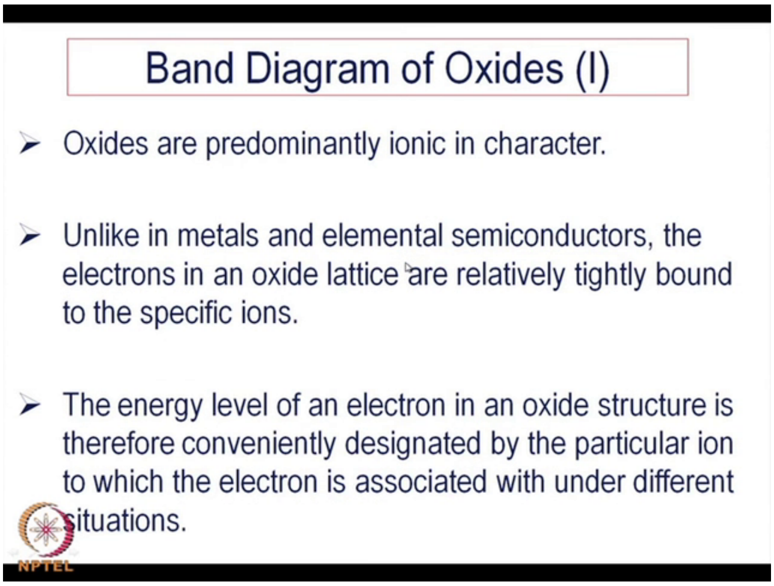

Band Diagram of Oxides (I)

- Oxides are predominantly ionic in character.
- Unlike in metals and elemental semiconductors, the electrons in an oxide lattice are relatively tightly bound to the specific ions.
- The energy level of an electron in an oxide structure is therefore conveniently designated by the particular ion to which the electron is associated with under different situations.

So with this background let us try to look at what happens in the band diagram? Because band diagram is one of the basic concepts to understand the various different ((Refer Time: 08.49)) transport system or electrical conduction or resistance in a material. So we look at how exactly we arrive at the different band diagrams and particular oxide in particular. The oxides are predominantly ionic in character.

Their bond a chemical bond is ionic in character mostly unlike in metals and elemental semiconductors. The electrons in oxide lattice are little bit tightly bound to this specific ions because of the strong interaction between the ion core, and they are strongly positive and the elections are strongly negative or there be cat ions and anions.

So the electron, which are negatively charge species. And they have a much stronger bond with a positive ion. And therefore their situations are slightly different compared to what we get in metals or in semiconductors. In metals it is a electron cloud and they are completely un localised or delocalized whereas, semiconductors is little more localised.

And in oxides it much more localized. So, that they are actually much tightly bound to the ion core. So, the difference to the band the nature of the band is certainly different. And we will also designate these bands in a different way. So that is what we like to look at the energy levels of electron in an oxide structure is therefore, conveniently designated by the particular ion to which the electron is associated with under different situations.

So the electrons or the band are actually designated as the bands associated with the particular cat ion or the anion. We will look into it what exactly it means so the energy levels are designated by that particular cation or the anion, when the electron is associated with that particular ion.

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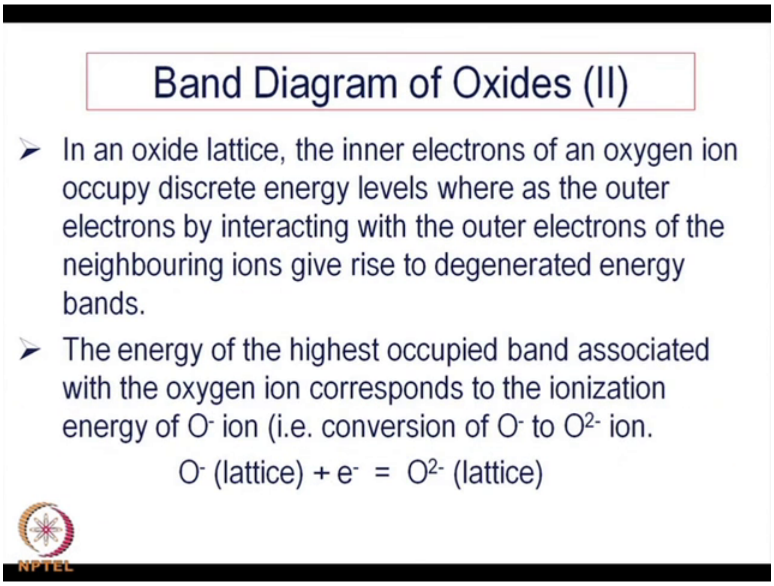

Band Diagram of Oxides (II)

- In an oxide lattice, the inner electrons of an oxygen ion occupy discrete energy levels where as the outer electrons by interacting with the outer electrons of the neighbouring ions give rise to degenerated energy bands.
- The energy of the highest occupied band associated with the oxygen ion corresponds to the ionization energy of O^- ion (i.e. conversion of O^- to O^{2-} ion.

$$O^- \text{ (lattice)} + e^- = O^{2-} \text{ (lattice)}$$

In a oxide lattice, the inner electron of an oxygen ion occupy discrete energy levels. Whereas, the outer electrons by interacting with the outer electrons of the neighbouring ions give rise to degenerated energy bands as we have discussed earlier. So degeneration takes place when there is overlapping of the electron cloud of the two atoms or the ions in this case.

The energy at the highest occupied band associated with the oxygen ion corresponds to the ionization energy of the oxygen ion. Of course, we are first considering the situation what happens in the oxygen ions. We can also consider very similar things for the cat ions or the metal ions. So, this is what happens the energy of the highest occupied band associated with the oxygen ion corresponds to the ionization energy of O minus ion that is the conversion of O minus to O 2 minus ion. So, the overall energy change, energy change is here. You are considering O minus ion that is not O 2 minus to start with. When you add this electron it becomes O 2 minus.

So, we are looking at what is the energy change, what is the change of energy with this. So, in fact it will be from the free space as if we are adding an electron from the outside to the oxygen minus ion in the lattice. And as a result we are getting O 2 minus in the lattice. We look into what is the energy change.

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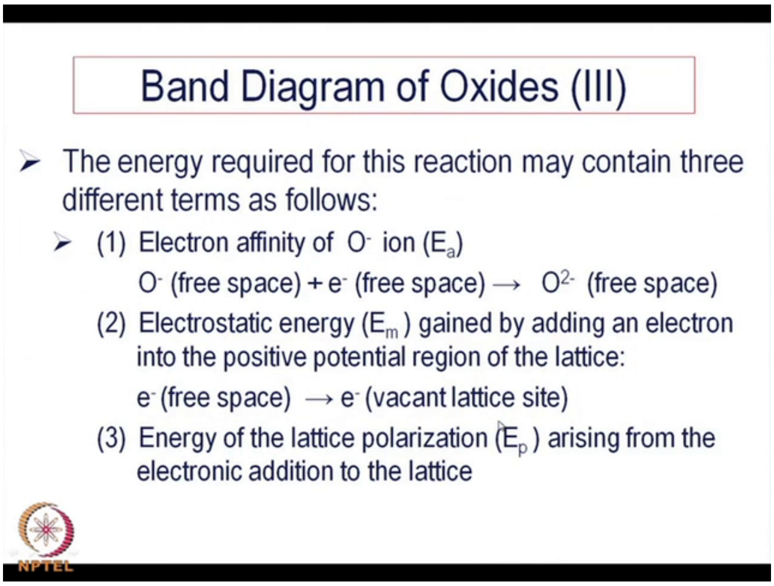

