# Electroceramics
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## Lecture - 5

So, in this lecture, we will talk about a completely different topic. In the previous lectures, we discussed on structures of ceramics, what are the fundamental basis on which ceramics structures are formed and we discussed various type of ceramic structures like FCC based structures, HCP based structures and other structures, such as cubic packing of an ions etcetera. In this lecture, we will start with defect chemistry of these ceramic materials. Now, defect chemistry is very important from the point of view of properties, because none of these ceramics are perfect in nature. That is they contain defects which are equilibrium in nature, which are thermodynamically stable. We need to understand how these defects are formed and under what conditions, what kind of defects are stable, which would help us in understanding the property evolution in these ceramics.

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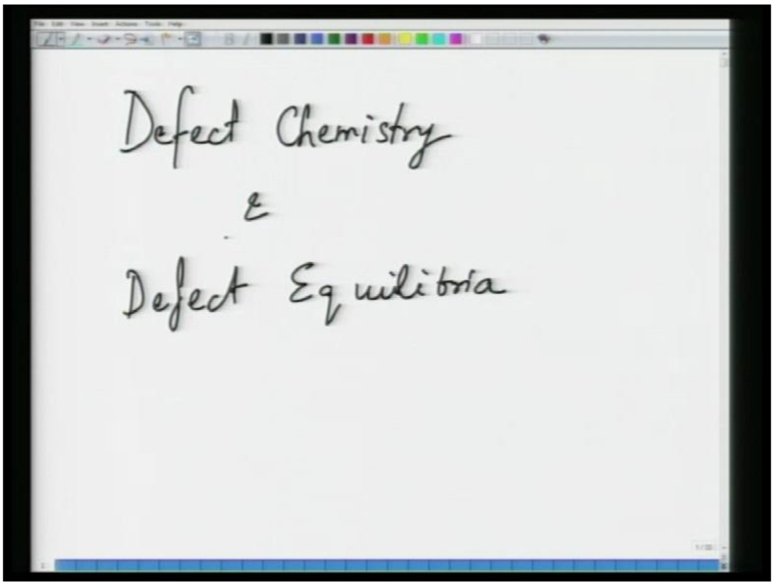

Defect Chemistry
&
Defect Equilibria

So, the first topic, so, the name of this module, I would put it as, so first we will look at defect chemistry followed by defect equilibria. So, these are the two topics that we will discuss in this module. Defect chemistry deals with thermodynamics of defect formation as well as defects, the various kinds of defects etcetera. Defect equilibrium is under various conditions of atmosphere etcetera, what kinds of defects are stable under the equilibrium. So, this also talks about thermodynamics.

So, to begin with the various kind of defects that are available, that are present in ceramic materials or other materials as well, you can have this locations which are one dimensional defects, you can have n boundaries, and you can have various other kinds of surfaces, twins etcetera. But here, we are mainly concerned with defects which are point defects, which are 0 dimensional defects and which are also called, which are basically vacancies or interstitials. Now, in contrast to metals, the vacancy or interstitials, since ionic solids or ceramics are entities which contain charges, since because since you have presence of oppositely charged ions, as a result to maintain the stoichiometry as well as charged neutrality, these defects tend to be charged and which makes them pretty special.

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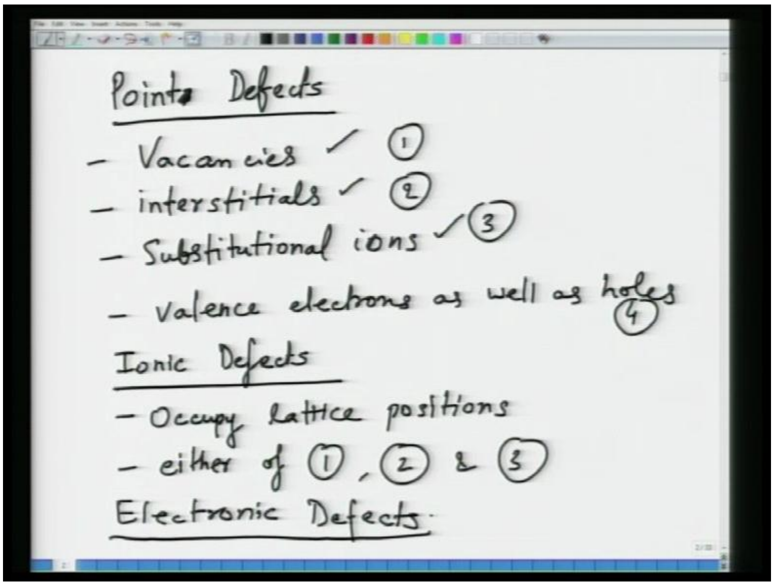

Point Defects

- Vacancies ✓ ①
- interstitials ✓ ②
- Substitutional ions ✓ ③
- valence electrons as well as holes ④

Ionic Defects

- Occupy lattice positions
- either of ①, ② & ③

Electronic Defects

So basically, we are interested in learning about point defects and these defects are basically deviation from the perfect atomic arrangement in a perfect solid. These can be called as you know vacancies, which are atoms or atoms is missing from their positions, it could be interstitials. Interstitials are typically foreign atom or it could be a host atom sitting inside an interstitial site. You know what interstitials site is after a discussion in lecture 1 module 1. It could be substitutional ions. So, you have an impurity, which substitutes for the host atom. You can have presence of valence electrons as well as holes.

