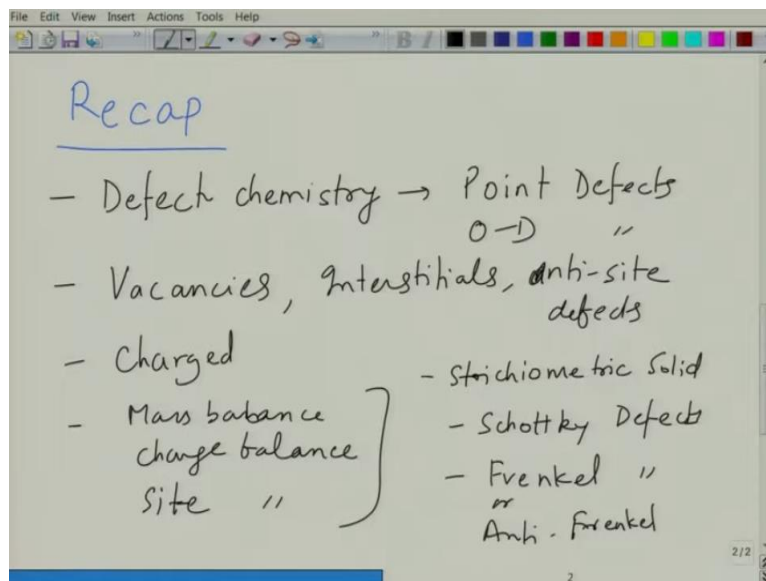


Fundamentals and Applications of Dielectric Ceramics
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Lecture No 09
Defect Chemistry: Non-stoichiometric oxides

So, welcome again to this new lecture of the course, Fundamentals and Applications of Dielectric Ceramics. So, we will just do a brief recap of previous lecture.

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So in the last lecture, we learnt, we started our discussion on defect chemistry and this defect chemistry basically deals with point defects, it does not deal with dislocations or surface defects, just with point defects, which are also called as zero dimensional defects. And there are various defects, that can exist in the material, so you can have vacancies, vacancies of metals and cations and anions, then you can have interstitials, you can have anti-site defects, and so on and so forth.

And these defects are also, if they are completely ionized, these defects are also charged. So depending upon the nature of defect, whether it is oxygen vacancy, metal vacancy, oxygen interstitial, metal interstitial, it could be positively or negatively charged and we will assume complete ionization of all these defects. And then we looked at the conditions or writing defect reactions, so you have to have mass balance, charge balance, and site balance.

So all these balances have to be obeyed while writing the defect reactions, which means you

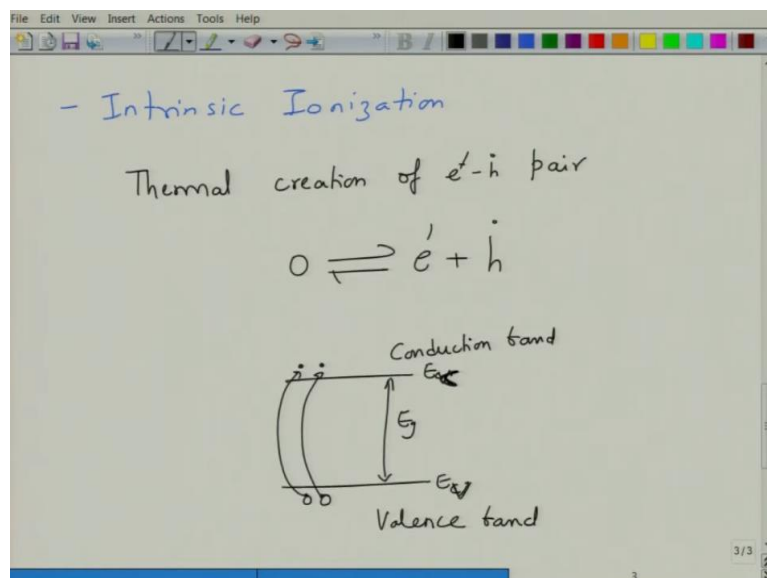
should not have any dis-balance in mass transfer, you should not have any imbalance in charges, solid has to be charged neutral, so as a result, all the positive charges must be equal to negative and sites must be conserved, which means if you have a host structure MO, then number of M sites and O sites depending upon the stoichiometry will always remain conserved.

