Electroceramics
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Lecture - 10

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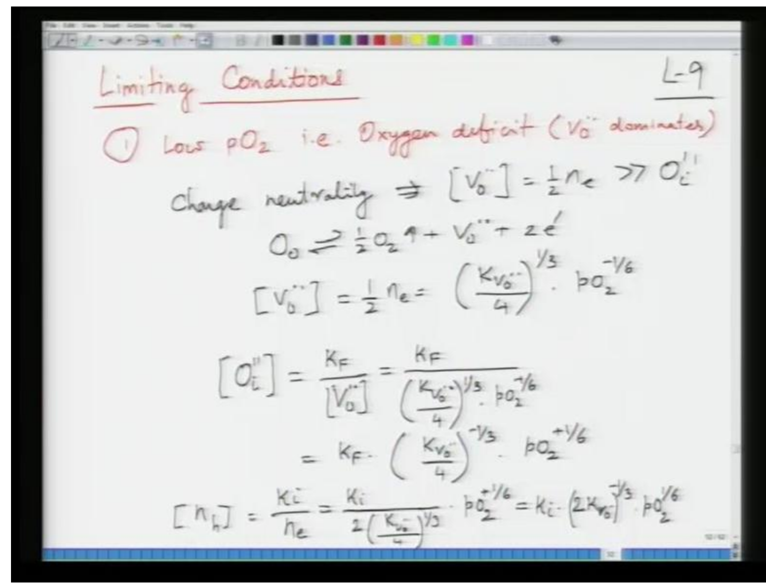

So, welcome to this new class. So, in the last class, we were determining the limiting conditions to determine the equilibrium diagram of concentration versus partial pressure. So, the first condition we took was low pressure of oxygen that is, when oxygen deficiency dominates, that is oxygen vacancies dominate in this particular material. And then charge neutrality, you can establish the charge neutrality condition, where oxygen vacancy concentration is half of electron concentration and which is much higher than interstitial concentration.

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And then you can determine what is the concentration of all the defects and then I can work out since V O is much greater than O i, I can work out what is the p O 2 condition at which this should happen. So, this is first limiting condition.

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Second limiting condition would be in high pressure region. So, in this case opposite prevails that is oxygen interstitials are much larger in concentration than oxygen vacancies, again write down the charge neutrality condition and write down derive the concentration of all defects.

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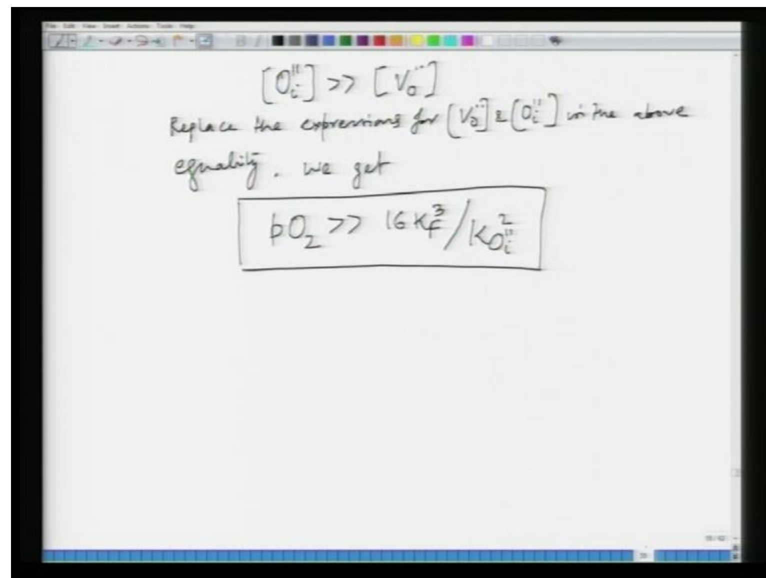

And then we work out what is the what is the regime of partial pressure of oxygen, which is given in terms of k k's of different reactions. So, p O 2 must be larger than 16 k F cube much larger than 16 k F cube divided by k O i square and then the last region which is remaining is the stoichiometric condition.

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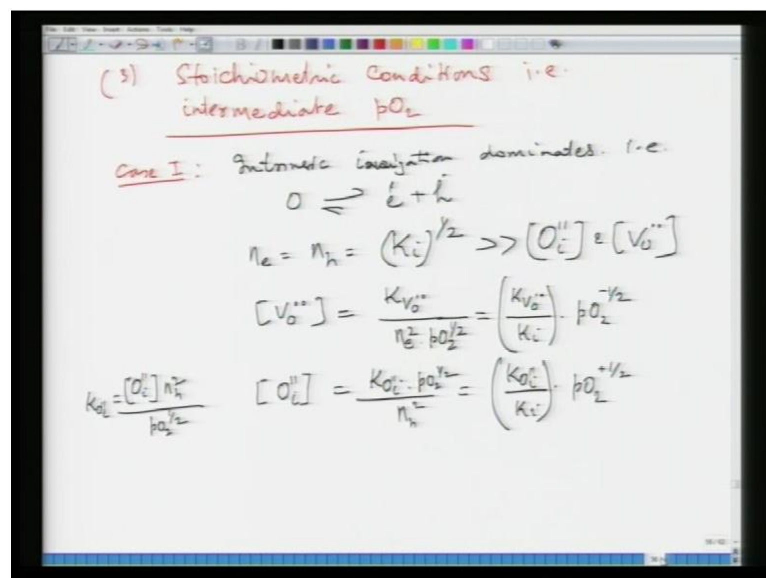

In that case we take two conditions, case one when intrinsic ionization dominates, that is intrinsic creation of electrons and holes. In such a situation, the electron and hole concentrations are equal they are equal to k i to the power half and these two concentration are much larger than oxygen interstitial and oxygen vacancy concentration.

So, when you determine V O and O i concentrations, then n e is given by this expression. So, here as a result oxygen and oxygen vacancy and oxygen interstitial concentrations are vary as p O 2 to the power minus half p O 2 to the power plus half in the intermediate range.

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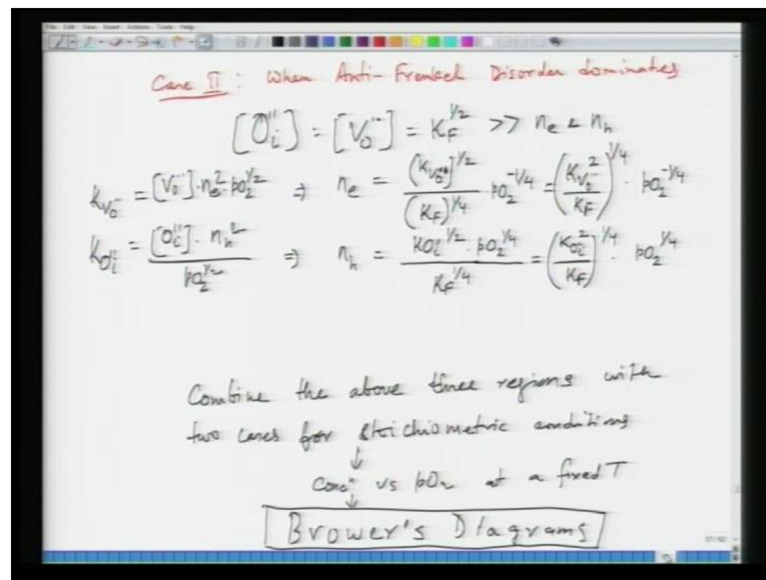

Second scenario that we could take, was when anti Frenkel defects dominate, that is in that case vacancy of oxygen is equal to vacancy of oxygen interstitial, which is equal to k F to the power half and these two are much larger than electron and hole concentration. So, we work out from the reduction and oxidation reactions. The electron concentration and hole concentration, the only thing you do here is because V O and O i is now fixed as k k F to the power half. You replace these as values of V O and O i in the expressions which are shown below. Then you can work out what is the what is the concentration of electrons and holes which goes as p to the power minus 1 by 4 or plus 1 by 4 and if we combine all these three regions with the limiting conditions, we get a equilibrium diagram which is called as Brower's diagram.