So, all these make point defects, which are interesting from the point of view of property determination in these solids. Point defects in metals tend to be electrically neutral, simply because you have only one kind of atom present there. Whereas, in ceramics, which are typically ionic materials these tend to be neutral electrically charged. So, we can define further point defects into two categories. First category could be ionic defects. In terms of ionic defects, these are the ones which occupy lattice positions, which are the regular positions. They can be either of either this or that or that. So, if I say number 1, number 2, number 3 and number 4. Then either of 1, 2, and 3 and you can have electronic defects. These are basically created due to deviation from the ground state electron orbit configuration. So these, typically you can think of, since these ionic solid have a band gap, as we will see later on, since these are their band gap is above in most cases 2 electron volt, 2.5 electron volt, the electrons from the valence band get exited into the connection band due to either thermal means or any other means, which means this prescribes to creation of electron in whole pairs.

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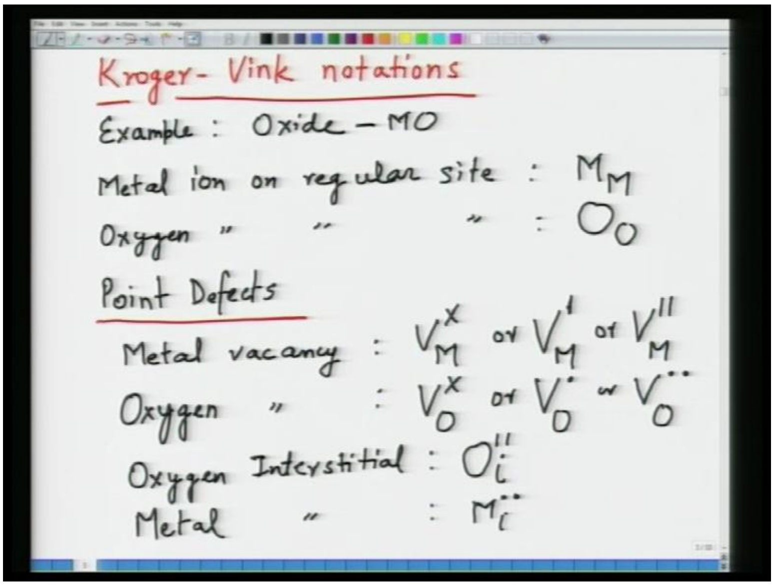

Kroger- Vink notations

Example : Oxide – MO

Metal ion on regular site : $M_M$

Oxygen " " " : $O_O$

Point Defects

Metal vacancy : $V_M^x$ or $V_M^{'}$ or $V_M^{''}$

Oxygen " : $V_O^x$ or $V_O^{\bullet}$ or $V_O^{\bullet\bullet}$

Oxygen Interstitial : $O_i^{''}$

Metal " : $M_i^{\bullet\bullet}$

So now, we will look at first some of the conventions. The conventions for, since the defects are charged, there are certain conventions and these conventions are known as, we define them as Kroger Vink notations. So, let us say example is an oxide MO. So, where metal is a bivalent cation. So, if you have, so, metal ion regular site, it is known as M subscript m. So, this is how a regular metal ion will be. Similarly, oxygen ion on regular site will be given as O o. Or, if you had a cation X, anion X, then it would be X

X. Then you have host of these point defects. So, for example, a metal vacancy is represented as V M and if it is, so, if you have a neutral vacancy, the vacancy which does not contain any charge, it will be V M X. If it is charged, then it would be V M dash or if it is completely charged, as in case of a metal oxide, the divalent metal cation would be maximum negatively charged with two negative charges.

So, this would be, when the vacancy is completely ionized and these are the states when vacancy is not completely ionized. Similarly, an oxygen vacancy is written as V O, neutral oxygen vacancy will be V O X, singly charged oxygen vacancy will be V O dot and completely charged oxygen vacancy would be V O double dot. So, double dot will represent two positive charges, and double dash will mean two negative charges. If you have oxygen interstitial, which means oxygen is going to an intestinal site, this would be O I. If it is completely charged, it would be O I dash dash and if you have a metal interstitial, this would be M I. If it is completely ionized, it would be M I double dash. So, we are taking, so, all these number of charges, all these number of dashes or dots represent for an oxide M O. So, if you have M O 2 or M 2 O or M 2 O 3 M 2 O 5, the number of dots and dashes will change for metal cation and for oxygen, it will remain same.