So the conservation of mass, charge, and site is important to write defect reactions and then we looked at the defects in stoichiometric solids. And we started with Schottky defect, which does not change the stoichiometry of the material, so which means for oxide MO, you form one vacancy of oxygen and one vacancy of metal, so stoichiometry is not disturbed and number of vacancies of metal are equal to number of vacancies of oxygen for MO, but it could be different for M_2O_3 , MO_2 , M_2O_5 .

And basically, number of vacancies you form will be determined by the charges of the valences of cations and anions. And then we look that Frenkel defects, which is again a stoichiometric defect, Frenkel or anti-Frenkel. And Frenkel defect was formation of vacancy and interstitial. So, it could happen with both cations and anions. If it happens with cations, it is Frenkel defect, if it happens with anions, it is anti-Frenkel defect.

Both of these defects do not lead to change in the stoichiometry of solids.

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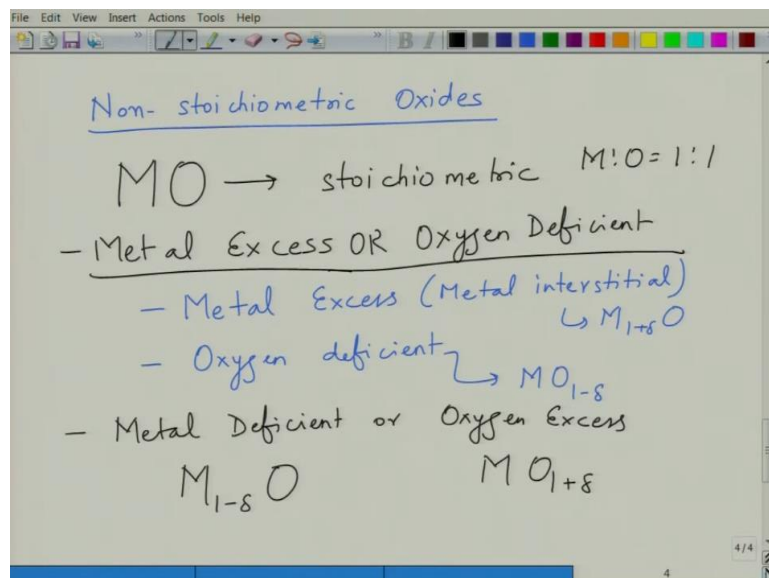
And the third thing that we wanted to introduce, we wanted to talk about is, intrinsic ionization, which means formation of electron in hole pairs and so basically it is thermal creation of electron hole pair. So, basically it is written as electron plus hole. So, essentially, it is nothing

but, you have a solid, which is, oxides are generally semiconductors in nature, semiconductor insulators, so as a result they have a band gap, this is the band gap, this is the valence band edge, this is the conduction band edge.

So, the temperature can excite these electrons from valence to conduction band, sorry, this is E_c and this is E_v . So, this is conduction band and this is valence band. So, excitation of electrons from valence to conduction band causes formation of holes in the valence band and electrons in the conduction band. This is nothing but thermally created electron hole pairs, which are created in any solid depending upon the temperature.

So, these are the three methods which do not change the stoichiometry of materials, but oxides are not only, they not only consists of these defects, but there are several instances where you will see oxides are non-stoichiometric.