Band Diagram of Oxides (III)

- The energy required for this reaction may contain three different terms as follows:
  - (1) Electron affinity of O^- ion (E_a)
    O^- (free space) + e^- (free space) → O^{2-} (free space)
    (2) Electrostatic energy (E_m) gained by adding an electron into the positive potential region of the lattice:
    e^- (free space) → e^- (vacant lattice site)
    (3) Energy of the lattice polarization (E_p) arising from the electronic addition to the lattice

So, the energy that is required for this reaction contain three different terms as follows. First is the electron affinity of the O 2 minus ion that is designated as ea. The electron affinity what is the energy change by that process of adding one electron to the O minus ion. Then it becomes we can write O minus free space and also E minus in the free space. That means a singular oxygen ion is there and a singular electron is there. We are adding together what is the energy change in Ea. And both of them and finally, O 2 minus which is also in the free space. It is not hindered by any other interaction in the surroundings.

So, the electrostatic energy that is the second term E m gained by adding an electron into the positive potential region of the lattice. That means free space is coming to the vacant lattice site E minus that is another energy term that is, another energy term, which is Em. This is the first energy term this is the second energy term and the energy of the lattice polarization E p arising from the electronic addition to the lattice. So when electron is added to the system then it surrounds a electrical field it generates a electrical field. And that electrical field interacts with the other surrounding ions. And the lattice gets polarized the lattice get polarized. And so, the re-adjustments takes place. And that is also requires certain energy.

So there are three different energy terms Ea, electron affinity. Then is the energy gained by the system because of the, because of electronegative atom is being added to the system. Positive potential of the lattice and then the polarization because of the addition of the charge to the crystal lattice.

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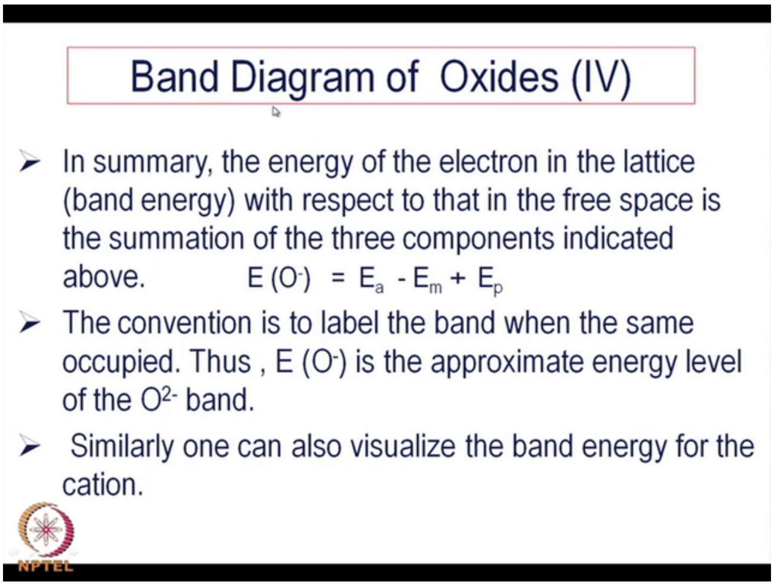

Band Diagram of Oxides (IV)

- In summary, the energy of the electron in the lattice (band energy) with respect to that in the free space is the summation of the three components indicated above. $E(O^-) = E_a - E_m + E_p$
- The convention is to label the band when the same occupied. Thus, $E(O^-)$ is the approximate energy level of the O^{2-} band.
- Similarly one can also visualize the band energy for the cation.

So, the total energy change in summary… The energy of the electron in the lattice band or the band energy ultimately with respect to that in the free space is summation of the three components indicated above. So, it is E minus E minus equal to I mean E O minus sorry E O minus equal to Ea, which is the term explained earlier this is a negative term because energy is gained by this by this process, by this particular process.

This is the gain in energy, this one. And then E p is the polarization. The convention is to level the band, when the same is occupied that means thus E O minus is approximate energy level of the O 2 minus band. The convention is we do not designate this is O minus. Although we are talking about what happens to O minus. We are adding an electron that means a O minus ion is changing over to an O 2 minus by accepting one electron from the outside. By that process whatever change is there that is the change or that is the energy level of O 2 minus band, O2 minus band similarly.

One can also visualize the band energy of the cation. So, we have just discussed the how we can designate the energy level of an electron associated with O minus or O2 minus.

Basically the band will be designated as O 2 minus. It will be clear in a minute when we discuss show the picture.

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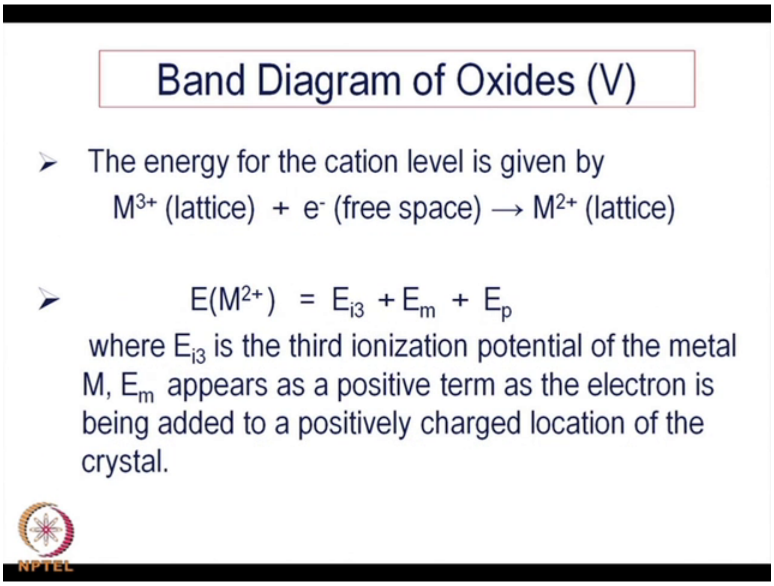

Band Diagram of Oxides (V)

- The energy for the cation level is given by
  M^{3+} (lattice) + e^- (free space) → M^{2+} (lattice)
- $E(M^{2+}) = E_{i3} + E_m + E_p$
  where E_{i3} is the third ionization potential of the metal M, E_m appears as a positive term as the electron is being added to a positively charged location of the crystal.

Now in the case of, in the case of the cation the energy for the cation level is given by similar terms M 3 plus. Now it is electron is getting added to a cation. So, we start with as if we have a 3 plus ion M 3 plus ion, when the electron is added to the system from the free space from outside the lattice. Then we are actually changing over to 2 plus. So, band ultimately will be designated as M 2 plus. So, the M 2 plus band of the M 2 plus is I 3. i 3 is the ionization potential the third ionization potential of the metal ion.

In case negative ion, which is primarily electron affinity and positive ion is the ionization potential is the same thing. So, E m appears to a positive term here as the electron is being added to a positively charged location of the crystal. So, this is becomes this E m which was earlier negative term is now a positive term these two remains a positive term.