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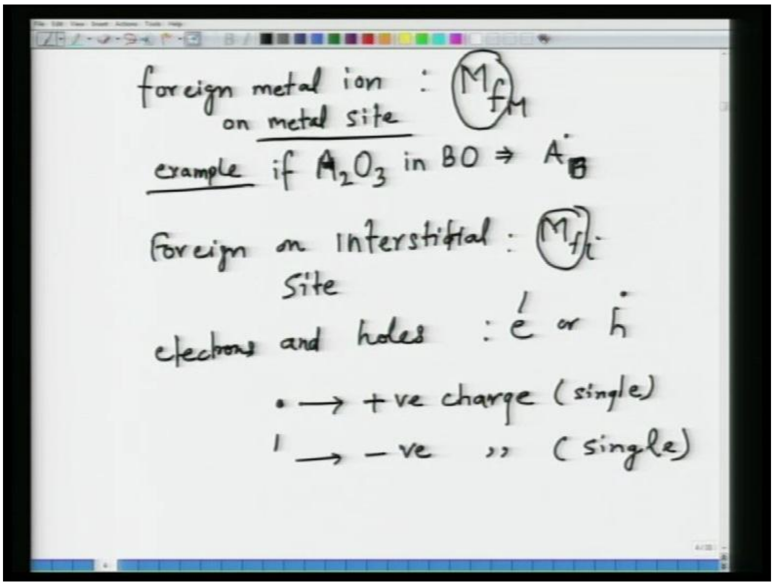

foreign metal ion on metal site : $M_{f_M}$

example if $A_2O_3$ in BO ⇒ $A^{\cdot}_{B}$

Foreign on interstitial site : $M_{f_i}$

electrons and holes : $e'$ or $h^{\cdot}$

• → +ve charge (single)

' → −ve ,, (single)

So, and a foreign metal ion, it would be represented as M f M f M. So, foreign metal ion on metal site, which is the regular metal site, so, this could be regular metal site. So, if the oxide was MO, so, you have this foreign metal ion M f. M f going to regular M site will make it as M f M and number of dashes here will depend upon the charges which are carried by foreign metal ion. So, for instance, if you have, let us say we had, let us say A 2 O 3 in B O. So, I am not writing the complete reaction. I am just writing, if A goes to M site, so, this would be A B. In this case, since A contains plus 3 charges and B contains plus 2 charges, it would be as a result net plus 1. So, this is the example. Vice versa, if you have A 2 A O 2 A 2 O in B O, then it would contain 1 negative charge.

So, the number of dashes or dots will depend upon the type of substitutional for an atom. So, this is foreign metal on regular metal site. If you have foreign cation on interstitial site, it will be known as M f I. So basically, either here M f or either here M f, basically means a foreign metal ion. You can denote it as A or B or whatever you like just to simplify it. For electrons and holes, it is e dash or h dot. So basically, one dot is positive charge, single positive charge and one dash represents. So, this is the convention which we have to follow when we are going to do this defect chemistry exercise for all these defects.

So now, the second thing is, second most important thing is how to write these defect reactions. Now, these defects are formed and you have to at least believe me that they are stable and we will prove the thermodynamic basis in a little while and they are stable. So, the formation of these defects can be represented via reactions like chemical reactions and these are called as defect reactions. So, there are certain rules for writing these defect reactions.

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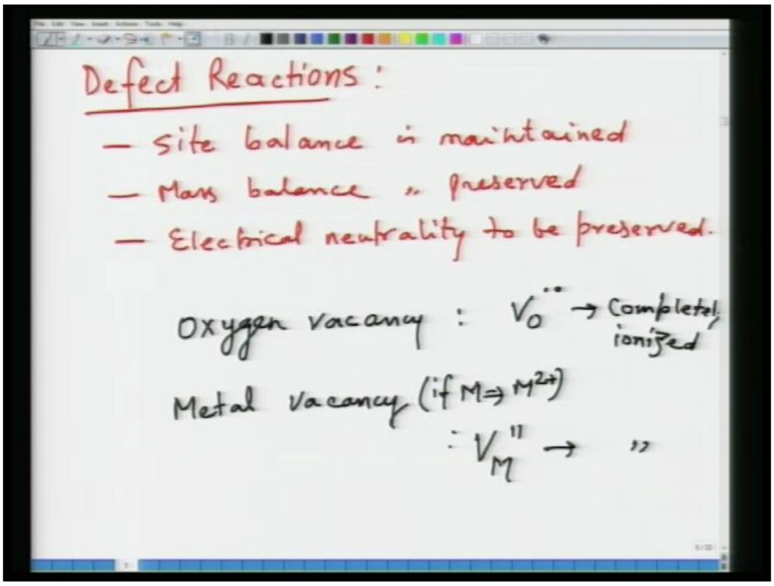

Defect Reactions :

- site balance is maintained
- Mass balance " preserved
- Electrical neutrality to be preserved.

Oxygen vacancy : $V_O^{\bullet\bullet}$ → Completely ionized

Metal vacancy (if $M \Rightarrow M^{2+}$)

: $V_M''$ → "

These rules are, so, you have defect reactions and there are certain rules for writing defect reaction. The first rule is, site balance is maintained, which means number of metal site to number of oxygen site or anion site is always maintained according to the chemical formula. Mass balance is preserved and then you have to maintain the electrical neutrality. The system on the whole after writing the defect has to remain in electrically neutral state. So, electrical neutrality is to be preserved. We can do thermodynamic analysis to work out what is the ionic defect concentration in the whole exercise that we would undertake in these lectures. We will assume that all the defects are completely ionized, which means, if you have oxygen vacancy, we will take it as V O dot, completely ionized. If you have metal vacancy and if metal was M 2 plus, then this would be V M dash dash and this will also mean it is completely ionized.