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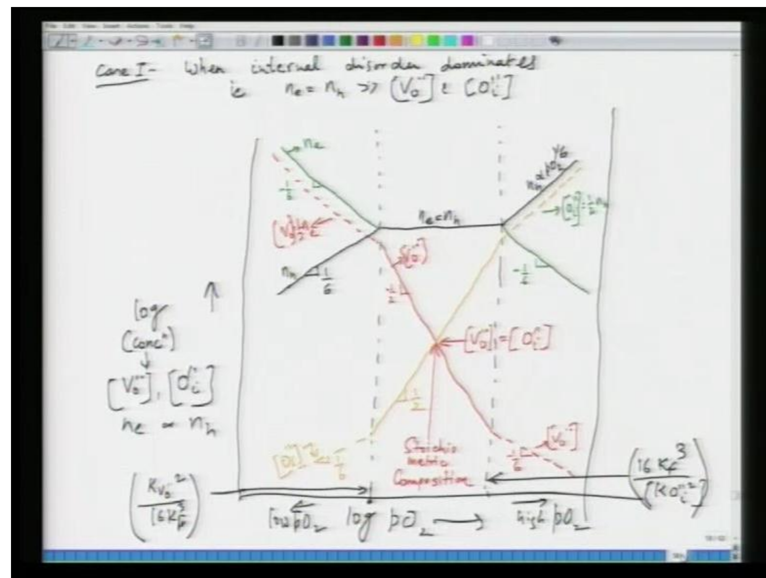

So, first one is when internal disorder dominates. So, I first draw n e is equal to n h in the stoichiometric region then I extend n E and n h in to high and low pressure regions, whose expressions are given as the expressions we have worked out. Then accordingly we can also draw O i and V O concentration, this is O i and V O concentration. So, O i concentration we start drawing from high pressure region because we know that it is equal to half of n h and then, we then the, since the continue composition has to be continuous it varies as p O 2 the power plus half in the stoichiometric region and then again varies as 1 by 6 in the low pressure region.

In case of V O it is equal to half of n e and this goes as minus 1 by 6 in the low pressure region, followed by minus 1 by 2 in the stoichiometric region, followed by minus 1 by 6 of p O 2 to the power of p O 2 to the power of minus 1 by 6 as in the high pressure region. So, this is the diagram that you get, when you when you assume that internal disorder dominates in the material.

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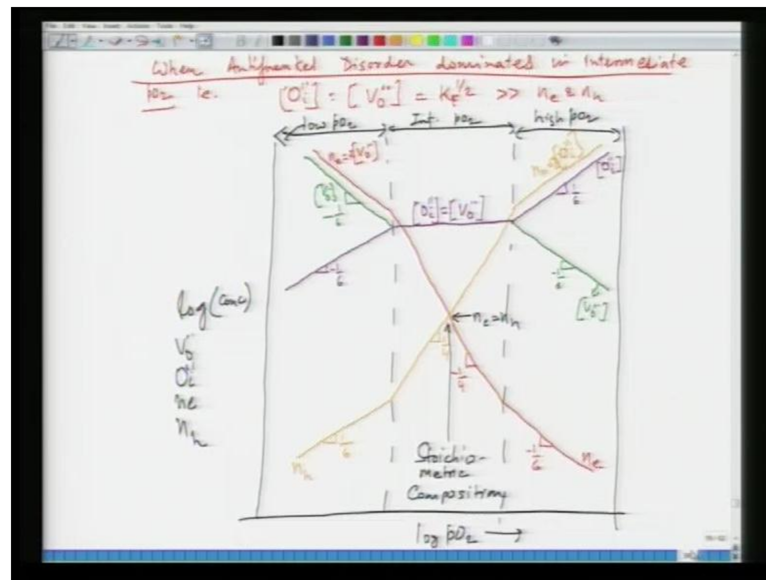

On the contrary, if you have anti Frenkel disorder which dominates in the intermediate p O 2 range, then stoichiometric composition, stoichiometric status or intermediate pressure state is governed by O i is equal to V O. Then you extend O i and V O into high and low pressure regions, according to the expressions that we worked out previously. Then since, we know n e is equal to 2 of V O, n h is equal to 2 of O I, we draw the lines for both n e and n h as per the slopes that are obtained in each of these regimes. So, these are two equilibrium diagrams, that we developed and these are very easy now as you can see. They look complicated, but they are much more easier to derive, if you know the fundamentals well, if you write the defect reactions properly.

We also, and choice of internal anti Frenkel or Schottky defects or whatever the kind of defects which prevails in the intermediate p O 2 range, usually those defects are the defects which prevail in the low or high pressure regime. So, your intermediate. So, for example, for example, if an oxide is prone to having Schottky defect, in that case the intermediate pressure, intermediate p O 2 range would be V O is equal to V M. So, the So, the defects that would dominate in the low and high pressure regime would be either V O or V M. So, you do not have O i or M i.

So, that is how it would change or if you had Frenkel disorder dominating then you would have V M and M i. So, the kind of defects which are going to dominate in each of these regime are governed are to a large extent governed by, what is the situation in the intermediate p O 2 range and that makes our life much more easier. So, as you can see if

you write the defect reactions properly, if you if you work out the limiting conditions, then you can work out what is the diagram, Brower's diagram for which is nothing, but log of concentration versus log of p O 2.

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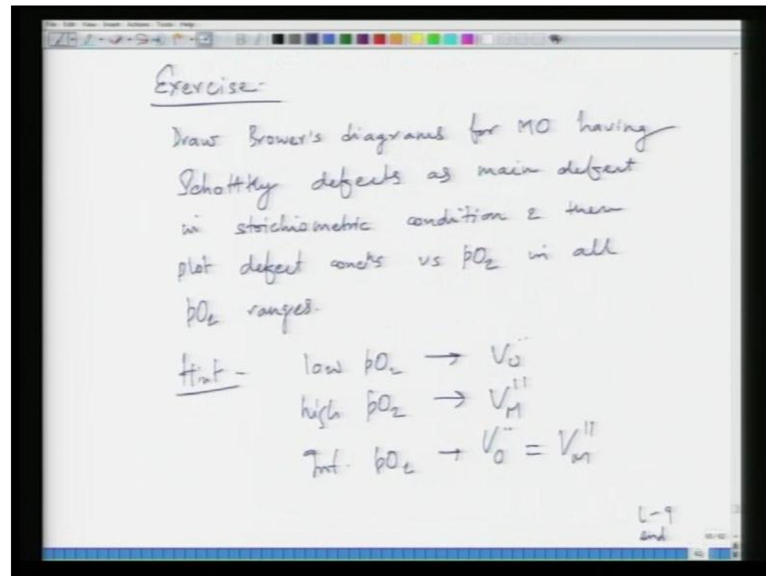

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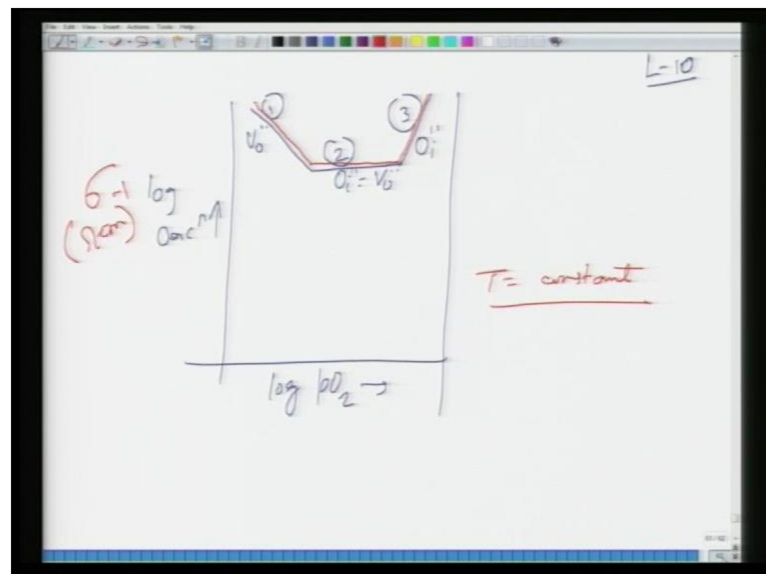