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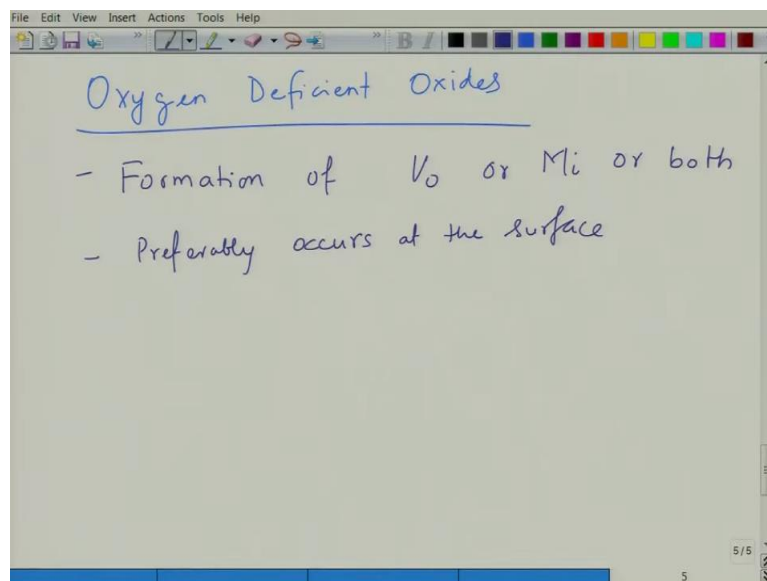
So, we look at the cases of non-stoichiometric oxides now. So, non-stoichiometric oxides, so we will start with MO, but you can have any oxide. So, if you have MO, MO is stoichiometric, right. The M:O ratio is 1:1. What happens when you have little bit of extra of M or a little bit of extra of O. So, there are two cases; one case is metal excess. When you have metal excess, then what it may mean is that you may have either metal excess in the form of metal interstitial.

And what it may also mean is that it is deficient in oxygen deficient. So, in this case you may have $M_{1-\delta}O$, where delta is very small, it could be 0.01, 0.1, or 0.001 and oxygen deficient would mean $MO_{1-\delta}$. So, these are the two possibilities that may exist, you may call them metal

excess or oxygen deficient, alright. Second case is that of metal deficient or oxygen excess and this case will mean that we have $M_{1-\delta}O$ or $MO_{1+\delta}$.

So, now, what is going to be prevailing depends upon various conditions, it depends upon temperature, it depends upon partial pressure of oxygen, it depends upon the thermodynamics. So, there are a lot of factors which determine inherently what would be the nature of material and most importantly, it is governed by the conditions under which they exist. So, we will see the effect of some of those conditions on the evolution of these defects.

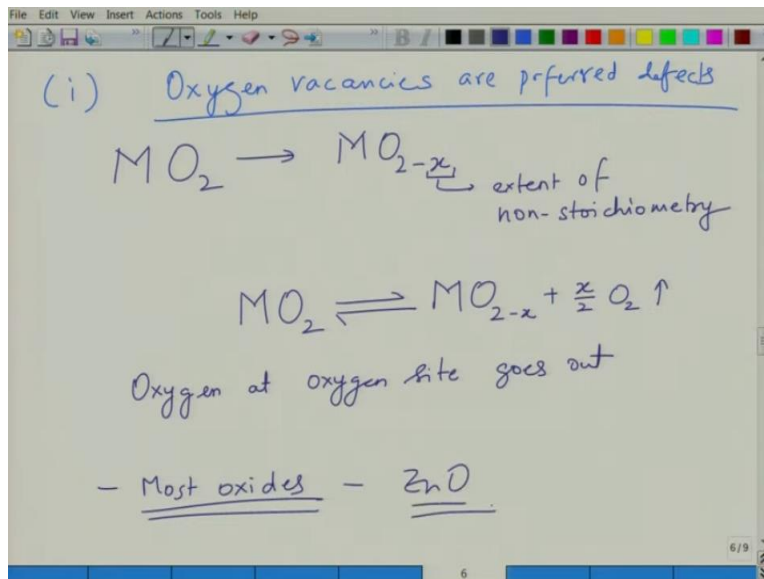
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So, again, you have to ensure that electrical neutrality is preserved, mass balance is there and site balance is there. So, all these three conditions have to be obeyed when this happens. So, let us first look at the cases of oxygen deficient oxides and we start with oxygen deficient oxides because oxygen deficiency is one of the most common scenarios in most oxides. And basically oxygen deficient oxides means you may have formation of either V_O or you can formation of M_i or both, there is a possibility that both might occur, okay.