So, we will assume complete ionization of these defects while writing these defect reactions. But you have to maintain the site balance, the mass balance and the electrical neutrality. You have to preserve these three things to correctly write these defect reactions. Unless you write these defect reactions correctly, you cannot calculate the defect concentration and related to thermodynamic parameters accurately. So, this is something which is important. So, first we will consider the cases of defects that are present in stoichiometric solids.

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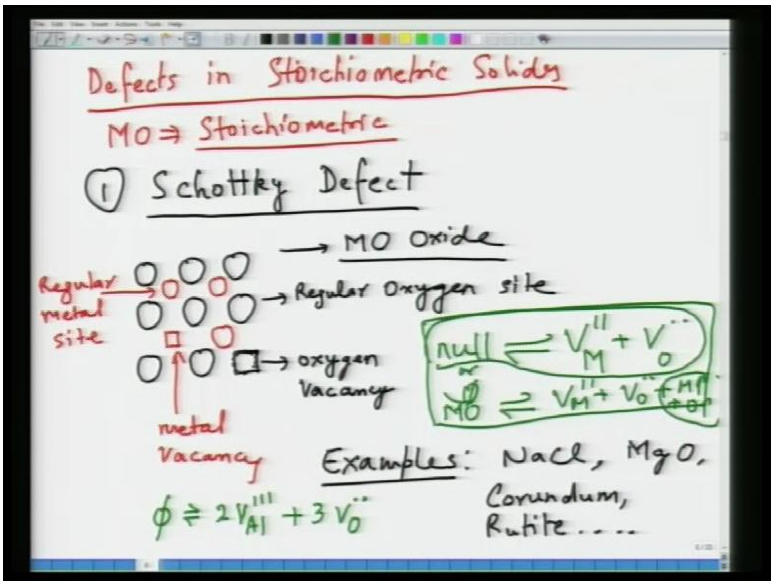

Defects in Stoichiometric Solids

MO ⇒ Stoichiometric

① Schottky Defect

→ MO Oxide

$\text{null} \rightleftharpoons V_M'' + V_O^{\bullet\bullet}$

or

$\overset{\phi}{\cancel{MO}} \rightleftharpoons V_M'' + V_O^{\bullet\bullet} + M_M + O_O$

Examples: NaCl, MgO, Corundum, Rutile . . . .

$\phi \rightleftharpoons 2V_{Al}''' + 3V_O^{\bullet\bullet}$

So, here we will take, in this first, we will consider defects in stoichiometric solids. What it means is that, the stoichiometric solids will mean the oxides or solid which tend to preserve their chemical integrity. So, if it is M O, it would mean M O, which means where each oxygen atom, there is M present. There is nothing, so, you do not have this disbalance of metal and oxygen in a stoichiometric material. So, if you create a point defect for a particular ion, which means the complimentary defect for that another ion or that particular site has to be created, so that, you maintain the stoichiometric nature of the solid.

So, you can have various combinations. You can have combination of a metal vacancy compensated by a oxygen vacancy and you can have a metal interstitial, which means a regular metal ion messing from its site going to interstitial site. But it has to be compensated by a metal vacancy, because side balance in that case has to be maintained. So, it has to be complete package. So, various combinations are possible and we will take example of some of these cases. First of such cases is called as schottky defect or schottky disorder. So, here when we wrote M O, it would be in stoichiometric. So, in case of schottky defect, what happens is that, typically these defects are normally formed as the outer surface or at the defects such as dislocations or at the inner surfaces. If the defects form inside the crystal, then eventually it diffuses out on the surface towards the crystal until you reach equilibrium. This defect is like, so, I can draw this defect as, suppose these are the bigger ions; let us say which are the anions. Now, if I draw the cation, the cation lets say goes here. So, each of these has four nearest neighbors. So, this makes M O kind of solid. So, this would be, in this case M O oxide.

Now, this is a perfect solid. Now, what happens in schottky defect is, one of these metal site is missing and to compliment that, any of one of these, so, oxygen site will be missing. So, what it will look like is, so, this will be or sometimes it is also represented as square and in this case, it would be represented by red square. So, if I denote this, so, this would be your oxygen vacancy and this would be your regular oxygen site. This would be your metal vacancy and this would be your regular metal site. So here, what you see in a otherwise perfect lattice is creation of a pair of vacancy, out of which one is metal and one is oxygen.

So again, you see that you maintain the site balance for each oxygen site, which metal site is missing, which means the whole stoichiometry of the crystal is maintained. Now, how do you maintain the charges? So, the way you write defect reaction is, so, the way I write this defect reaction is, I write this defect reaction null which is equivalent to 0, because the creation of a vacancy pair actually basically it leads nothing. Right? So, null leads to V M plus V O. Now, if they were completely charged, V M would be double dash and V O would be double dot. So, this is or I can write 0. So, this is what is formation of schottky defect.

So here, you can see the charged neutrality is maintained for two charges of metal vacancy which are negative and you have two charges of oxygen vacancy which are positive. Now, the question arises, you must be wondering why these vacancies have charges. Now, you can understand this like, suppose you have a metal. You consider this as regular site. Now, regular metal site have a metal ion sitting, which is plus 2 in nature, which means, the site to which this plus 2 ion is attracted has to have a charge which is complimentary in nature. So, when this metal ion goes away, the resulting vacancy will contain minus 2 charge. Similarly, same is true about the oxygen vacancy. This is a very simple way of understanding why these vacancies have charges. These defects are typically present in most of the materials, especially when metal and oxygen are of comparable sizes.