The top part of this, if you look at the top part, top part of this diagram for example, if I and this was the exercise which I gave you, which hope you follow. Then top part of this diagram would go as if you. So, basically no matter what the top part of the diagram would look like is. So, when you may now top part of the diagram is basically the majority concentration. So, this is regime 1, regime 2, regime 3. So, let us say in this

regime you have V O, in this regime you have O i, in this regime O i is equal to V O. So, when you make conductivity measurements, conductivity measurements in so this is p O 2 on log scale and this is concentration. So, when you make conductivity measurements.

So, now if I make conductivity measurements then, conductivity measurements would depend would scale as similar manner. So, from the conductivity measurements you can work out what the defect scenario in each of these materials going to be, which makes life little bit easier because and in this of course, the temperature is constant. These all these measurements are done at constant temperature. So, I hope the situation is clear now with respect to defect equilibria. Now, what we will do is that, we will look at the comparative performance of couple of oxides versus oxygen pressure. What happens in two different materials, let us say at different oxygen partial pressures.

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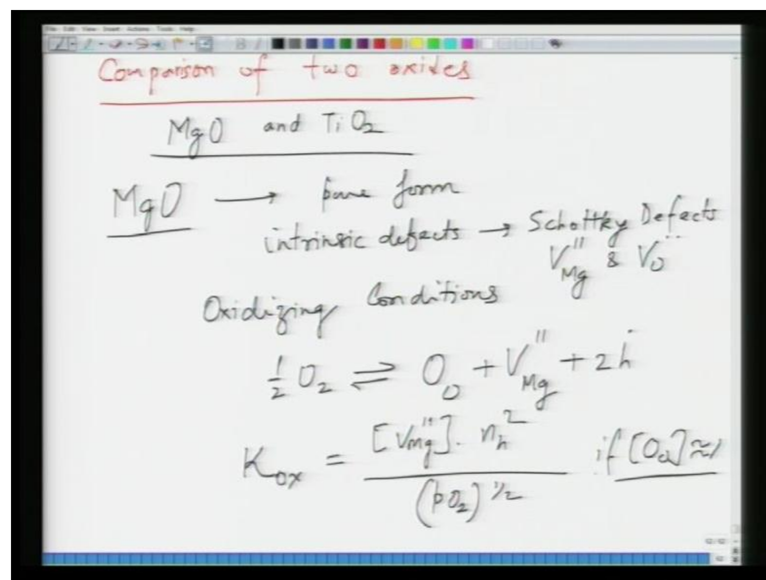

So, this is here this is. So, what we will do is that, comparison of two oxides. So, we will take M g O and T i O 2. So, first we will take the case of M g O. Now, M g O if it is pure form, then intrinsic defects are as we know we have talked about Schottky defects. So, M g O is prone to most of the close packed materials are prone to having Schottky defects, which means V M g and V O, these are two dominating defects. So, what would the defect reaction under oxidizing conditions? So, under oxidizing conditions, you will have oxygen coming into the system and this would go to oxygen site.

Now, you have created one oxygen site compensate for that, you will have one

magnesium site, which would be vacant and that will give rise to two holes. So, this would be the defect reaction and k for such a reaction would be, k ox let us say, this would be V M g multiplied by n h square divided by p O to the power half if, O O was equal to 1.

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If I take a dilute solution, now k experimental value for this reaction is 7.2 into 10 to the power 63 to exponential of minus of 610 plus minus roughly 10 percent, 680 divided by R T and this is kilo joule per mole. This is the experimental value of k and the units are centimeter to the power minus 9 M P a to the minus half. Now, you can see from this expression that what happens as you increase the temperature. Now, as you increase the temperature since this is minus sign is here, the k value also increases. As a result what it means is that that M g O can be oxidized at higher temperatures, which means producing more and more intrinsic magnesium vacancies and holes if no other defects were present, if no other extrinsic defects were present.

So, from the electrical neutrality condition you can write, electrical neutrality condition gives you n h is equal to 2 of V M g. So, let us take two two examples of different temperatures. So, let us I mean, even though in reality even though the concentrations are very small, but they still vary as a function of partial pressure of oxygen as well as temperature. So, for example, we take melting point of T m of M g o is about 2480 degree, 2480 Kelvin. So, let us say T is equal to 0.8 of T m and atmosphere is air which means, 0.21 p O 2 is equal to 0.21 atmosphere. Under these conditions V M g can be

worked out as 2. So, you know what the temperature is, I can just put the value of temperature here to get the value of k and I know from the previous slide that k is equal to V M g n h square by p O 2 to the power half.

So, I replace n h is equal to 2 V M g which means this whole expression becomes 4 V M g cube. So, 4 V M g cube will be equal to p O to the power half multiplied by k ox and k ox is experimentally determined as a function of temperature. So, when you make these substitutions. So, so V M g would be your. So, I write 4 V M g cube is equal to k ox multiplied by p O to the power half, which means V M g is equal to 1 by 4 to the power 1 by 3 into k ox to the power 1 by 3 p O to the power 1 by 6. So, I can determine k ox from this expression, as a function of temperature and I know p O 2 is equal to 0.21 atmosphere. So, if I make appropriate substitutions then what I get is V M g is equal to 2 into roughly 10 to the power 16 per centimeter cube. This works out to about 0.6 PPM in M g 1 minus x O. So, this x would be 0.6 PPM because magnesium deficient would mean M g 1 minus x is the level of deficiency and level of deficiency is equivalent to vacancy of magnesium and this works out to around 0.6 PPM.

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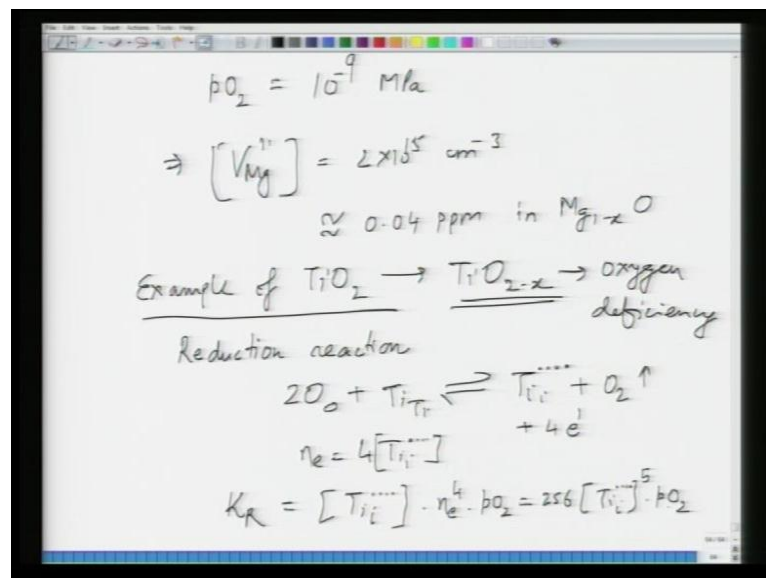

Now, if you change the partial pressure of oxygen. So, if you take p O 2 is equal to minus sorry if you take p O 2 to be equal to 10 to the power minus 9 minus 9 M P a in such a situation again, you recalculate and this gives to V M g concentration of about 2 into 10 to the power 15 centimeter, per centimeter cube. This is equivalent to 0.04 PPM in M g 1 minus x O. So, if you compare these two values, in previous case we got 0.0,

0.6 PPM and now we have got 0.4 PPM.

So, by reducing the partial pressure of oxygen by about 9 orders of magnitude, we we get only a difference of an order of magnitude in the magnesium vacancy concentration. So, this is about magnesium oxide. So, here we see that, when you change the pressure for example, at a fixed temperature of 0.8 of melting point you do not see an appreciable change in the concentration of magnesium vacancies. On the other hand if you take example of T i O 2 now, T i O 2 is also an oxygen deficient oxide. So, it is very proned to non stoichiometry. So, the in this case, this is let us say. So, modify a little bit T i O 2 minus x. So, this is going to have oxygen deficiency. In case of M g O we looked at magnesium deficiency and here we look at oxygen deficiency. So, there are that. So, the reaction is of course, the reduction reaction.