So, ultimately the total summation is E i 3. The third ionization potential energy of M 3 plus if it happens. And then E m the here is also E m component that is the energy gained by the electron into the positive zone. That is what we have discussed here and here also the E m is there, but it is a positive term. Earlier it was a negative term, it was a positive term now and this is E p polarization is always positive.

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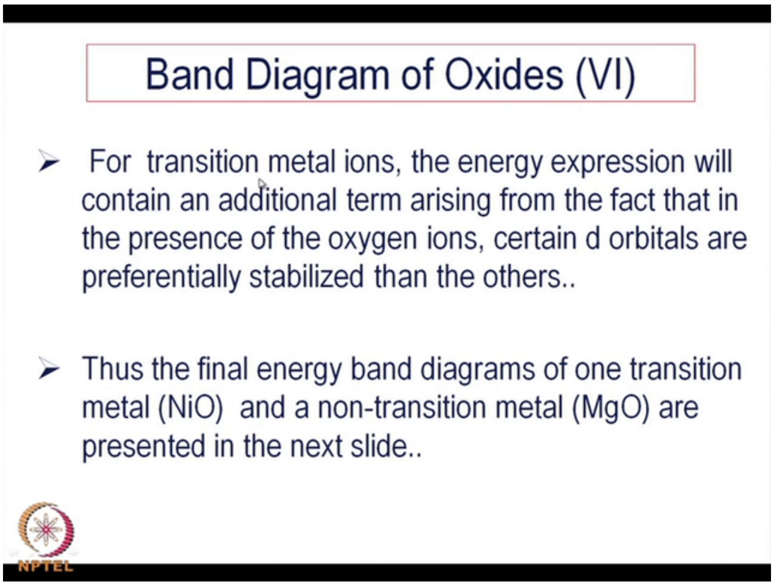

Band Diagram of Oxides (VI)

- For transition metal ions, the energy expression will contain an additional term arising from the fact that in the presence of the oxygen ions, certain d orbitals are preferentially stabilized than the others..
- Thus the final energy band diagrams of one transition metal (NiO) and a non-transition metal (MgO) are presented in the next slide..

So, for transition metals of course, that is general things for non-transition metal oxides. For the transition metal ions. The energy expression will contain an additional term arising from the fact that in presence of the oxygen ions certain de-orbital's are preferentially stabilized than the others. So, there is slight adjustment, there is a slight adjustment in the energy term particularly, when the transition metal ions are.

So, there will be the fourth term, which is not designated here. There is small change and that will be a fourth term particularly for the transition metals. There is a final energy band diagrams of one transition metal NiO and the non transition metal MgO are given in the next slide. So, in reference to that particular diagram it will be more clear.

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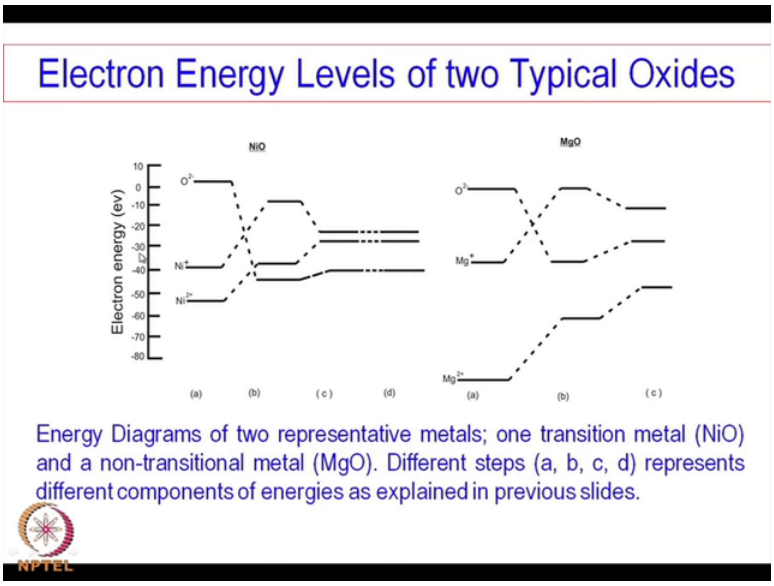

Electron Energy Levels of two Typical Oxides

Energy Diagrams of two representative metals; one transition metal (NiO) and a non-transitional metal (MgO). Different steps (a, b, c, d) represents different components of energies as explained in previous slides.

This is what it looks like and these are the different steps. These are the different steps three steps we have discussed. Particularly for the non-transition metal oxides and the transition metal oxides like NiO the fourth step mentioned is because of the preferential stabilization of some of the d shells. There will be slight change in energy. So what by step by step how the energy levels are changing the energy level associated with this cation. Both the cations and the anions the energy of the electron associated with the cations or the anions.

So, the energy diagram here represent two representative metals one transition metal Ni O and a non-transition metal MgO. Different steps a, b, c, d represents different components of the energies as explained in previous slides. So, whatever we talked about that is what is given here, but this is the energy scale. We started with let us say for transition metal or let us say for the non-transition metal to start with. We have MgO so, we have bands like this Mg 2 plus, Mg plus, O 2 minus. These are the three levels of the… These are in isolated ions isolated elements.

So, if you take the isolated elements it becomes like that and then or sorry not the isolated it is for the first step. That means the electron affinity and ionization potential. If you just look at the electron affinity and ionization potential of these ions. The relative energy levels are like this. Mg 2 plus is the lowest energy, Mg plus is the next highest energy and O 2 minus is the highest energy. Incidentally this is the more or less the situation in the other oxides also non-transition metal oxides also to start with. To start with Ni 2 plus has the lowest, Ni plus has next lowest or next highest and then O 2 minus has the highest energy level. So far as the electron affinity and ionization potentials are concerned.

Then we have added the electron as soon as the electron here the impact the energy goes down from there to there and these goes up. So, the energy level goes up here, whereas the oxygen goes down. So, the cation energy goes up the energy level of the electron added to the cation. Then there is a polarization because of the polarization all these energies again the Mg plus will go down where as oxygen will go up and Mg 2 plus will also go up.

So, these are the different components of the energy level energy associated with the different steps involved. And finally, you will see that Mg plus is the highest O 2 minus is in between and Mg 2 plus is the lowest. So, this is the lowest energy this is the next energy or intermediate energy and this is your highest level of energy. This is in comparison to here in the transition metals is more or less same, but slightly different. This comes down much below Ni 2 plus. Here oxygen does not come below Mg 2 plus. So, oxygen is in between, whereas here oxygen comes much below the two cations or the two state of the cations Ni 2 plus and Ni plus.

So, these are the conduction oppose as I mentioned there is an additional round of fourth step. And, but there is change of energy is very insignificant where as this fourth step is not there in the MgO Vacancy insulating oxides or non-transition metal oxides. So, you will get finally, these are the energy levels of as I said they are designated according to the status or the charge level of the cations or the anions when the electrons have being put in there. So, in this case in the non-transition transition metal oxides the highest level is Ni plus the next lowest level is Ni 2 plus the oxygen is much below.

In case of non-transition metal oxides the highest level is Mg two plus not the Mg plus as in case of nickel, but the next lower level is not the cation the oxygen comes in. So, this becomes your valence band and this becomes the conduction band here. Whereas here it is between nickel 2 plus and nickel plus. So, it is between the two cations that is the valence band and the conduction band. That is an important difference between the transition metal oxides and the non-transition metal oxides or insulating oxides and semiconducting oxides here.