So, examples of materials which follow this structure are, so, examples are, for example, NACL MGO or corundum or rutile etcetera etcetera. All these materials, first two are rock solid structure compound and then you have A l 2 O 3 and then you have TIO 2. So, all of these oxides or compounds are prone to having schottky defect formation. So, I have written defect reaction for a binary metal oxide, which is M O, which host formulize is M O. Now, the defect reaction formula would change. For example, AL2 O3. In case of AL2 O3, how would you write it? In case of AL2O3, it would mean null is equal to 2VAL. In this case, it would have three charges, because aluminum is plus 3, plus 3 V O.

So now, if we see the defect reaction here, you have site balance as well as charged balance and you have maintained the mass balance as well. So, you can write mass balance would be, suppose you had this M now and schottky defects are typically formed during the stage of formation itself. So, the regular sites on which you would have metal and oxygen going to, they do not occupy those. Since, formation of solid which is nothing, but nucleation in growth and growth is a more like a random walk phenomena because of diffusion. As a result, when you write the defect reaction, you say that they start from nothing and you start from nothing because these sites were anyway empty to begin with and they were not occupied by metal and oxygen. As a result, it is V M plus V O.

You can also think of this in this way, M O being V M plus V O. Now, M goes out and O goes out. O will of course go out in the form of half O 2, But M, unless the metal is volatile, it would not go out. So, I mean this is not very accurate way of writing, but you can understand this in this fashion as well. So, whatever M O, hypothetically that are present there, it has gone out. But since the defect forms during the formation stage itself, the more accurate way of writing is this above line. If you look at these equations, you have to maintain the site balance, mass balance, as well as the charged balance. So, this would be schottky defect formation in the solids.

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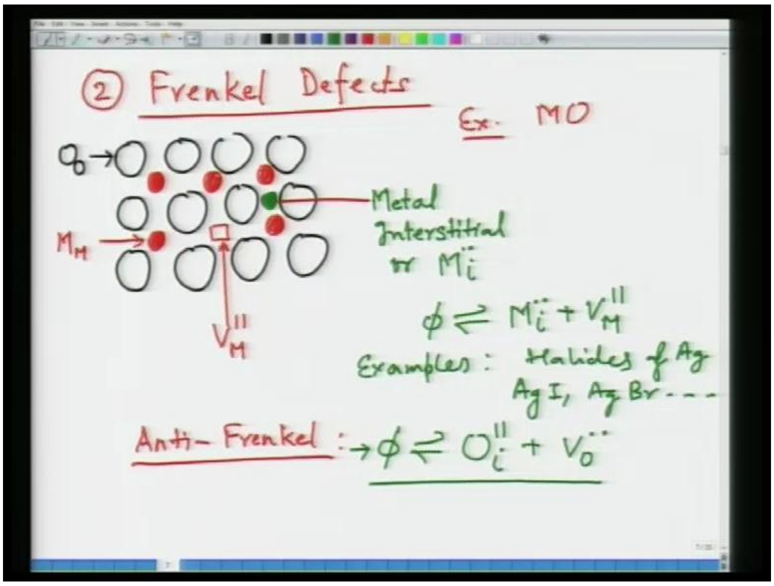

Now, we will look at the second another important defect, which is in present in stoichiometric materials. Its name is, so, the second one is frenkel disorder. Frenkel defect or frenkel disorder. Now, these frenkel disorders are defects where a particular ion goes missing from its site, but it does not leave the solid. It is present inside the solid in an interstitial site. So, what happens is, you have is, again I will draw the structure. So, you have, now you again put these. So, this would be present in the solids where you have empty interstitial site. So, for example, this particular ion which is missing from its position, let us say this is the position and this is regular metal site. So, this would be, I would say M M and this would be O O.

Now, let us say this particular ion goes missing from its site. So, what did is created here is, so, it has created a vacancy, which is V M. For example, I take M O, and then it would be V M double dash. Now, how does this gets compensated? You do not have any missing anions. So, side balance is all right, but mass balance is not there. So, where does it go? It goes somewhere in the solid itself. So, let us say, it goes in one of the other interstitial sites. So, in this case, let us say it goes here. So, this would be here. I will have to color it differently. So, this would be your metal interstitial or M I. Since, it has plus 2 charges, it would be M I dot dot. So, how do you write the defect reaction? The defect reaction would be again 0. So, what it means is that, basically a metal ion which would have been present on its regular site is not there. Rather, it goes to an empty interstitial site. So, this would be M I plus V m. So, here you can see the charge and mass balance as well as the side balance.