So, 2 O O plus T i at T i side they go to, T i interstitial plus O 2. So, since oxygen is gone out, the titanium side is also lost and it has become a interstitial and this gives rise to 4 electrons. So, the electrical neutrality condition we know is, equal to n e is equal to 4 of T I, assuming the titanium interstitials are. So, and k R would be T i sorry T i i T i i multiplied by n e 4 into p O 2 and if you make this to be equal to. So, this 256 T i i to the power 5 multiplied by p O 2.

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So, T i i concentration becomes k R divided by 256 to the power 1 by 5 into p O 2 to the power minus 1 by 5. Let me have a just look, minus 1 by 5. So, this would be your T T i

concentration. Now, I know that k R experimentally is determined as 6.55 multiplied by 10 to the power 22 into exponential of minus 960 kilo joule per mole divided by R T and this has a unit of M P a centimeter inverse. So, now again I take T is equal to 0.8 of T M and which is nothing but about 1690 Kelvin in titanium oxide. So, I work out. So, if you put the value, this value of temperature you can work out, what is T what is k R and p O 2 let us say. So, let us say in air, p O 2 is 0.21 atmosphere.

So, if you work out T i now. So, make sure you put the right units in every place because units are very important and what you get here is 1.4 into 10 to the power 18 per centimeter cube. So, first of all if you compare the magnitude with respect to magnesium, in case of magnesium we got around 10 to the power 16 per centimeter cube atmospheric pressure and here you have two orders of magnitude high. So, even at room even at atmospheric pressure at the same temperature, that is 0.8 of melting point, titanium oxide has much more two orders of magnitude higher defect concentration in comparison to M g O and this works out to roughly 93 PPM in T i O 2 minus x. So, this x is 93 PPM.

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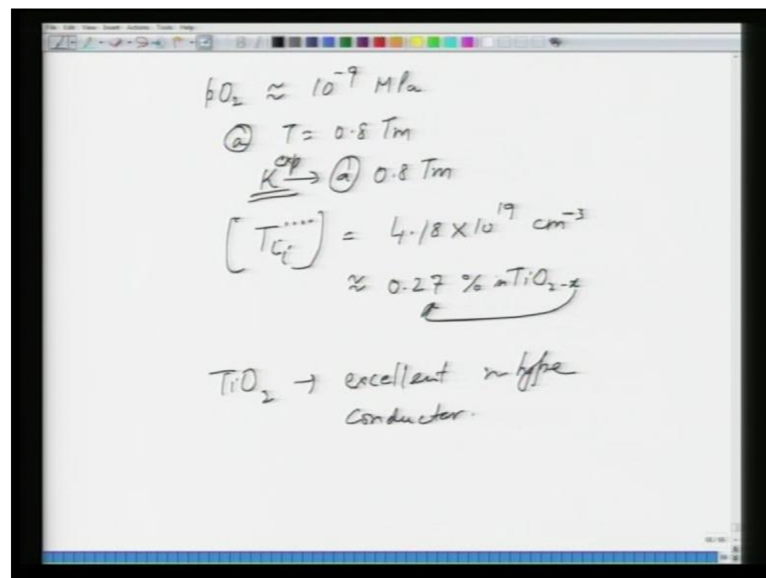

Now, if you take p O 2 is roughly 10 to the power minus 9 megapascal same pressure as in case of M g O and again at 0.8 of T M, then you work out what is k. k experimental will give you the value of k at 0.8 and then you know what is T i i expression. So, T i i would be under such condition is 4.18 into 10 to the power 19 per centimeter cube. So, you have seen that, although the although the change relative change in the magnitude at

two pressures is only about one order of magnitude, but this is equivalent to roughly 0.27 percent in T i O 2 minus x. So, this x is 0.27 percentage. It is a significantly large number.

So, because of this reasonable, because of this large change, large difference in the defect concentrations of two oxides that we have taken T i O 2 makes a excellent n type conductor, but M g O does not. So, if you want to make M g O conducting, you need to put impurities. That is you need to work through extrinsic defects and that we have seen earlier what happens when you put defects in M g O.

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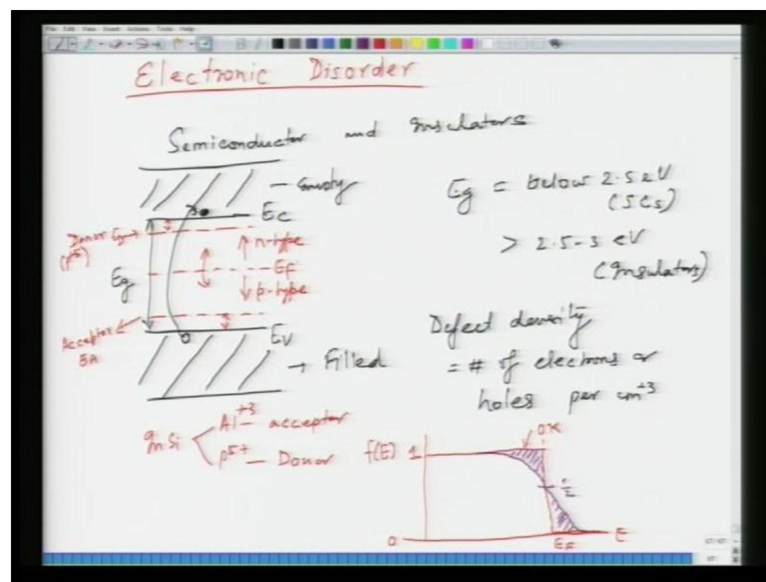

So, this I hope clarifies some of the basics related to ionic defects. Now, we will look at some of the fundamental things related to electronic disorder in the material. We have talked in very brief about electronic disorder and just by writing a defect reaction. Now, unlike intrinsic point defects which are your vacancies or interstitials or electronic defects are typically created by either thermal means or optical means, which means what happens in these materials is basically, you have two types of materials one is semiconductor and insulators and oxides typically form in any of these two categories. They are different from the metals in such a sense that they have a forbidden energy gap.

So, this is your energy gap in the energy band diagram and this is E g which means nothing exists. So, this separates basically your valence band and this is your conduction band. So, this valence band is typically at 0 k would be filled and this would be empty.

So, any conduction, which has to take place in these materials having a particular band gap. So, this E g value of E g would be would be about typically below 2.5 electron volt for semiconductors and greater than 2.53 electron volt for insulators. So, any if these guys have to conduct any electricity or any charge conduction has to take place, the electrons from the valence band which is here, they have to be excited across this energy gap to go there and as a result it gives rise to a hole. Now, this can this process which means the process which has to occur here it can be thermal process or an optical process because you need to supply an energy which is at least equal to or higher than E g. So, that is where. So, that is why these defects are little bit different in terms of.