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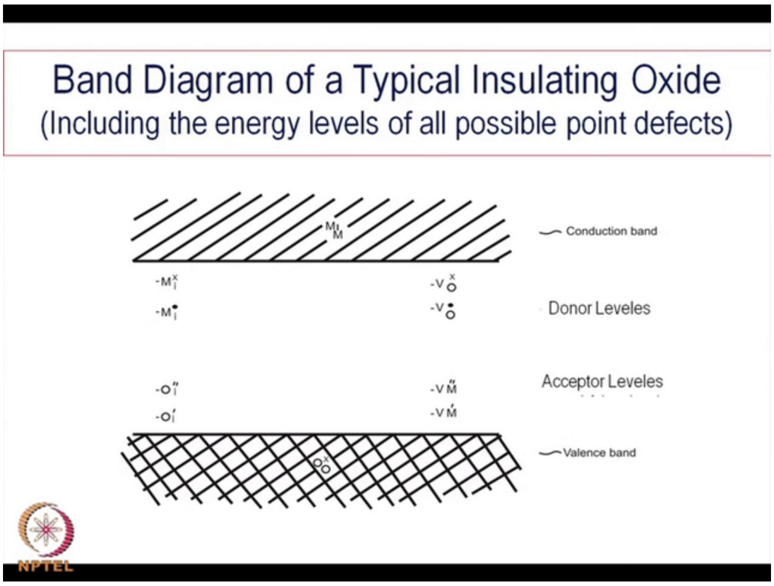

Band Diagram of a Typical Insulating Oxide
(Including the energy levels of all possible point defects)

With this we go to the… Now we are talking about the band diagram of an oxide, of an oxide as per the earlier designation. So the band diagram of a typical insulating oxide this is an insulating oxide including the energy levels of all possible point defects. Now in this is… For example, we have seen an insulating oxide here so the O 2 minus and Mg plus. So, this is actually O 2 minus.

It can be O 2 minus it had been written in a different way of course. Here MM that is M at the M site with a negative sign. With a negative sign it need not be written like that. One can also written differently, but what is more important here is that… What I am trying to show is this two levels, these two levels are basically the valence band and the conduction band.

And the other important issue I want to mention is the position of some of the defects. So, the defects also has some energy levels. We have earlier discussed about the point defects of different types metal vacancy, oxygen vacancy. They are charged are neutral vacancies and metal interstitials as well as oxygen interstitials. So these different varieties or different types of point defects also have energy levels. That means electron associated with that have energy levels, which falls within the band gap the main band gap of that particular oxide.

So, this is the two bands, two bands the valence band and the conduction band and once again this is an M x kind of oxide. So, you have metal interstitials a neutral x here denotes the neutral that means it is not a charged defect it is a neutral defect. Similarly, oxygen vacancy it is a neutral defect these are non-negative signs these are actually levels indicated, level indicators.

So, this is the level compared to that or compared to this energy and so, these are not negative signs. Here you have metal vacancy with a positive charge one positive charge and metal vacancy with double positive sorry these are negative charges. Effectively negative charges because the positive charge is negative. So, it is effectively a negative charge. Now, these are the two… In each case there are pairs this Mix Mi dot VOx VO dot. Here it is VM single dash or single prime, single prime as well as double prime here is Oi prime and Oi double prime.

Now these are actually the status state of ionization this is singly charged and this is doubly charged. Because M are basically two charges M 2 plus this is M 2 plus O 2 minus. So, here both the charges are not there so it is singly charged, whereas next level it goes to the double charged. Now these are more prominent or more predominant defects the doubly charged ones this one or this one or this one and this one.

Now there is a difference also have to be noticed. Here it is doubly charged, but this has not been shown as doubly charged or positively charged. Only single dot has been put. This is single dot and this is single dot, whereas this is neutral and this is neutral. On the other lower side you have both single charge and double charge. Single charge as well as double charge on the top it is actually single charge a sorry neutral and single charge, neutral and single charge.

That is because they the way you have designed it, designated it. When the electron is there actually it is a single charge. It was originally a single charge since it has been occupied by an electron so single charge has gone to neutral. And that is designation as per designation because we have made a statement earlier. That the energy levels are designated when the electrons are occupying that energy level. So, that is reason a single charge has been designated as neutral because it was single positively charge one electron goes there it becomes neutral. This is also single positive charge when electron comes here becomes neutral.

Here the neutral to the neutral one electron has been added not added actually removed. So, it becomes a positive charge effectively positive charge. So, this is one kind of designation. The other thing is this is our valence band and the energy levels closer to that is actually the acceptor levels. Because they will accept electrons from here and create holes in this valence band so they will accept electron. If they accept one electrons from here it will change to this.

If they accept two electrons they will change to this. Similarly, same case with this. This will accept one electron it becomes negatively charged one negatively charged it accepts two electrons it will negatively charged like this.

Here it will donate electrons. A neutral atom has already it will donate electrons and becomes a neutral and this… Sorry a positively charged interstitial will donate electron and becomes neutral. Then one more electron when will be donated it will be actually negatively charged. Sorry, singly positively charged. So, both Mi and Vr and vacance, which can donate electrons, are actually act as a donor levels. Whereas the VM or the vacance and the oxygen interstitials which can accept electrons are actually acceptor levels.

So, compared to other semiconductors here it is little different in the sense. The defects itself… We do not have to add an impurities to create acceptor level or donor level. The defects points themselves act as acceptor donor levels within the oxide. So they have their energy level and they are within the band gaps. So, they actually create stets energy stets, which can act as donor or acceptor levels. So this is a very important difference from the normal semiconductor when we talk about the oxides with that.

So, without adding any impurity you can have ap type conduction and an n type conduction. Which we have discussed earlier, which we have discussed earlier when we were discussing about defect formation as a function of partial pressure of oxygen. Some of them do act as a acceptor or p type conductor. Some of the others act as n type conductors.

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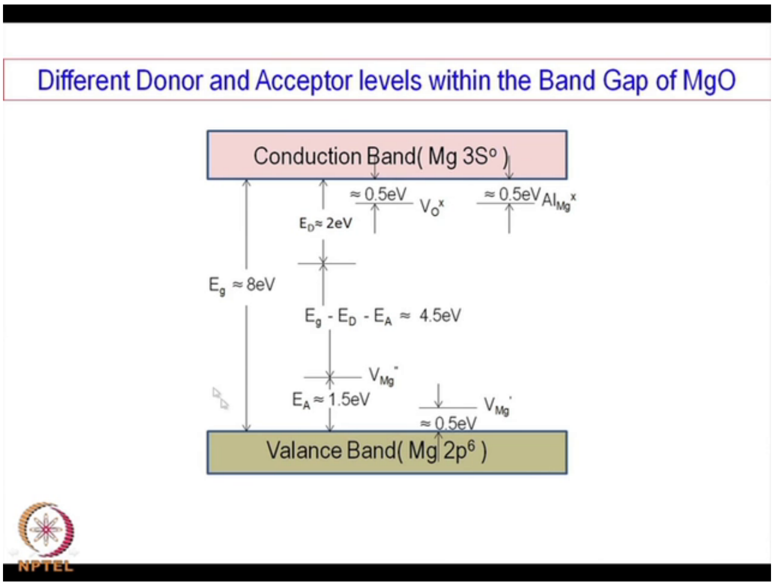

Different Donor and Acceptor levels within the Band Gap of MgO

This is a very specific example of a MgO and this is the valence band of MgO and this is the conduction band of MgO and this is the 3, that means the electron has been is not there. But once we add the electrons it becomes 3 S 2 here it is already electrons are there. So, the valence band 2 p 6 or Mg 2 p 6 actually acts as the valence band the next highest level. This is Mg 3 s 0 it becomes the conduction band.