Now, these defects can form typically inside the crystals. It generally happens when metal ions are considerably smaller as compared to oxygen ions, because as you can understand, the metal ion has to go to interstitial site and try to expand the lattice, which means, the size of the voids and the metal ions themselves, size of the voids have to be larger than the or at least equivalent or comparable to the size of metal ion, which means the metal ion have to be smaller in nature. If it happens with the, typical examples are halides of silver. So, for example, silver iodide, silver bromide etcetera, these follow this kind of structure. So, if it happens with metal interstitial, it is called as frenkal defect. If it is happened with oxygen or anion, it is called as anti-frenkal. So, in case of anti-frenkal, what will happen is, so again, site and charge and mass balance have to be maintained. So, just that you have to place here, in case of frenkal, you have metal vacancy and metal interstitial formation and in case of anti-frenkal, you have oxygen interstitial and oxygen vacancy formation.

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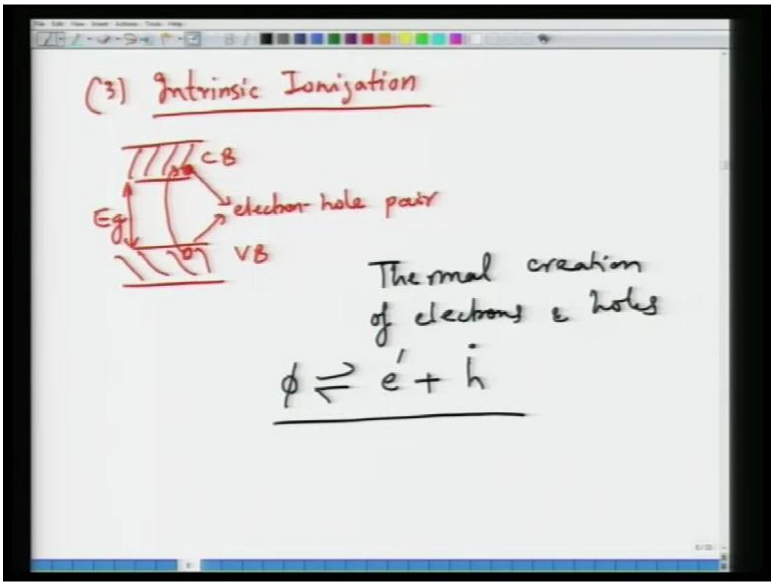
(3) Intrinsic Ionization

Thermal creation of electrons & holes

$$\phi \rightleftharpoons e' + \dot{h}$$

The third defect in stoichiometric solids is called as intrinsic ionization. In this case, you have thermal creation of electron hole pair. So basically, you have, this is your conduction band, this is your valence band and this is your band gap and electrons from valence band jump into conduction band giving rise to formation of an electron hole pair.

So, this is called as thermal creation of electrons and holes and the defect reaction is again written as, since electron hole pair combination is 0 charge, it would be formation of electron plus hole. So, this is your intrinsic ionization reaction.

Now, these are the cases or most common cases for stoichiometry oxides. Similarly, but oxides are not only stoichiometric. They can also be non-stoichiometric, which means, what it means by non-stoichiometry is that, for example, for in an oxide M O, you can have excess of oxygen, you can have excess of metal or you can have vacancy of deficiency of oxygen or deficiency of metal. These are all the stable forms. In these materials, when they are non-stoichiometric, the defect structures are, they depend upon the level non-stoichiometry. So, let us see how it works in case of non-stoichiometric materials.

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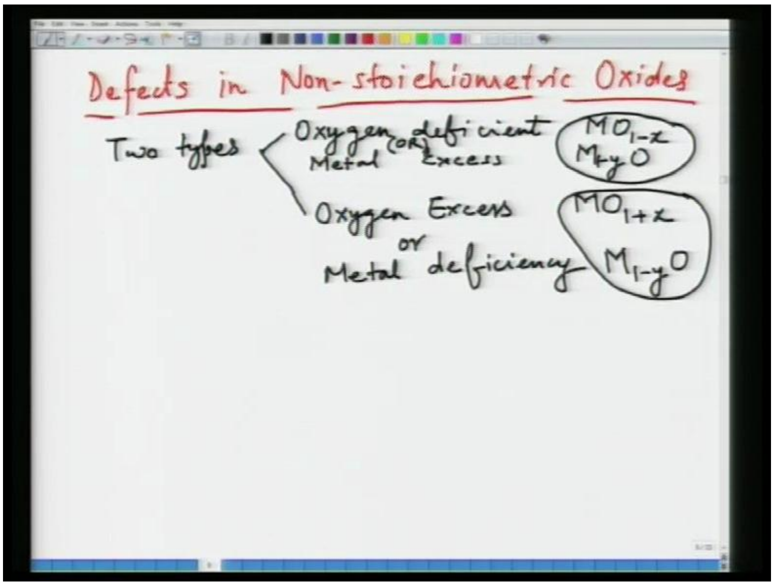

Defects in Non-stoichiometric Oxides

Two types
- Oxygen deficient (OR) Metal Excess — $MO_{1-x}$, $M_{1+y}O$
- Oxygen Excess or Metal deficiency — $MO_{1+x}$, $M_{1-y}O$

So now, we will look at defects in non-stoichiometric oxides. We will take examples of oxides because oxides are first of all examples of ionic materials or electroceramics and most of the electronic and magnetic ceramics tend to be oxides. These are the materials which are more prone to having this non-stoichiometry

So, typically of two types. So, first one, you can have oxygen deficient. Oxygen deficient would mean M O 1 minus x. What it also means is that, it could be metal excess. So here, I can write M 1 minus y O. So, metal deficient or oxygen deficient or metal excess are typically in the same category. The second could be your oxygen excess or metal deficiency. So, oxygen excess would be M O 1 plus x or y or delta. I mean choice of x y z or delta will depend upon you and it would be M 1 minus y O. So, this is one category and this is another category. So, these are the two major categories.