So, basically you can consider this energy band gap as an energy, which is equivalent to your defect formation energy in terms of intrinsic point defects. In terms of intrinsic point defects if you look at the statistical model, then in order to create certain number of defects you need to overcome the energy barrier of defect formation energy that is, delta h F. Now, here you need to overcome E g in order to create a electron hole pair or to create electronic disorder or electronic defects. So, defect, density as a result is nothing but number of electrons or holes in the material and you can express in terms of per centimeter cube.

Another another thing that is of interest in these materials is something called as Fermi energy and this Fermi energy for intrinsic semiconductors sits at the middle of the band gap and the once the semiconductor or insulator it start becoming extrinsic, which means you start putting in defect then this Fermi level moves up or down. So, if you want to if you make it n type the Fermi level will move up for n type and for p type it will move closer to valence band. When you start putting in impurities, then you also introduce something called as donor or acceptor levels. So, this would be your acceptor level, which means it will accept electrons from the valence band giving rise to large hole density in the valence band and this will donate its extra.

So, this is this is typically for example, in silicon if you take. In silicon your aluminum would be an acceptor because aluminum is plus 3 atom. So, it would attract an it will it will receive an electron from the valence band, creating a hole in the valence band. So, this is an acceptor level which and this difference in the energy is very small it is it is of the order of few milli electron volts which can be easily, which can easily happen at room temperature. Similarly, this level will be called as donor level. So, I can write this

as E d, I can write this as E a and again this energy difference E c minus E d is very small, is of the order of few milli electrons volts. So, that all the excess electrons from donors for example, P 5 plus phosphorous.

So, electrons from the donor impurities can be excited into the conduction band, without spending any extra energy at room temperature and this gives rise to large density of conduction electrons in the conduction band. So, and the Fermi energy is an energy you know what Fermi energy is. So, when you plot for example, So, this is let us say, E f this is E versus. So, this is from from the Fermi derived statistics which means all the energy at 0 k, all the energy levels below Fermi energy. So, an f E would represent the probability of occupation. So, what it basically tells you is that, all the energy levels below E f are filled at 0 k and nothing above E f is filled. So, this is your 0. So, this is at 0 k and as you increase the temperature.

So, at a finite temperature this will go through half. So, this would be your half point. So, number of electrons. So, the number of electrons from the levels just close to Fermi energy will leave and go into the adjoining parts. So, this would be your definition of Fermi energy.

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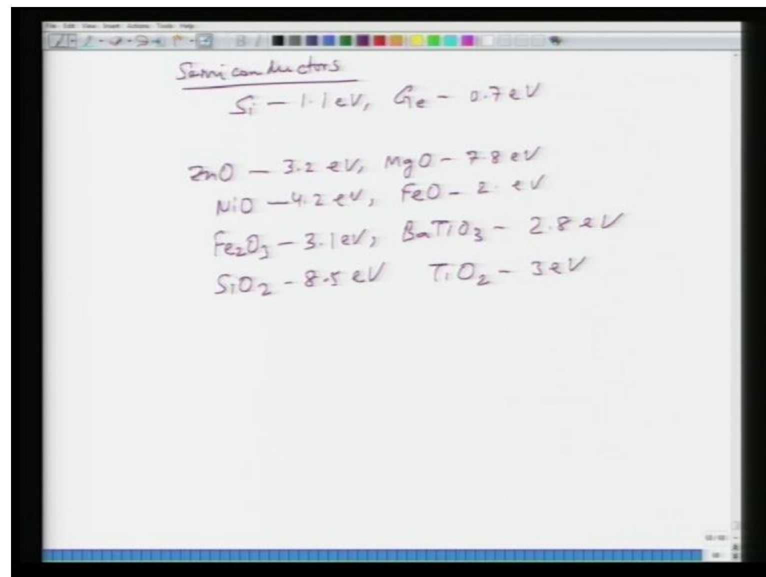

So, typically for a intrinsic semiconductor it sits right in the middle of the band gap. Some of the band gap values for example, in case of semiconductors your silicon has about 1.1 electron volt, germanium has 0.7 electron volt and in case of oxides for

example, zinc oxide has about 3.2 electron volt, magnesium oxide has 7.8 electron volt, nickel oxide has roughly 4.2 electron volt, iron oxide is close to 2. something electron volt, close to 2 electron volts your F e 2 O 3 has about 3.1 electron volt, barium titanate very important material for many practical applications is about 2.8 electron volt and so, on and. So, forth silicon oxide for example, has large band gap of 8.5 electron volt, T i O 2 has 3 electron volt and you can you can find many more values in the literature and. So, these are the some of the band gap values.

So, typically higher the band gap is, less conducting the material is in the intrinsic state. Unless you create defects from some other means. So, the defect concentration since we know that it depends upon since we know that you have to provide enough energy which is, the thermal energy to over thermal or optical energy in order to overcome the energy barrier it can be written in terms of probability of electrons or electrons crossing and this gap.

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So, so concentration of electrons or holes are equal in intrinsic. So, n e is equal to n h in an intrinsic solid and this is given as n e is equal to n c exponential of minus of E c minus E f divided by k T and you know what is E c and E f is. So, this is your E c conduction band edge, the bottom of conduction band and E V is top of valence band. So, N c where N c is the effective conduction band density of states density of states and similarly n h is given as N V into exponential of minus of E f minus E V divided by k T. So, basically you can see that now, for intrinsic semiconductor E c minus E f would be equal to for an

intrinsic semiconductor E c minus E f is equal to E f minus E V is equal to half of E g because its right in the middle.

So, you can see that this would change to minus of E g by 2 k T and this would also change to minus of E g by 2 k T and you can see as. So, if that is the case then, as E g increases what would happen to n e and n h, both n e and n h would decrease and also as temperature increases both n e and n h would increase and this n V, I forgot to mention would be effective conduction, slash valence band density of a states depending upon which case you are referring to.

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N c and n v values are given as N c is equal to 2 into 2 pi M e star k T divided by h square and to the power 3 by 2 and n v is equal to 2 into 2 pi M h star k T divided by h square to the power 3 by 2 and M e star and M h star are effective mass of electron and this is effective mass of hole and k is Boltzmann constant, h is Planck's constant and that you can. So, at about. So, at about 300 k which is the free room temperature, N c is equal to n v is roughly 10 to power 19 per centimeter cube if, M e star was equal to M h star which means mass of free electron effective mass of free electron is equal to effective mass of hole. Now, that is not necessarily a true condition, but just for the sake of doing it. We know that n e is equal to n h for an intrinsic semiconductor I can write E F to be equal to E c plus. So, if you make n e and n h equal to what it becomes is that E c plus E v by 2 plus 3 by 4 k T l n M e sorry M h star divided by M e star and this E c plus E v by 2 is nothing, but E g by 2.

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So, this becomes. So, your E F becomes E g by 2 plus 3 by 4 k T l n, M e M h star divided by M e star. So, if this would was equal to 1 then, E F was equal to E g by 2 for an intrinsic semiconductor that is what we assumed to begin with, So, but typically in oxides your effective masses are about 2 to 10 times of M e or effective mass of free electron. Let us say M e naught which is a free electron mass. You know that atomic density of solids is roughly 10 to the power 23 per centimeter per cube. So, density of states is about 4 and 4 to 5 orders of magnitude lower than in semiconductors.

So, this gives you an idea about the density of states value in the oxides. Now, if M e and M h were equal then you can write n e to be equal to n h to be equal to n c n v to the power half into exponential minus E g by 2 k T. Now, this expression is very similar to what you see for defect concentration. For defects we worked out n by N is equal to exponential minus delta H F by k T 2 k T right. So, in case of Frenkel defects. So, you can see the relation, here you need to overcome energy of delta H F in order to create the defects here you need to create an overcome an energy of E g in order to create electronic defects. So, it's very very similar these expressions are very similar because the fundamentals concepts are similar, you need certain energy in order to overcome energy barrier to create the defects.