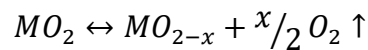
Because both of them represent the same scenario. So, there is a possibility that both might coexist and this is a very realistic scenario. And since the vacancies have to be formed, generally this is preferably happens on the surface. Because if the vacancies have to be formed, which means oxygen has to diffuse out of system and diffusing from inside is more difficult than from outside and that is why formation of vacancies is preferable on the surface than in the interior.

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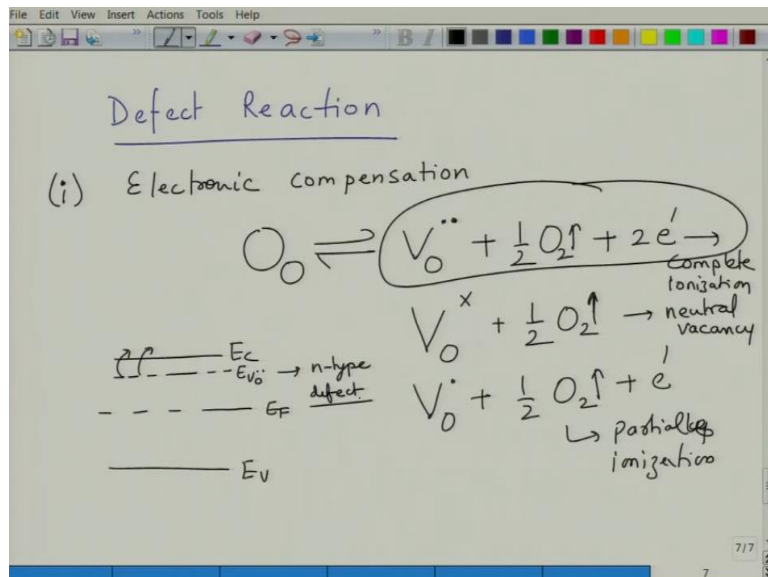
So, let us say first scenario where we say oxygen vacancies are preferred defects, okay. So, let us say for a change, a different material, let us say we start with oxides called as MO_2 and this MO_2 can be written as MO_{2-x} or δ whatever you can write, where this x is the extent of non-stoichiometry, okay. So, the defect reactions is written in this way. So, you write it as, MO_2 and these are all thermodynamic reactions, reversible defect reactions.

So, this is written as



So, basically MO_2 converts to MO_{2-x} releasing some of the oxygen outside in the ambient. So, now, when this reaction happens, what must happen, you have formed MO_{2-x} , which means, there was some oxygen at oxygen site goes out. So, what happens to charge balance and site balance and mass balance?

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So, the defect reaction then you write as, defect reaction is written as, there are various possibilities, the first possibility is electronic compensation and the electronic compensation is written as oxygen at oxygen site goes out giving rise to vacancy of oxygen, which means the sites are preserved, the site which was filled earlier is preserved. We have created one vacancy of oxygen. What about the mass balance?

Mass balance is not preserved as yet, because we have to account for this oxygen, this oxygen goes out, half O₂. Now, the mass is also preserved, but the charge is imbalance because these are two positive charges, which means you need to create two electrons in order to have the charge balance, okay. This is what basically means ionization of oxygen vacancies. If the vacancy was not ionized, you can write this reaction, if it was let us say not ionized, you can just write this reaction as V_O^{\times} not star.

Generally it is written as cross plus half O₂. Now, there is no charge problem, right. But vacancy is not ionized, but if the vacancy is ionized, which is determined by conditions such as temperature etc., then you would write the top reaction. There is a possibility that vacancy is also singly ionized, vacancy is not completely ionized, then you would have to write this in this fashion +1 electron. So, this is for complete ionization.