Now the total band gap is of the order of eight electron volt and as per definition it is insulator. However if some point defects are created. For example, Mg vacancy singly charged magnesium vacancy or a doubly charged magnesium vacancy. Will act as an acceptor they will accept and the typical energy levels are about 0.5 electron volt in this case. And about 1.5 electron volt in this case. So, this is singly charged and this is doubly charged we mostly get doubly charged ions. So, it gets a energy states within the bands and therefore, conduction is possible to some extent conduction is possible.

Here it is a oxygen vacancy, intrinsic vacancy. This is magnesium vacancy and this oxygen vacancy. Once again it is about 0.5 electron volt here this is doubly charged. Sorry it has not been mentioned here. This is, this is next ionization of this level. So, this is about 2 volt 2 electron volts from the top. Here is a another type of defect which is aluminium has been added as an impurity to the magnesium site. And this is the aluminium at magnesium site with a neutral charge and that is about 0.5 electron volt.

So this a typical band diagram of an insulating material like MgO. And then by adding or creating vacancies or creating some defects either metal vacancy or oxygen vacancy. We actually add certain states. Energy states within the band gap and one can increase the conductivity of them. So, aluminium by adding aluminium we are actually creating a step. So, the electron transfer can takes place here.

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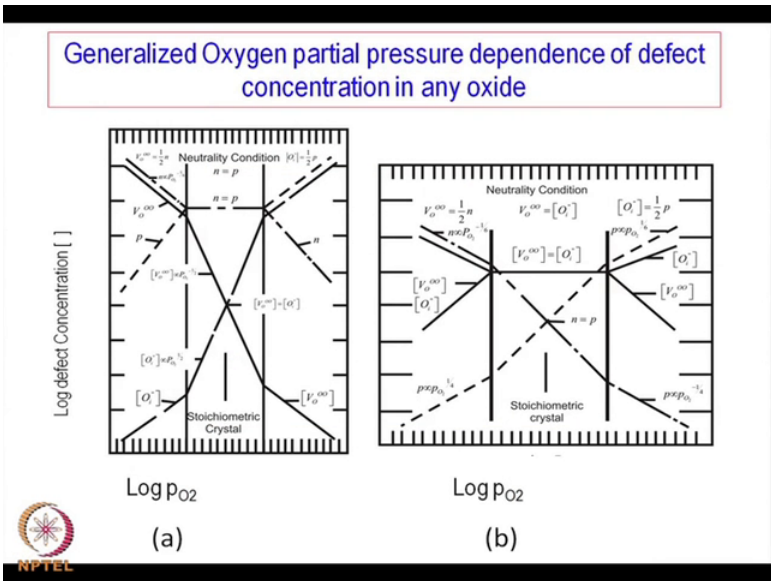

Generalized Oxygen partial pressure dependence of defect concentration in any oxide

This we have already discussed earlier. Once again I will try to look at it in a slightly different context. Once again, all the ceramics the charge carrier density is strongly dependent on the partial pressure of oxygen. In which it is getting equilibrated and looking at it as I mentioned earlier. When you just trying to discuss the defect concentration. This the diagram was considered earlier in the association the defect concentration. But here we are talking about the conductivity and here there is a strong correlation between the defect concentration and the conductivity here.

It is an ionic conductor or an electronic conductor for the time being we are looking at this part of the diagram or this part of the diagram. Here you will see then highest conductivity or the highest concentration is actually n or the electron concentration. So, this is the relationship. This is the neutrality condition here. And this is the neutrality condition there. So it is oxygen because it is a high oxygen rich site.

So, oxygen interstitials are possible and corresponding. You have positive holes so, that is the neutrality condition here, whereas on the lower side you have oxygen vacancy.

And therefore, you have negative electrons are n type conductivity. The highest defect concentration is this. So, it is p type on this side this is stoichiometric crystal. So, it is n equal to p it is an intrinsic semiconductor. And then it is a n type semiconductor on the lower Po 2 side.

Here also we find defect concentrations are like this. It is n on the lower Po 2 side and here P on the higher Po2 side. The only difference here is this value this electronic concentration or electronic compensation, or the equilibrium constant for n and P is lower than the oxygen vacancy the oxygen interstitials.

So, this value is higher. The plateau here is because of the this neutrality condition. That is oxygen vacancy and oxygen interstitial. That means, in this region it is the ionic defect concentration or the ionic compensation is predominant over the electronic concentration. So, the concentration of oxygen vacancy and oxygen interstitials are much larger than the concentration of electrons or hole. In this diagram it may corresponds to another oxide. This diagram may be may be valid for one kind of oxide and this may be valid for another group of oxide. So, the difference here between this and that as I have mentioned here. This is the stoichiometric crystal it is the ionic compensation, which is important.

So, the neutrality condition is that oxygen vacancy to oxygen interstitials here. Here neutrality condition is electron is to hole or the concentration of the electron is equal to the concentration of hole. So, this is an electronically conducting material particularly in the stoichiometric crystal range. And here it will be an ironically conducting material. So, an ionic conductor will have a diagram like this, whereas a electronic or semiconducting oxide will have a diagram like this. This will be a stoichiometric and non-stoichiometric compound basically or non-stoichiometric oxide. Whereas, this will be stoichiometric or mostly stoichiometric oxide until unless they have equilibrated with very very low Po 2 or very high Po 2.

So, those may be attend may not be attend, but it all depends which particular region of the material has been equilibrated. With respect to this diagram the atmospheric pressure where exactly it lies. The atmospheric pressure for some oxides may be here. For some other oxides it may be there the atmospheric oxygen partial pressure. So, depending on that either one oxide will be permanently or predominantly a ionic conductor or predominantly an electronic conductor.

So, this is the importance of this diagram. And on this diagram we have to place the atmospheric condition with respect to that particular oxide. So, this is these diagrams have been of course, drawn only for a constant temperature. We are not considering the temperature effect here it is only the partial pressure dependence at a particular temperature.

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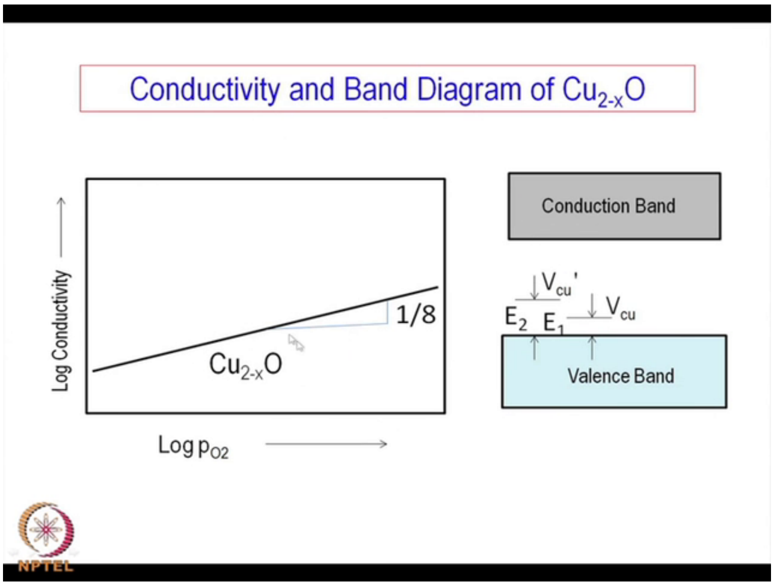

Conductivity and Band Diagram of $Cu_{2-x}O$

Now in that context these are being discussed earlier also, but I will just give you some examples. For example, Cu 2 minus xO that means a cation vacancy and because of the monovalent this is copper. Here is monovalent therefore because if the cation vacancy it will be P type conductor and if you plot log Po 2 to conductivity you have a positive slope. In this case it is one eighth positive slope band diagram will look like this as we have discussed in case of MgO.