So, density of electronic states in a in a material can be can be thought of as equivalent to density of vacancies in the lattice sides. So, expressions are equivalent that is why you can make them equivalent and the and the depiction in terms of chemical reaction if you

want to in terms of in terms of.

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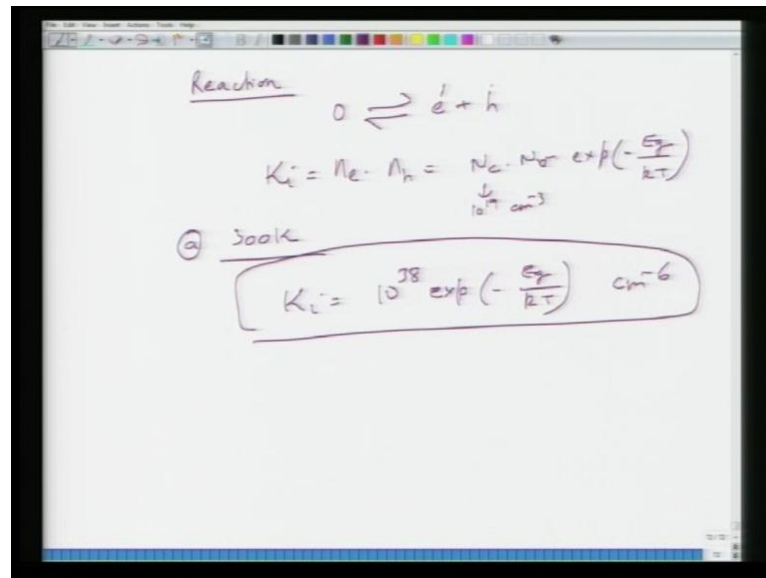

So, reaction of course, as we saw was electrons plus holes and this was for this reaction constant would be n e multiplied by n h which is equal to n c into n v into exponential minus E g by k T at about 300 k and this k i is approximately 10 raised to power 38 because this is 10 to power 19. So, this will be 10 raised to power 38 exponential of per centimeter cube. So, this would be 10 to the power for 38 exponential minus E g by k T and this would be centimeter power minus 6. So, this is how you can determine what could be the values of k i for intrinsic ionization.

So, now. So, in summary basically what we have seen is, for electronic disorder that the oxides typically have ionic solids or semiconductors covalently bonded solids they have an energy gap, in order to create electron and holes you need to overcome an energy which is nothing but the band gap and depending upon how much energy you provide you will create certain electron hole concentration. This equation is pretty much similar to the vacancy concentration or Frenkel defect concentration that we worked out in case of equilibrium defect concentration. So, concepts are similar except that that type of energies are different. So, now we will move on to some of the examples and for example, we will take what is the, we will take the case of M g O and we will see what the intrinsic electronic and ionic defect concentration is.

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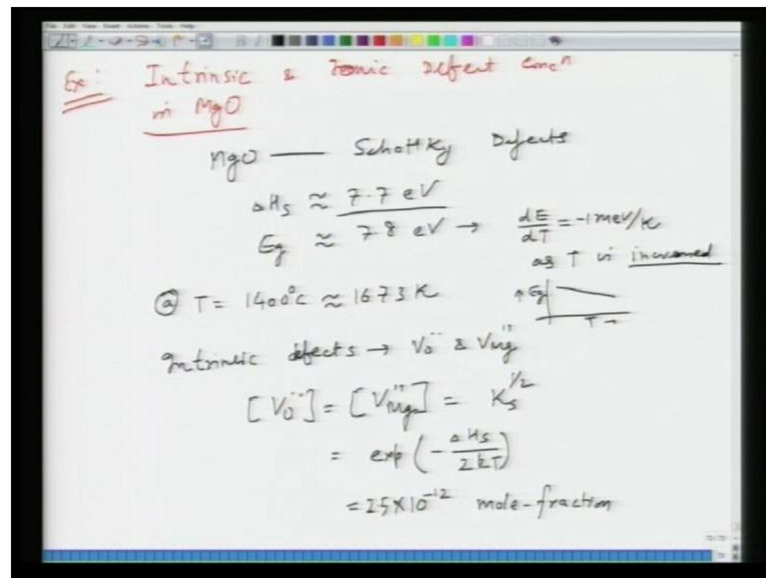

So, what we will see is that because the point here is just to see which one dominates and we will see later on that which one is more likely to be present, in that particular environment. So, this is an example. So, consider. So, M g O as we know has Schottky defects and the defect formation in energy delta H s is about 7.7 electron volt. Since we since, they have Schottky defects it is 7.7 electron volt and the band gap E g is about 7. what we saw earlier is about 7.8 electron volt and this band gap changes as you as you as you increase temperature of M g O. So, this minus of. So, basically your band gap is going to decrease as you increase the temperature.

So, the question is now in an completely pure and stoichiometric magnesium oxide which defects are likely to be created and or who which defects are going to be going to dominate is it ionic or electronic. So, let us say a temperature. So, let us say temperature is equal to about 1400 degree centigrade and that is 1673 kelvin. So, we can write the defect. So, intrinsic defects are V O and V M g. So, concentration of V O is equal to concentration of V M g and this is equal to nothing but your k s this is your Schottky defect Schottky defect reaction to the power half and this is nothing but equal to exponential of we will we are taking it this in mole fraction.

So, exponential of minus delta H s by 2 k T and if you put in the value of delta H s and at this temperature this comes out to about 2.5 multiplied by 10 to the power minus 12 mole fraction. Now, how do you calculate the electron and hole concentration. Just use the formalism that we have used earlier.

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So, we know that n e is equal to n h is equal to k i to the power half which is equal to N c N v to the power half into exponential minus E g by 2 k T right and this would be given as 2 into k T to the power 2 pi h square into M e star into M h star to the power 3 by 4 . So, exponential minus E g by 2 k T. So, what I have done is if you go to previous slides n N c and N v were equal to yeah.

So, what I have done is basically replace the value of N c and N v in those expressions. So, this is how it becomes and in M g O. We know that M e star is equal to 0.38 of M naught or M M e naught and M h star is equal to 0.77 M e naught. Typically effective mass of hole is much more higher as compared to effective mass of electron and what we find is n M e naught is equal to nothing but this particular thing is 9.1 into 10 to power minus 31 k g. So, at the temperature of interest which is at 1673 kelvin. You know that the band gap also changes.

So, you need to cover work out what is the E g. So, E g will be equal to 7. how much was it. So, we have taken 7.8 7.8 minus that difference of 1673 with respect to. So, that that value was given as at. So, basically delta t 1673 minus room temperature multiplied by d E by d T and this would be, this would come out to approximately 6.2 electron volt. This would give you n e is equal to n h is equal to if you replace the value of temperature here take the Boltzmann constant, the Planck's constant M e and M h naught we know what is E g and if to that you get about 4 into 10 to the power 10 per centimeter cube. So, now if you compare these 2 concentrations here it is 4 into 10 to the power 10 to power

10 centimeter cube and in the previous case it was 10 to power minus 12 mole fraction. So, the question now here is how to convert it to say per centimeter cube.

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So, V M g conversion into per centimeter cube. So, basically 2 into 10 to the power minus 12 mole fraction multiplied by you will have to multiply it by density of M g O n grams per c c multiplied by N a which is avogadro number, which is number per mole. This has to be divided by molecular weight of M g O which is gram per mole. So, if we do that this is 2.5 into 10 to the power minus 12 multiplied by density is 3.58 multiplied by N a 6.023 into 10 to power 23 divided by molecular weight of M g O is about 40.3 and this would come out to around 1.4 into 10 to the power 11 per centimeter cube.