This is for neutral vacancy and this is for partially ionized vacancy. But in general, partial ionization, okay. But in general, we will consider this as the most plausible scenario, okay. Oh sorry, yeah O₂, yeah in this case O₂. So, these are the possible defect reactions, so you can see now, you have site balance, we have not created an extra site or we have not lost any site. So, site of oxygen is now preserved by vacant site, mass is preserved, the oxygen which was

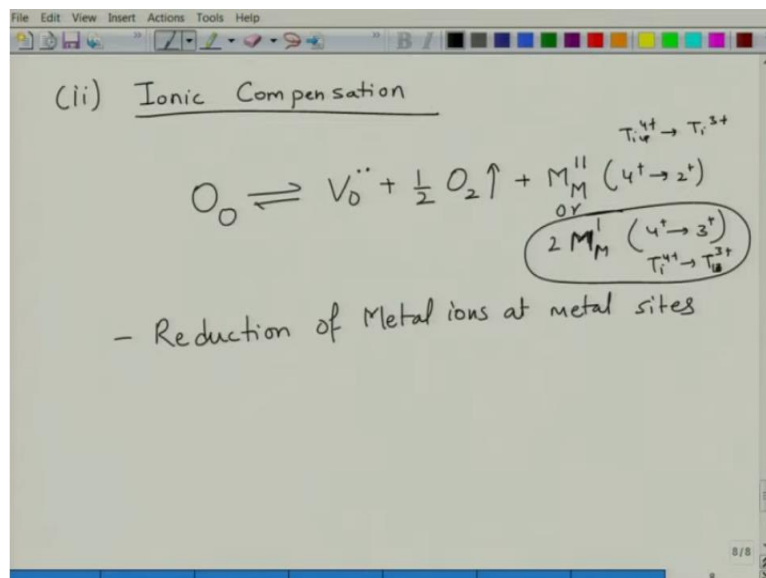
present at oxygen site has gone out of system.

So, we account for the masses, however, the vacancy which is created is positively charged. As a general rule, the metal vacancies are negatively charged and oxygen vacancies are positively charged. Metal interstitials are positively charged and oxygen interstitials are negatively charged. So, to account for the charges created at the vacant site, you need to create two free electrons in the system.

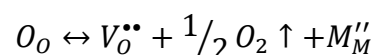
Energetically, you can represent this as, so basically, so this is E_c , this is E_v , this is Fermi level of oxide, this is very much like creating a n-type defect, right. In silicon when you add phosphorus you create an electron, extra electron. So, here we are creating extra electron by creating oxygen vacancies, so for oxide MO, vacancy of oxygen will create this E, I do not know, how do you write it, E_{V_o} let us say, the energy level with respect to oxygen vacant sites, which will donate electrons to conduction band.

That is how some of the oxides, which are otherwise wideband gap semiconductors turn to become semiconductors or metals because there are a lot of vacancies, which are present in them. And they donate sufficient number of electrons to the conduction band making them electrically conducting, okay, even though they are oxides with large band gap. So, basically you can say it is an n-type defect, okay.

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Second scenario that may prevail is the following, second scenario that may prevail is called as ionic compensation.



So, in this case, you do not form electrons, rather the oxygen and oxygen site goes out, giving

rise to vacancy of oxygen plus half O₂. Now, what may form is you may have oxidation or reduction of metal site depending upon the charges. So, here you have created two charges on the oxygen sites, which means metal at the metal site will reduce.

So, it will have two negative charges, okay, or there is a possibility you might have to 2M_M dash, the two metal ions will reduce, so in this case we had taken an example of MO₂, so 4+ will become 2+ or 4+ will become 3+, okay. So, for example, it was titanium, titanium will become Ti⁴⁺ + 2, Ti³⁺ and here Ti⁴⁺ will become Ti³⁺. It will depend upon what kind of valences are more stable. So, generally this will be preferred over the first one because Ti²⁺ is an unstable form of Ti more unstable.

As a result Ti⁴⁺ to Ti³⁺ is more plausible as compared to Ti²⁺. So the bottom ones, so basically what you form here is vacancy of oxygen plus the oxygen that goes out, plus two metal sites which have now reduced from higher to lower valence to accommodate the charge imbalance that is created. So, this is called an ionic compensation. So, basically here what happens is reduction of metal ion at metal sites, okay.