Here generalized band diagram. Here the vacancy the metal vacancies will have the acceptor like characteristics and these will be the neutral vacancy. And this will be single vacancy or this will be singly charged vacancy. So, this energy will be below this energy will be high. So if you have a singly charged vacancy it will give rise to a conductivity like this. And it will act as a P type and therefore it is a acceptor. So, electron will transfer from this valence band and this acceptor level and will get a hole there.

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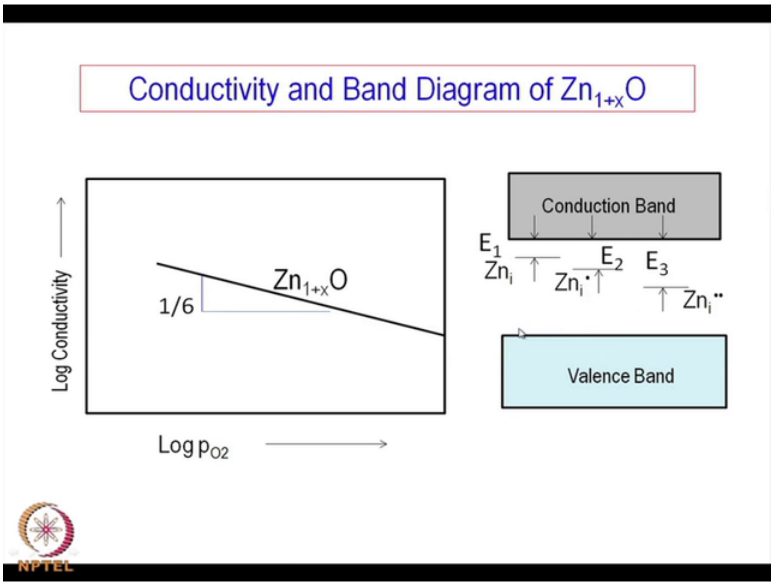
Conductivity and Band Diagram of $Zn_{1+x}O$

So, that is a typical situation of Co 2 O minus x Co 2 minus x O and this another example of a semiconducting oxides. Once again created because of non-stoichiometry, and this non-stoichiometry here is because of metal interstitial, metal interstitial act as donor. Therefore, it is n type semiconductor with a negative slope with Po 2 non-conductivity log Po 2 with a negative slope, and the energy levels will be like this.

Now in this case zinc this divalent. So, there are three energy levels possible one is neutral level. Another one is a singly charged level, and the other is a doubly charged level. So, E1, E2, E3, E3 will be higher than E2 than E1 and they will act as a donor levels. And this point effects will act as donor level and they will act as a, and the overall conductivity will be n type conductor.

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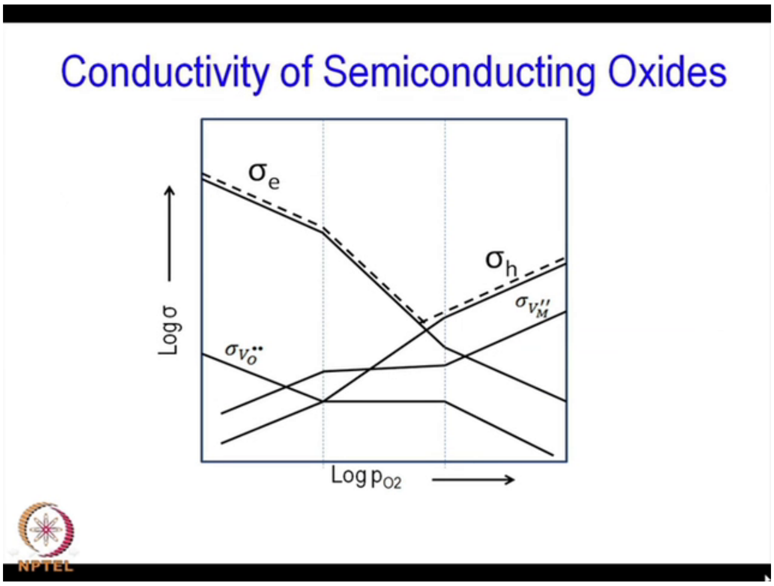

Conductivity of Semiconducting Oxides

Now, we have seen this diagram earlier. This is just a modification of that and this was, that diagram was shown the generalized diagram, which was shown in terms of the log concentration.

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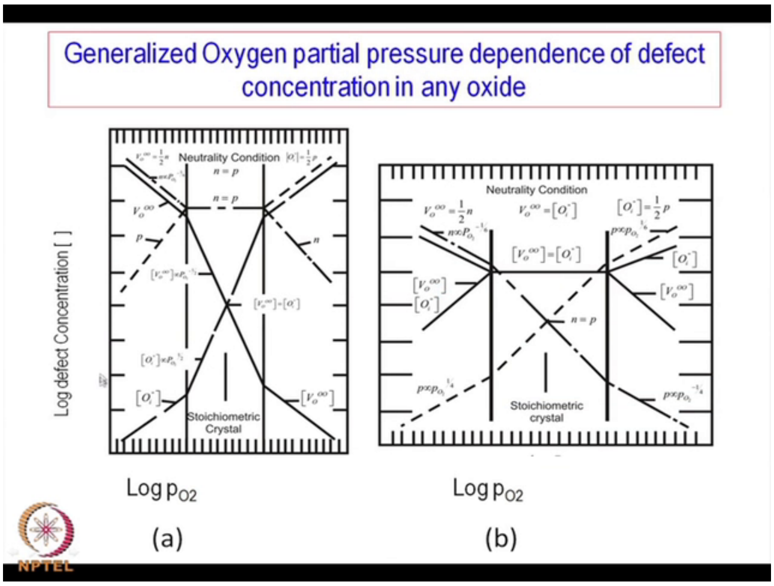

Generalized Oxygen partial pressure dependence of defect concentration in any oxide

We are not talking about the conductivity there. We are talking about the concentration. Of course the concentration is very much related to the conductivity.