So, if you compare these two magnitudes now, here you get 4 into 10 to power 10 and here you get 1.4 into 10 to the power 11. So, at 1400 centigrade if you compare these two energies now, if you if you look at the previous energies. The energy at that particular temperature the defect formation energy 7.7 electron volt and the band gap is about 6.2 electron volt. So, there is a difference of 1.5 electron volt, but still the defect concentration in M g O is Schottky defects concentration is much larger is an order of magnitude about a larger as compared to electronic concentration. So, you can see that at a particular given temperature which defects will dominate using this enough analysis.

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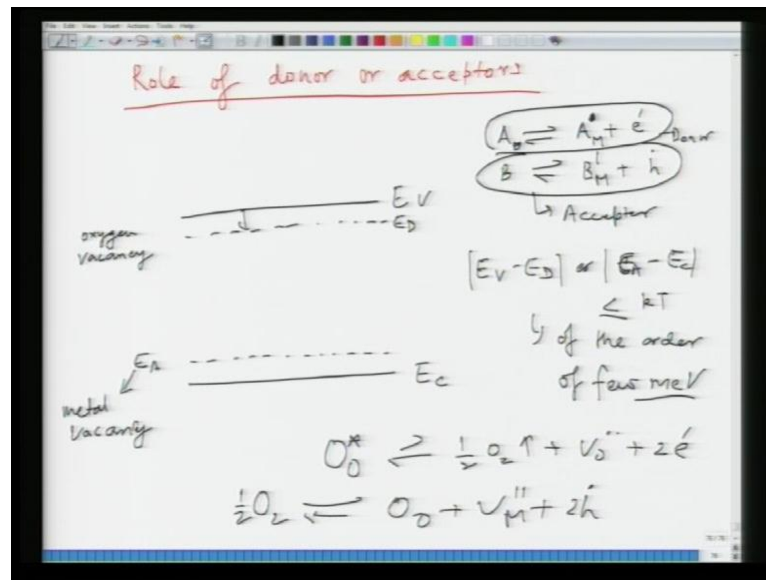

So, another thing that you would like to see is the role of impurities, role of donors or acceptors. Now when I make a band gap like this is your E c this is your E v, I said that in a semiconductor when you put an impurity. So, an impurity which let us say A you put and if it becomes . So, A star let us say A or B So, A dot and it goes to let us let us say M side and if you put B, B goes to M side if it gets reduced gives rise to a hole.

So, this kind of impurity will be a donor impurity and this kind of impurity would be an acceptor impurity because it creates an hole. So, the typically the acceptor level is very close to as I just explained in the previous slide. this is your E A and this is your E D and the E v minus E D or E A minus E c are equivalent to or smaller than k T. So, basically of the order of few M e v's in a typical semiconductor. Now, in case of for example, in case of oxides if you form oxygen vacancies for example, O O goes out it gives rise to half O 2 which goes out gives rise to oxygen vacancy gives rise to 2 electrons. So, here formation of oxygen vacancy has given rise to 2 electrons, which means oxygen vacancy acts as a donor impurity.

So, the this would be in an oxide for example, oxygen vacancy and acceptor would be your for example, metal vacancy. So, if you have if you have this reaction, then this would be metal vacancy. Similarly your oxygen interstitial would go at this side. So, acceptor levels would be typically metal vacancies and it or cation vacancies anion anion interstitials and donor level would be your anion vacancy and cation interstitials. The difference in energy would depend upon the fact that, how much what is the level of

ionization of these impurities or these defects? Whether they are singly ionized completely ionized or neutral and this would determine their basically level of typically what you will find is that that as the ionization increases the energy also the difference in the energy also increases. So, although we have taken most of the cases in our module as completely charged charged impurities and the defects may not defects or impurities may not be completely ionized.

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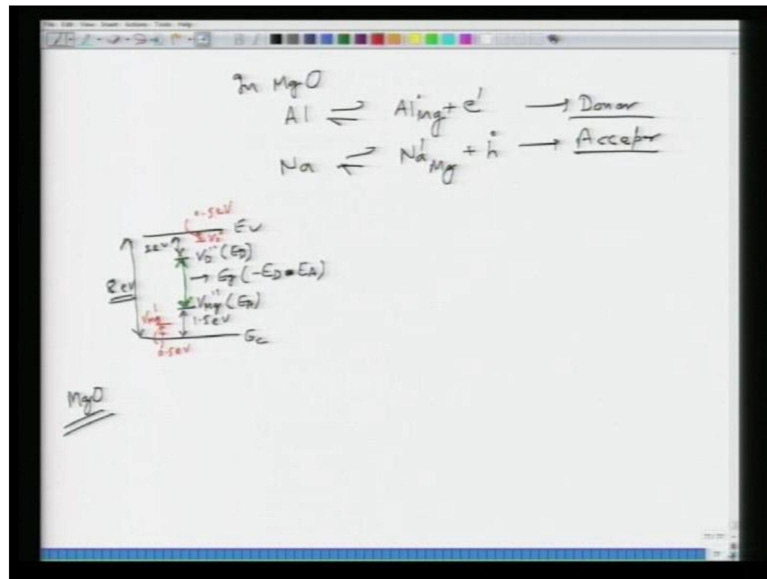

In case of impurity, if you take for example, in M g O aluminum if you are putting aluminum then aluminum goes to magnesium side, this would be positively charged. So, donor and if you put sodium sodium at magnesium side, this would be negatively charged giving rise to a hole. So, this would be acceptor. Now, the depending upon type of inbuilt defects are created level of their ionization, these energies the difference that that donor and acceptor the distance of donor and acceptor levels with respect to conduction and valence band edge would change. So, for instance in case of M g O. So, this is your E c this is your E v in case of in case of M g O.

So, if your V M g dash dash is about 1.5 electron volt. So, this is E A and your this is your V O E D and this is about 2 electrons volts and you know that in case of M g O the band gap is about roughly, let us say 8 electron volt about 7.8 or 7.9 electron volt and depends upon the temperature as well. So, this would be your E g minus E D plus E g minus E D minus E A and if you if. So, here we are talking of. So, if you if you talk about V o x then this would be much more smaller about half electron volt. If you take

singly ionized magnesium vacancy this would be roughly 0.5 electron volt. So, depending upon the level of ionization this, the difference in the energy levels would change and similarly, if you put aluminum and sodium they would also introduce their energy levels respectively at various places.

So, finally, we will just cone to final topic now, and final topic is just to consider electronic and ionic compensation of solutes. So, for example, you take the, which one is more preferable.

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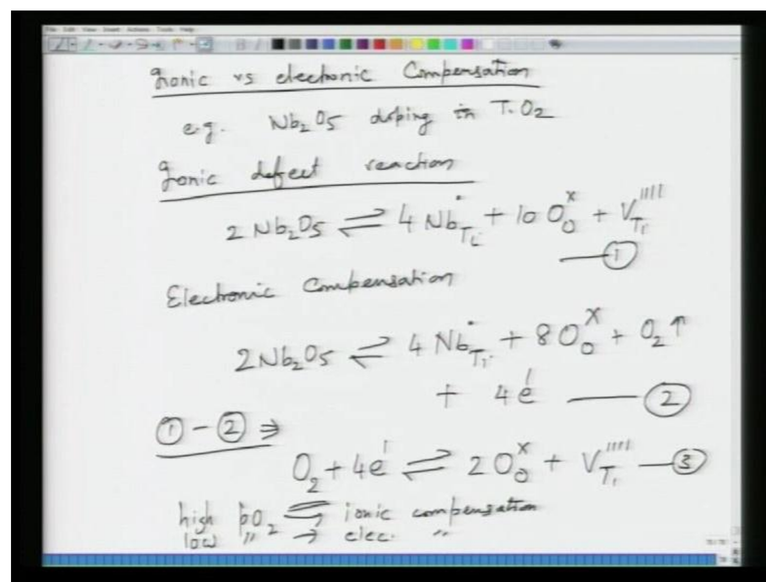

So, example we take of. So, ionic versus electronic compensation. So, example we take is N b 2 O 5 doping in T i O 2. So, what is the defect reaction the ionic defect reaction would be. So, ionic defect reaction means, no electronic defects is clear and defects are created. So, which means something is going to happen at cations side. So, you put 2 N b 2 O 5 I am going to write balance defect reaction. So, all those 4 niobiums goes to titanium side, which means niobium is plus 5 titanium is plus 4. So, it is going to carry 1 positive charge plus all the oxygen's go to oxygen side. So, now, there is a problem here. Since all the 10 oxygen go to that oxygen sides, but only 4 niobium goes to titanium side whereas, stoichiometric requires 1 cation side for 2 anion sides, which means I create a vacancy of titanium, which would be 4 charged minus 4 charged.