So, these are the two possible scenarios which happen, one is electronic compensation, second is the ionic compensation. Now, let us say if first scenario that we have taken is the oxygen vacancy are the preferred defects, so, here I can write A and here I can write B.

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(ii) Metal Interstitials dominate
 $M_{1+\delta}O_2$

(a) Ionic Compensation
 $MO_2 \rightleftharpoons M_i^{\dots} + (4 M_M^{\prime}) + O_2 \uparrow$

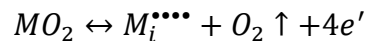
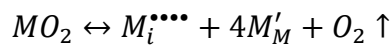
(b) Electronic Compensation
 $MO_2 \rightleftharpoons M_i^{\dots} + O_2 \uparrow + 4e^{\prime}$

Band diagram showing energy levels E_c , E_v , and E_m with arrows indicating electron transitions.

Materials listed: TiO₂, ZrO₂, CeO₂, Nb₂O₅

And now the second case is metal interstitial dominate. If that is the case, what will happen? So, in this case, generally we depict the oxide as M_{1+δ}O₂, okay. So this is the defect reaction,

where delta is the extent of non-stoichiometry. Defect reaction you can write,



so now that you understand how to write the defect reaction, the first is you can say ionic compensation and the ionic compensation is basically M_M metal at metal site going to $M_i + 4 M_M$.

So, the metal at metal site goes to the interstitial site and this forms the, sorry no, not the metal from metal site, it is the metal which comes from, it is the metal excess, so metal excess will mean you are putting in more metal. So, you are putting in more metal. So, you do not want to disturb the site ratio, which means M versus O is to be 1:2, okay. So, I cannot convert a metal at metal site into M_i , otherwise I will have to create a vacancy of metal, okay.

So, metal from outside will basically, so you can say MO_2 , so metal goes to metal site, metal goes to metal interstitial and the oxygen basically goes out. So, you do not create or disturb any site. MO_2 comes from outside, metal goes to metal interstitial, does not disturb the site balance. As a result, oxygen goes out, so no site is created, no site is lost, but to accommodate for the four valences, positive valences, you need to create four negative valences, which are in terms of reduction of four metal ions, okay.

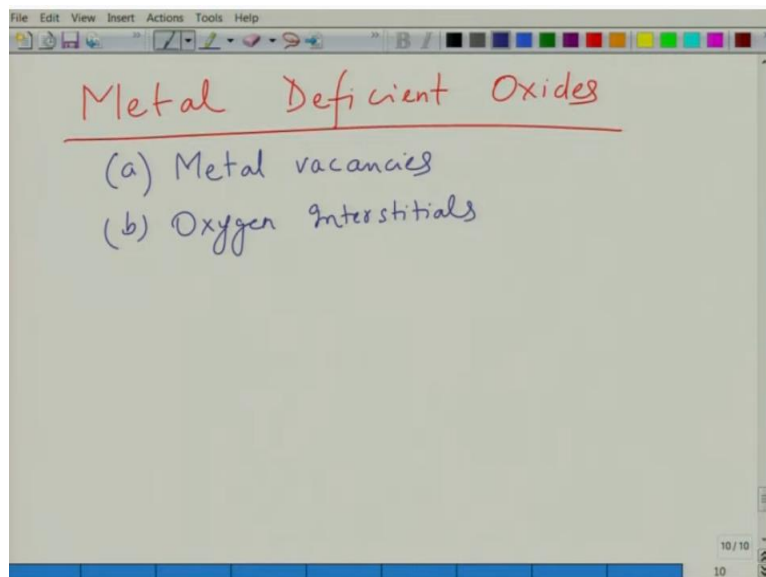
So, one molecule of MO_2 , out of one molecule, the metal goes to metal interstitial site, the oxygen goes out thereby not creating any extra sites. So, which means site conservation is not there, but you have extra metal in the form of interstitial, not in the form of site, okay. And then site means the host site. So, we have not created any host sites, which means M:O = 1:2, it is preserved. So, we preserve the sites, we preserve the masses, and we preserve the charges. So, this is ionic compensation.