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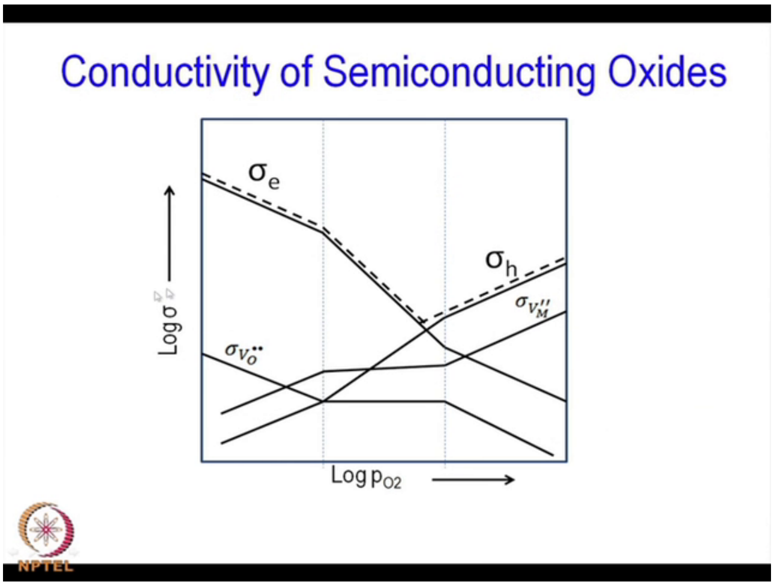

Conductivity of Semiconducting Oxides

That is why this has been plotted as conductivity and nothing it is as we have seen the conductivity is just ((Refer Time: 47.13)). So, the n is the number of concentration of the charge carriers. So, the here the highest level or the higher concentration is of the n type and on this side is P type.

So, the dotted line is actually the conductivity and the final conductivity. So the whole material throughout the Po 2 range will act as a semiconductor because the highest concentration level is because for the electrons or the holes. However, they change their character at some intermediate Po 2. There is no unlike the earlier diagram you have the flat portion here where n is equal to P that means, it is a intrinsic semiconductor. In this Po 2 range it is a intrinsic semiconductor. And then it becomes a kind of extrinsic semiconductor because of the vacancy creation, or because of the interstitial creation or vacancy creation on the site.

So in this diagram that particular portion is missing. There is no intrinsic either it has a negative and then positive. There is no intrinsic region. These concentrations are not are immaterial to us. Although there are some plots that means calculation can be done, but in the actual in reality. This is the concentration that dominates. Therefore, that with whatever conductivity we get. It is because of this highest concentration and not the lower concentration.

So, that also need to be remember so the conductivity arising from the oxygen vacancy in the same material will be like this. There is a constant region, but these are immaterial to us because that will not get reflected in the ultimate measurement or ultimate property. What will reflect in the ultimate property is the highest concentration. Whatever is the highest concentration in this region that will be electron concentration on the lower side lower Po 2 side and the hole concentration on the higher Po 2 side. They will dominate in the conducting area conducting property. These are only for sake of our understanding.

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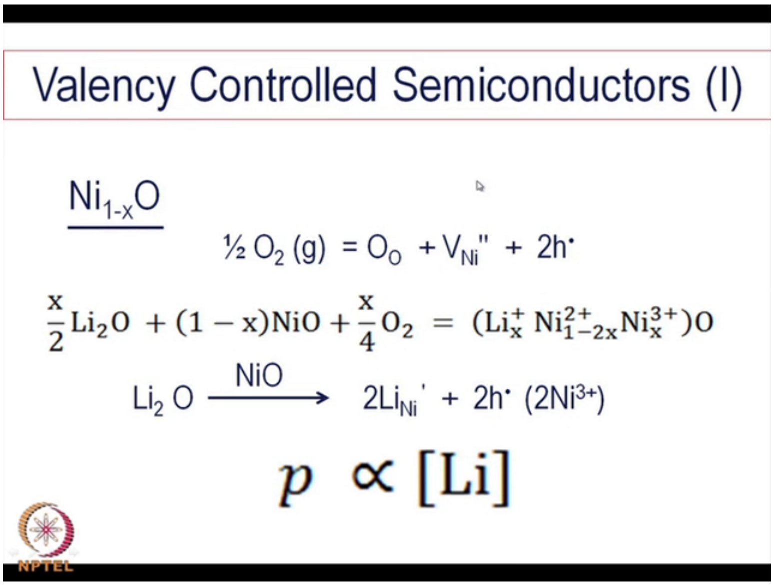

Valency Controlled Semiconductors (I)

$Ni_{1-x}O$

$$\tfrac{1}{2} O_2 (g) = O_O + V_{Ni}'' + 2h^{\bullet}$$

$$\frac{x}{2}Li_2O + (1-x)NiO + \frac{x}{4}O_2 = (Li_x^{+} Ni_{1-2x}^{2+} Ni_x^{3+})O$$

$$Li_2O \xrightarrow{NiO} 2Li_{Ni}' + 2h^{\bullet}\ (2Ni^{3+})$$

$$p \propto [Li]$$

Well having discussed all these. Let us have a different kind of semiconductor it is called valence controlled semiconductors. So, far we have discussed kind of intrinsic behaviour under different partial pressure range. How the defect concentration changes? And how the temperature effect is also there? But we have not discussed what is the impurity effect just like in semiconductors elemental semiconductors germanium and silicon. You add some donor doping. If you add some donor doping or accepted doping you do get enhanced conductivity as well. As a change over from intrinsic conductor to the either P type or n type depending on the type of impurity we add.

In this case also in oxides also, one can add certain impurities add certain other oxides and make the conduction conductivity constant easily it can be independent of Po 2, it can be independent even with temperature. And this is what we call the valence controlled semiconductor. That is basically the valence of the host cation changes, which we have seen earlier because that also changes because of the creation of defects, the intrinsic defects, but here we are inducing some defects. Inducing some change over of the valence of the cation and that is how it is called valence controlled.

The valence is controlled by adding the impurities. An example here is Ni 1 minus x O or NiO basically which is a P type conductor and because of cation vacancy. So, we have a cation vacancy there so it is a P type conductor and intrinsic situation. If we do not add any impurity to this. This is a kind of defect reaction. Half O 2 g it is O at O site vacancy of the lithium with double prime considering a doubly charged situation not a singly charged situation.

Normally although for our discussion, we have discussed in earlier slides that singly charged defects are also possible, but they are not so favourable. Primarily the doubly charged things the, doubly charged defects are normally considered as the favourable defects. So, we have two holes positively charged holes. Now, in that we have added Li 2 O. Li 2 O is lithium oxide with lithium having monovalent, or single positive charge compared to ni double positive charges.

That is why by adding about x by 2 amount of moles of Li 2 O to 1 minus x and NiO. And then adding some oxygen this is a kind of compound or this is kind of solid solution you will get. Because lithium goes into solid solution with nickel oxides or it replaces nickel in the nickel oxides in the lattice. So, that is why we are adding about x amount of lithium plus 1 plus and removing 1 minus 2 x amount of lithium nickel. And then these are 2 plus by adding x amount of lithium x amount of lithium is converted to 2 plus to 3 plus.

That is what you are controlling the valence from outside by adding certain ((Refer Time: 54.16)) impurities like lithium. So Li 2 O goes into nickel creates 2 LiNi with an single prime because Li is one less positive charge. So it is effectively negative charge and in the process creates two holes. These two holes are actually written here as 2 Ni 3 plus.

So effectively these two holes are situated or getting attached to the nickel site or the nickel 2 plus site and converting it to nickel 3 plus. So, it is because of this nickel 2 plus and 3 plus we have a conductivity we are inducing conductivity by adding nickel. And the concentration if the holes P is proportional to Li the concentration Li. It is not dependent or not controlled either by Po 2 or by temperature.