So, this would be the side balance. So, in order to compensate for 2 extra oxygen's which are coming as a result of N b 2 O 5 you need to create 1 extra vacancy of titanium. So,

this is your ionic defect reaction. Now, electronic compensation. So, I can again write 2 N b 2 O 5 again all the 4 niobium's are going to titanium side oops. So, we must take plus 8 O O x plus O 2 which means for 4 titanium sides I taken only 8 oxygens, rest of the oxygens go out, but now I have to balance the charge. So, which means I have to create 4 electrons.

So, this is. So, let us say this is reaction 1 and this is reaction 2. So, if I now subtract the reaction 2 from reaction 1 then, what I get is N b 2 N b 2 O 5 cancel each other and N b T i N b T i will cancel each other, what I will have is O 2 plus 4 e. So, 1 minus 2 gives rise to O 2 plus 4 e 2 O O x plus V T i. So, what this tells you is that, as you increase the partial pressure of oxygen the reaction will move into forward direction. Which means at higher at higher partial pressure of oxygen, your formation of titanium vacancies is going to be preferred. Similarly, if you have lower pressure of oxygens, the reaction will push into the backward reaction which means electron electronic compensation is going to be favored at. So, high p O 2 you have ionic compensation. This is obvious from this reaction and low p O 2 will give rise to electronic compensation. So, this is pretty clear from this reaction.

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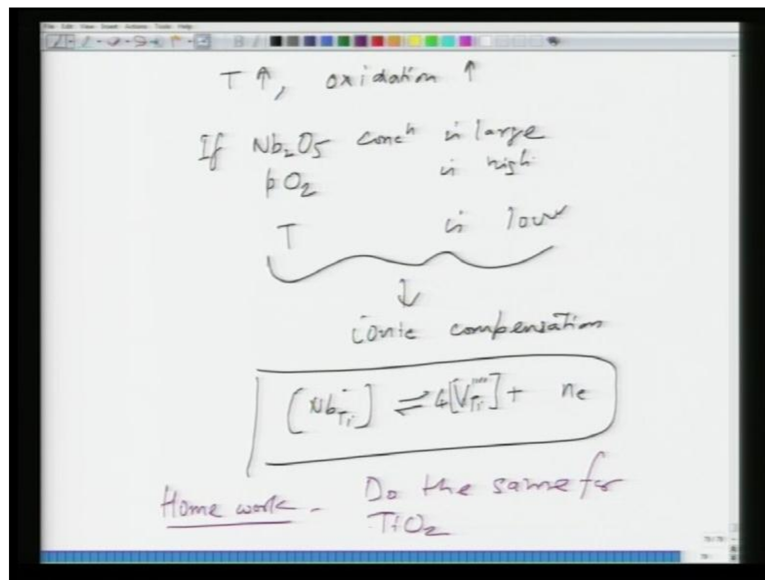

Now, similarly as you increase the as you as you decrease the temperature oxidation is again favored. So, so temperature increases means oxidation increases. So, as you increase the oxidation, then again formation of titanium we can see it is favoured. So, you basically put in the more oxygen in to the system. So, as now we can see. So, so N b

basically. So, you can create conditions like if N b 2 O 5 concentration is large p O 2 is high and temperature is low all these conditions prefer ionic compensation and converse is true in case of electronic compensation.

In any case you have to follow the electrical neutrality condition. The electrical neutrality condition would be N b T I, 4 V T i plus hang on just a second let me just see the, what the reactions are. So, I have here N b T i equal to electron N b T N b T i is equal to 4 of N b T i. So, N b T i is equal to N b T i is equal to 4 of b T i right. So, I will have N b T i will be equal to 4 of b T i plus n e because you have four times. So, in case of ionic compensation it is four times of vacancy concentration, in case of electronic compensation its equal. Similar effects you can see in oxides such as barium titanium etc. I can give you an home question, to work out for example, you can do the same exercise for material like titanium oxide. So, home work can be do the same for T i O 2 and for this you can refer the books which I have subscribed in the bibliography related to.

Similarly, same is true about calcium oxide doping in zirconium oxide again you can have a electronic compensation or the ionic compensation. So, I can, I will leave it to you to work out the defect reactions. What happens when you when you dope zirconia with calcia or atria. By this time we should be pretty much familiar with how the defect reactions are written and the one thing which I want to point out is that when you when you put all these dopants for example, into the host lattice they give rise to a change in the volume.

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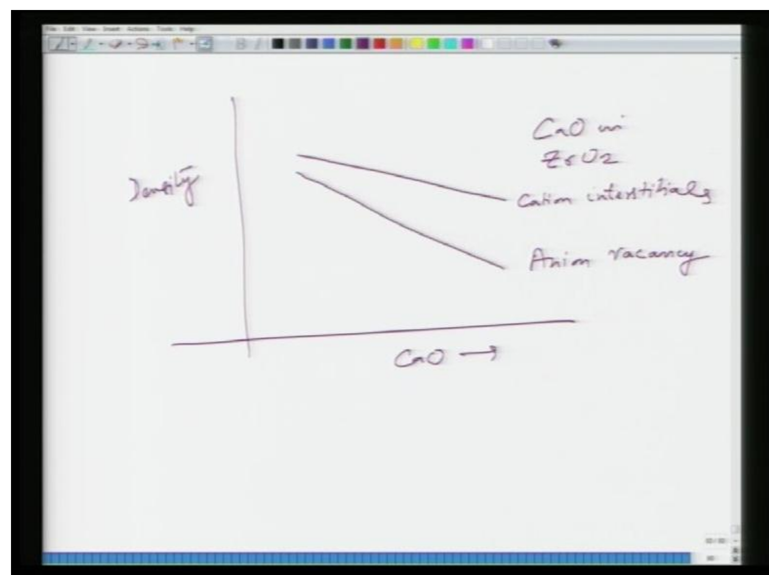

So, for example, when you dope zirconium oxide. So, C a O in Z r O 2. So, the density of these materials also changes at appreciable large concentration. So, when you put if cation interstitials are present it is like this, but if anion vacancy is present. So, depending upon what kind of defect you have, you will have difference in the level of reduction, but the volume changes are observed and as a result you have a volume or mass changes you can say, as a result you have changes in the densities. So, basically densities is the parameter which takes mass and volume both into account. So, level of type of defect would decide, the change magnitude of change, but you have a change in the density when you start doping the material.

If you want to go into details of these things you should go to the case studies given in the books, but as you can. So, what we have discussed in this module is, basically we have taken the defect equilibria. First of all we started with the defect how the defects are formed, what are the various defect reactions, how we can treat these defect reactions as chemical reaction the basis for that and then and we also worked out how the equilibrium concentration at fixed is calculated, what happens when you put impurities inside a particular material and then we looked at the conditions, the concentrations of defects at various partial pressures of oxygen by creating the limiting conditions in high and low pressure range and created an equilibrium diagram. Finally, we took some cases studies just to see what kind of defects dominate in which kind of material.

So, I hope this gives you a fair idea about the second module which would be instrumental in going to the third module, which is about now more applied in the sense that now, you now. We know about the defects what sort of defects are going to form what we will see in the next module is how these defects move and what sort of properties they give rise in ionic solids.

Thank you.