Then we write electronic compensation reaction, electronic compensation will mean formation of, so you will have MO_2 , okay. M goes to interstitial site, oxygen goes out and you create four electrons. Again, it is n-type defect, just like phosphorus and silicon. So this is phosphorus and silicon basically, but in phosphorus and silicon, phosphorus goes to substitutions site, not on the interstitial site, so basically it is not a $M_{1+}O_2$ type of defect, it is just, you are replacing silicon with phosphorus.

Here, you are pushing in extra metal, okay. So, the energetics is going to be again similar, this is conduction band, this is valence band and this Fermi level, somewhere here and you are going to have this E_{Mi} somewhere here, electrons are going to be pushed into the conduction band. So, it again is a n-type defect, creating extra electrons, alright. So, now, so, this is basically the possible scenarios and this happens in materials such as, you know, TiO_2 , ZrO_2 , CeO_2 , Nb_2O_5 , these are some examples in which this kind of thing happens.

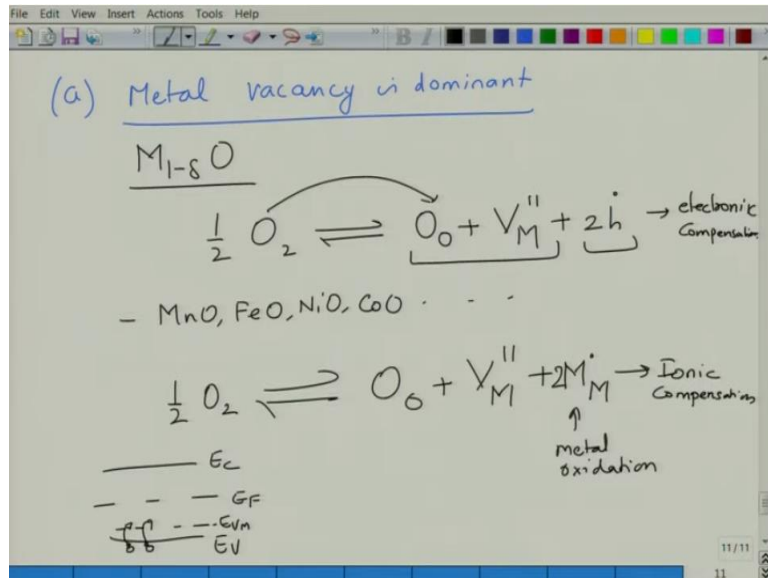
And oxygen defects are formed in many oxides, I mean, there are so if you look at the previous case, where oxygen vacancies are dominated, it happens in nearly most oxides show this kind of behavior. Oxides are generally oxygen deficient in nature as a result. So, for example, zinc oxide one of the famous example of its oxygen deficient, okay. Now, so, what we have seen is, we have seen the case of metal excess or oxygen deficiency.

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Similarly, you can have cases of, the other case that is, which is that of metal deficiency. So, second case is of metal, again metal deficient oxides can be divided in two cases also. So, the first could be metal vacancies and second could be oxygen interstitials, okay. So, again we will not go into similar details, but now I am sure you can write the defect reaction.

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So, if you write for the first case, let us say the first case is metal vacancy is dominant. If metal vacancy is dominant, then you can write the oxide as 1 – delta O, okay. So, this is the form of oxygen and the defect reaction would be oxygen comes from outside, oxygen goes to oxygen site, but you only bring in oxygen, which means, you need to create a site to maintain the site balance. So, if we have MO, which means the metal site is vacant, as a result we create two holes.

So, this is the donor kind of defect, the vacancy of metal is a donor kind of defect. So, we have maintained the mass balance, mass balance is one oxygen comes from outside, goes to oxygen site, this is mass balance, site balance is maintained by maintaining the ratio, one site of metal, one site of oxygen, the ratio is 1:1. It is just that one side of metal is vacant, but there are two sites; one for metal, one for oxygen and we have created holes to balance the electrons and electrical neutrality, alright.