So, it becomes more or less temperature independent except of course, there will be mobility term will change, but the concentration of the nickel on the holes the charge carrier here will remain fixed by the concentration of nickel. So any particular sample if you prepared with some percentage of nickel the conductivity of nickel oxide will remain constant. It will be independent of Po 2.

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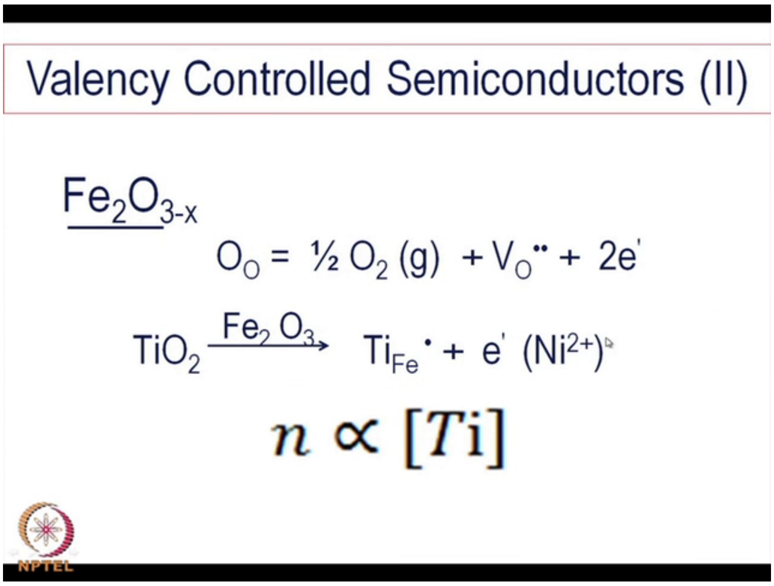

Valency Controlled Semiconductors (II)

$\underline{Fe_2O_{3-x}}$

$$O_O = \tfrac{1}{2} O_2 (g) + V_O^{\bullet\bullet} + 2e'$$

$$TiO_2 \xrightarrow{Fe_2O_3} Ti_{Fe}^{\bullet} + e' \ (Ni^{2+})$$

$$n \propto [Ti]$$

Another example is the similar example is Fe 2 O 3 minus x is an type conductor. This is an intrinsic defect reaction. Here it is TiO 2 gone to Fe 2 O 3. And since it is an 3 plus is getting replaced by 4 plus 3 plus is getting replaced by 4 plus. So, we have effective positive charge and corresponding electrons are generated. Earlier it was… Sorry there is a mistake over, there this is not nickel this is Fe.

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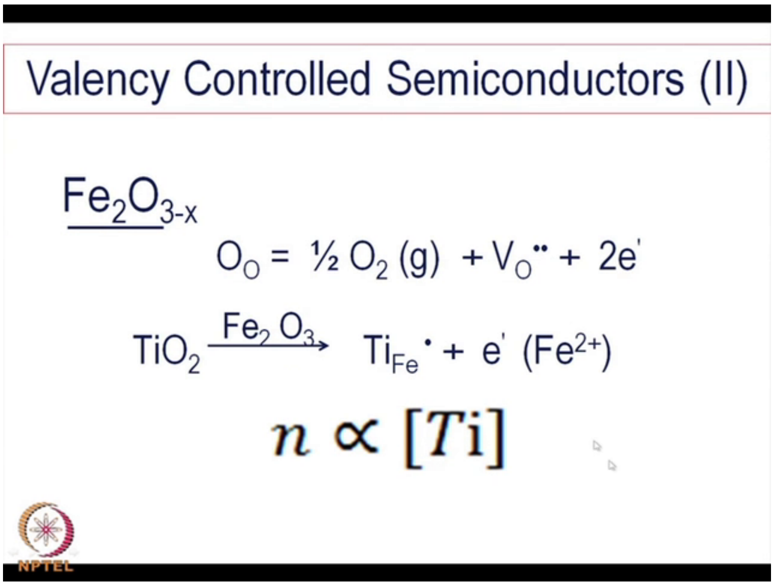

Valency Controlled Semiconductors (II)

$\underline{Fe_2O_{3-x}}$

$$O_O = \tfrac{1}{2} O_2(g) + V_O^{\bullet\bullet} + 2e'$$

$$TiO_2 \xrightarrow{Fe_2O_3} Ti_{Fe}^{\bullet} + e' \; (Fe^{2+})$$

$$n \propto [Ti]$$

So Fe 3 plus which was Fe 3 plus originally has gone to Fe 2 plus by adding one electron. So, this concentration of electron is actually proportional to the number of titanium added or the number of titanium atoms added. So, once again earlier example was a P type conductor controlled by the addition of impurity. Here an n type conductor is controlled by the addition of another impurity of a different valence. So, earlier it was a lower valence added to the higher valence. Here it is a higher valence added to the lower valence. So, that is the reason why to get the type of conductivity is different.

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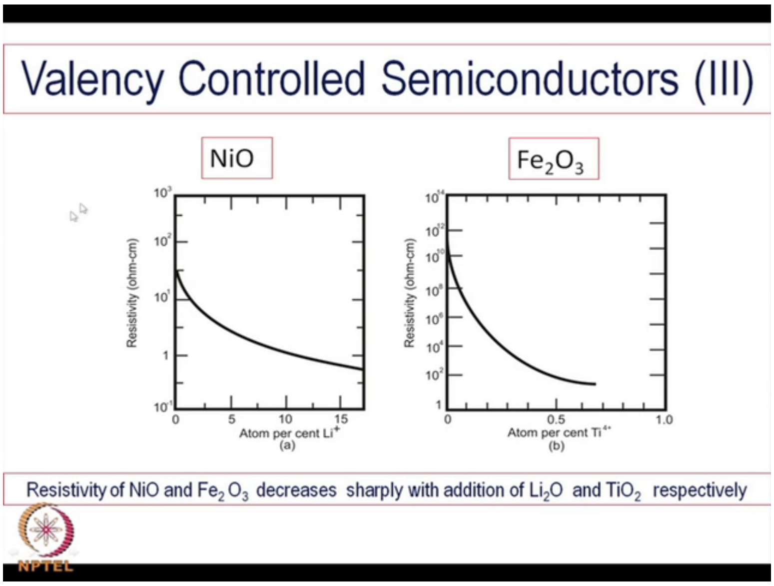

Valency Controlled Semiconductors (III)

Resistivity of NiO and Fe_2O_3 decreases sharply with addition of Li_2O and TiO_2 respectively

And these are the conductivity curves or resistivity curves here. As a function of lithium NiO and as a formation of Ti content for the Fe 2 O 3. There will be a sharp fall in the resistivity, when we add more and more of number lithium ions or more number of titanium ions Fe 2 O 3. So, both of them has a, you can control the resistivity or increase the conductivity by this kind of valence control mechanisms, or the oxides particularly. And these conductivity independent on Po 2 and mostly independent of temperature because of temperature of course will have some effect.

So far as the mobility is concerned the concentration remains constant. But the mobility may get changed. And therefore there will be some change in conductivity as a result of temperature. But Po 2 it will be completely independent of Po 2. Well the time is up. So we will close the discussion for the time being. We will continue this in the next class.

Thank you very much. Thank you for your attention.