The moment you have non-stoichiometry, which means the moment you have excess of deficiency of any particular ion, it requires the presence of point defects. You cannot avoid that. The concentration of these defects will be governed by what is the extent of non-stoichiometry. So, here again you have to maintain the electrical neutrality and electrical neutrality is preserved by either the formation of point defects and electronic charges or oxidation or reduction of the regular metal ions. Typically, oxygen does not have multiple balance state. It is typically metals which tend to have multiple balanced states. The creation of extra charges has to be taken care either by formation of extra electrons or holes or oxidation or defection cations. So, and of course, intrinsic ionization is always a possibility whether it is stoichiometric or non-stoichiometric material.

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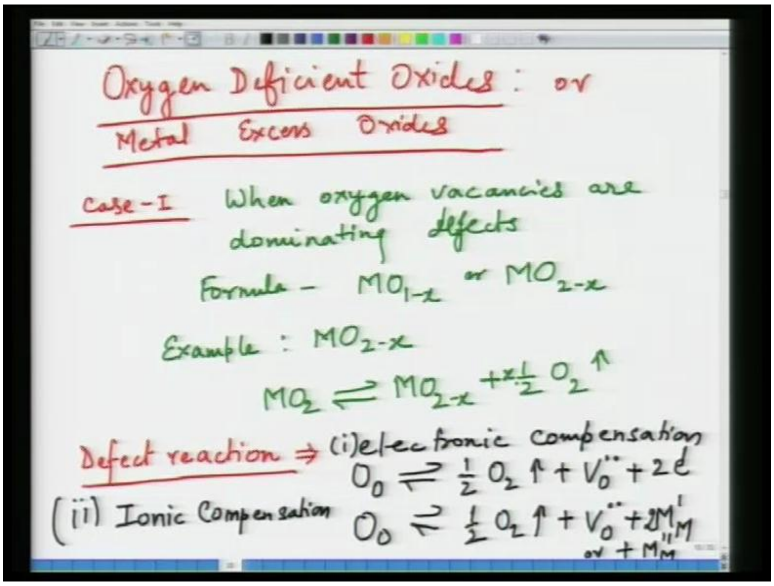

Oxygen Deficient Oxides : or Metal Excess Oxides

Case - I When oxygen vacancies are dominating defects

Formula - $MO_{1-x}$ or $MO_{2-x}$

Example : $MO_{2-x}$

$$MO_2 \rightleftharpoons MO_{2-x} + x \cdot \frac{1}{2} O_2 \uparrow$$

Defect reaction ⇒ (i) electronic compensation

$$O_O \rightleftharpoons \frac{1}{2} O_2 \uparrow + V_O^{\bullet\bullet} + 2e'$$

(ii) Ionic Compensation

$$O_O \rightleftharpoons \frac{1}{2} O_2 \uparrow + V_O^{\bullet\bullet} + 2M_M' \text{ or } + M_M''$$

So first, we will take example of oxygen deficient oxides. Now, so in this, in these, now I have not written oxygen deficient or metal excess oxides. So, if I write oxygen deficient oxides, it also means metal excess oxides. So, for the sake of clarity, I can write here or metal excess oxides. So, we will take these examples. So, formation of basically oxygen vacancy or interstitial, both is likely. Typically, formal formation of these vacancies occurs mainly at the surface. So, let us say, case 1, when oxygen vacancies are the dominating defects. Now, so here, in this case, we depict these by the formula. So, the formula is written as M O 1 minus x, if it was M O or M O 2 minus x, if it was M O 2 and so on and so forth. So, the overall reaction in this case would be, so, if you have for example, if I take M O 2 minus x, so, the reaction would be M O 2 which is the stoichiometric form. Now, this becomes M O 2 minus x plus half O 2 multiplied by x. So, this was oxygen has gone out of the system.

Now, you are left with after whatever oxygen has gone out of the system or oxygen is forced to go out of the system, whatever the reason is, due to loss of oxygen, the stoichiometry now is M O 2 minus x. So, due to loss of oxygen, what is the state inside the material? So, now we can write what is the defect reaction. So, defect reaction for example, the first case could be electronic compensation. So, if you have electronic compensation, then what it means is that, basically M O 2 minus x amount of oxygen is gone out and it gives rise to creation of certain defects. So, in this case, we can write the reaction as oxygen at oxygen site, now it goes out of the system. So, how it goes out of the system is, let us say it goes out as half O 2. Giving rise to naturally, if we are saying oxygen vacancies are dominating giving rise to oxygen vacancies. So, for each oxygen going out, you have one oxygen vacancy created.