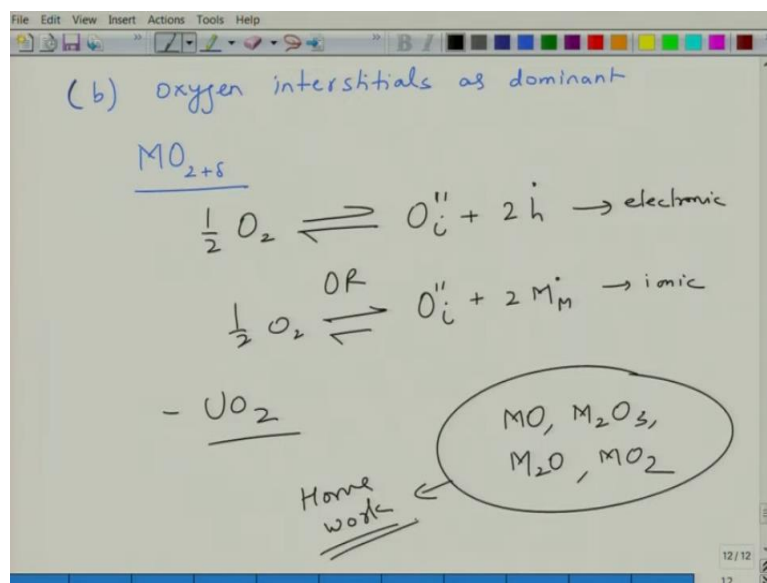
So, this is the scenario to create holes and this is something which happens in materials like MnO, FeO, NiO, CoO many of the systems are p-type oxides, so these are basically p-type oxides, which have hole dominance. Now, another example that may happen is, so similarly you can create, so this will be electronic compensation, right. What will be ionic compensation? So ionic compensation let me write partially and then I will tell you what should, you have to tell me what will happen, what will happen?

If you do not want to form holes, if the hole formation is not conducive, what will happen? Metal will oxidize, right. The metal at metal site will oxidize. So, two metals at metal sites

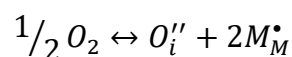
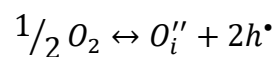
will oxidize and this is true in iron, iron is +2, it can easily become +3, manganese is +2, it can become +3. So, generally happens in oxides, the valence fluctuations are possible in those materials which are transition metal oxides, right, transitional metals, because you have multiple valences which are possible. So, this is ionic compensation, where you have metal oxidation, right, okay.

So, this defect, especially the electronic composition can be again represented in this form. So, it is a p-type defect, so you will form this E_{VM} somewhere here and the electrons will be transferred from here to here, leaving holes, okay. So, this is what will make a p-type oxide.

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So, now, the last scenario is electronic metal deficiency is dominant, if oxygen interstitials are dominant. So, in the first case we took metal vacancy is dominant, in the second case we take oxygen interstitials as dominant, then the oxide is depicted as $MO_{2+\delta}$, this is the form and the oxygen interstitial basically half O_2 . So, oxygen does not go to oxygen site, rather oxygen go to interstitial site. So this will be negatively charged, we do not create any extra site, so no metal vacancy has to be formed.



So, instead it will be $O_i'' + 2h^+$ or you can have similar reaction half O_2 , where you go O_i'' and two metal at metal sites will oxidize. So, this is electronic, the first one is electronic and this

is ionic. And this happens in materials such as UO_2 , thorium oxide and similar kind of materials, okay. So, I would like you to do these exercises for these two defects on MO type of materials, on M_2O_3 kind of materials, M_2O and MO_2 . So, just write the defect reactions for, so this is homework for you, okay.

So just practice this. Imagine both the scenarios of electronic and ionic compensations and write the defect reactions for both oxygen deficiency and metal deficiency, oxygen excess and metal excess. So, we will stop here today. We will move on to next lecture and we will see more about defect chemistry in the next one, okay. Thank you.