Now, this oxygen vacancy creates two positive charges. Now, what can this positive charge be compensated by? If this can be, if I am saying it is electronic compensation, then this is compensated by creation of two electrons. So, these two electrons will contain two negative charges, which will compensate these two positive charges. On the contrary, you can also have another kind of compensation which is called as ionic compensation. What will happen in this ionic compensation? The oxygen at oxygen site will go out. Oxygen is lost giving rise to oxygen vacancy, but you do not create electrons in this case. Rather, what you do is that, you see a reduction in the metal site, which means this creation of two charges, will have to be borne by something happening at the metal site.

Now, in that case, since oxygen vacancy contains plus 2 charges, a metal site has to contain two negative charges. But in this case, metal is, so metal at metal site, in this case, you have plus 4 metal ion. So, plus 4, either the plus 4 metal ions becomes plus 2 or 2 plus 4 sites become plus 3, which means, I can write this as 2 M m dash, which means, M m dash would, in this case means, reduction from plus 4 state to plus 3 state. Or it can also mean plus M m double dash, which means reduction from plus 4 to plus 2 state. However, this first scenario is more likely because it is reduction from plus 4 to plus 3 state, since the reduction oxidation happens in subsequent steps. So, the first scenario is more likely as compared to the second scenario. What decides which of these is going to be present depends upon the oxide entirely and various thermodynamics parameters as we will see later on in this course at some instance.

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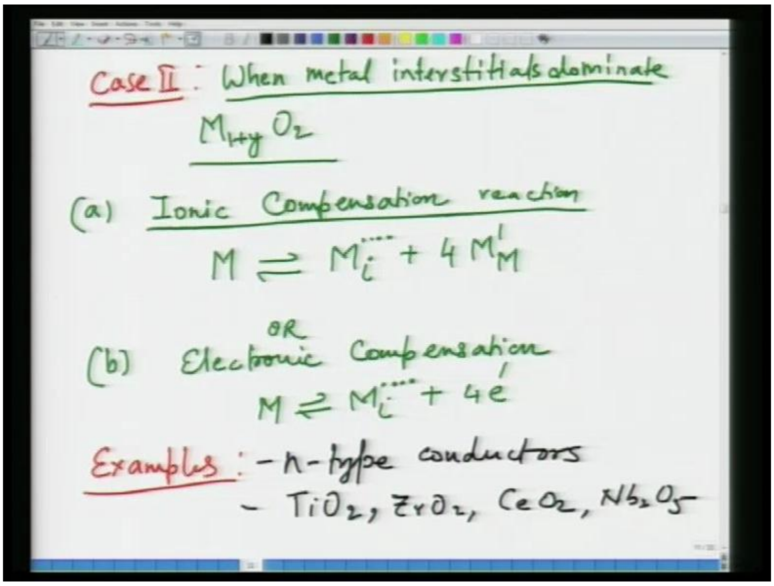

Case II : When metal interstitials dominate

$M_{1+y}O_2$

(a) Ionic Compensation reaction

$$M \rightleftharpoons M_i^{\cdot\cdot\cdot\cdot} + 4M_M'$$

OR

(b) Electronic Compensation

$$M \rightleftharpoons M_i^{\cdot\cdot\cdot\cdot} + 4e'$$

Examples : - n-type conductors

- $TiO_2$, $ZrO_2$, $CeO_2$, $Nb_2O_5$

So, this is the first scenario, when oxygen vacancies are the dominating defects. Second scenario could be, so, in the first case one and here I write as case two, when metal interstitials dominate. Now, when this happens, in that case we can depict the oxide as first of all M 1 plus y O 2. So, you have some extra metal there and y is x. It is just like x, where x determined the loss of oxygen and here, this is y would determine the loss of extent of non-stoichiometry or extent of excess metal. So again, the possible reactions are, first reaction could be your ionic compensation.

So, ionic compensation basically would lead to, in this case, when you have excess metal, the metal tends to go to metal interstitial site. So, what basically you have as a defect reaction is, M tends to go to M i. So, in this case, I have taken it as plus 4. So, it would be M I 4 dots plus 4 M M. So, what I have done is, the metal has gone to metal interstitial site giving us 2 plus 4 charges and those plus 4 charges are compensated by reduction of 4 metal ions on regular metal sites 2 plus 3 state. So, this is ionic compensation or electronic compensation. Electronic compensation is similar and easy, M I plus 4 electrons. So, this is the electronic compensation reaction.

Another change that you observe in two cases is, in the first case, for each oxygen, we can see you created two electrons. And here and there was a dependence on partial pressure of oxygen. Whereas, in this case, you have this, there is no dependence on partial pressure of oxygen. You create for each metal interstitial ion, you create 4 electrons. This is the difference between two reactions. These electrons, which are created in these two cases are called as quasi free electrons or if there is reduction in that case, then it is often referred as M M dash. In these solids, again the conduction, since you have quasi electrons present, these electrons can be source of conduction as well in these materials. As a result of presence of these quasi free electrons, many of these materials tend to be n type conductors.

So, typical examples could be n type conductors due to quasi free electrons. Examples are materials like T I O 2, Z R O 2, and C E O 2. So, all these A O 2 kind of oxides or you can have materials like NB2O 5, which are also prone to having this kind of defect chemistry. Second defect, second thing about non-stoichiometry oxides is metal deficient oxides and we will look at the case of metal deficient oxides in the next class.

Thank you.