Fundamentals and Applications of Dielectric Ceramics
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Lecture No 08
Defect Chemistry

So, welcome again to the new lecture of this course, Fundamentals and Applications of Dielectric Ceramics. So, in the previous few lectures, we looked at the structure formation of these dielectric ceramics. So, basically most of the dielectric ceramics are based on ionic bonding of cations and anions, as a result, they follow what we call us Pauling's rules, which are essentially based on formation of polyhedras by anions being bigger ions and cations occupying the interstices between them depending upon the radius ratios.

So, we looked at essentially FCC base structures, the cubic base structures and HCP packed structures, which are the most common ones. There are other structures as well, but these are the most common structures that we looked at in the last few lectures.

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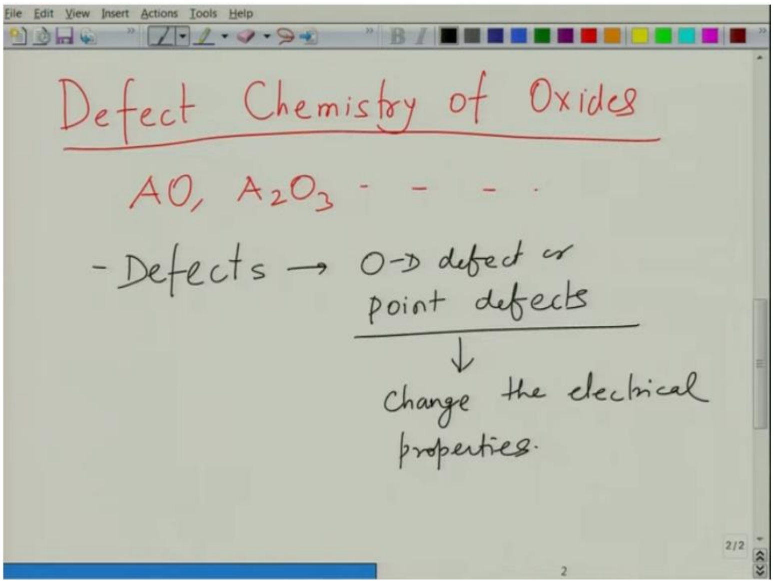

Defect Chemistry of Oxides

AO, A_2O_3 - - - .

- Defects → 0-D defect or point defects
↓
Change the electrical properties.

So, now, we move on to the new topic here, which is essentially based, which is important from the perspective of properties. So, here we are going to look at, what we call as the defect chemistry. Defect chemistry of basically oxides. So, because many dielectric materials tend to be oxides and in terms of their chemistry, defect chemistry plays a very important role because, what is defect chemistry is basically most of these materials, whether you have AO or A_2O_3, variety of these materials, they tend to carry defects which are not.

So here, we are not talking of defects like dislocations and grain boundaries and surfaces, here we are going to talk about the effects are mainly point defects, so defects basically which are 0 dimensional defects or point defects. So, these defects are very important, because these defects when they are present in them, they change the electrical properties and these electrical properties essentially are modified, especially the conductivity, the electrical conductivity changes quite extensively and this has very important ramification on the use of these materials.

And this is affected by chemistry, the environment in which they are used, the chemical reactions and variety of other things. In the next few lectures, we will look at a few fundamental aspects or defect chemistry of these materials, which can enable you to tailor the properties, when you work on them as a part of your research or industry or wherever you are.

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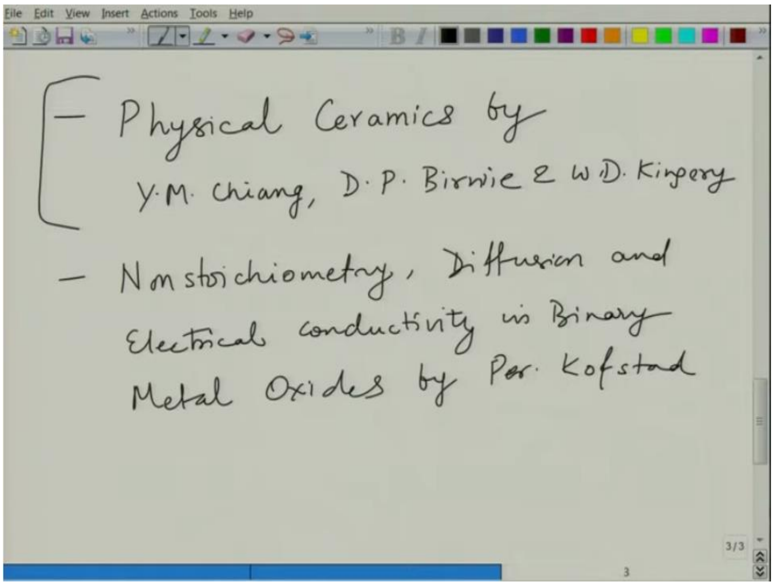

- Physical Ceramics by Y.M. Chiang, D.P. Birnie & W.D. Kingery
- Nonstoichiometry, Diffusion and Electrical conductivity in Binary Metal Oxides by Per. Kofstad

So, the books that we are going to follow, I told you the books earlier, but the books that we are going to follow basically, if you look at Physical Ceramics by YM Chiang, DP Birwie, and WD King Gary. So, this has a chapter on defect chemistry and then, if you are interested in deeper aspects, then you can look at Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides by Per Kofstad.

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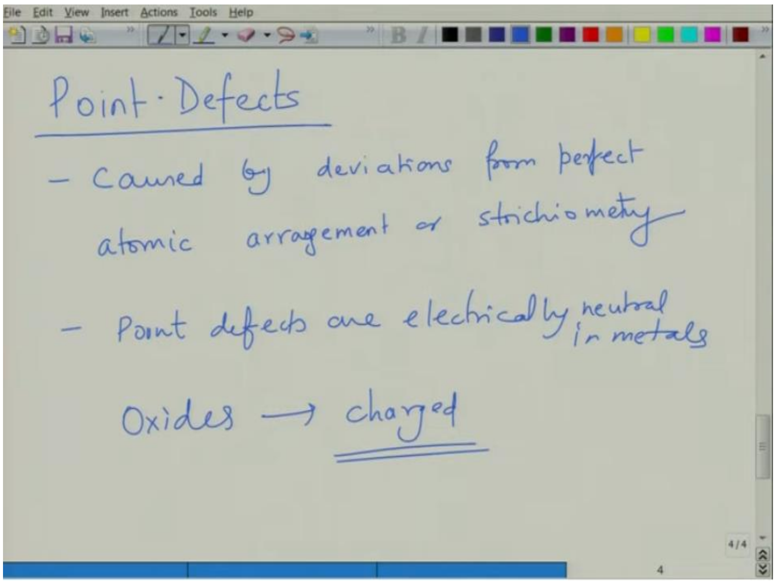

Point · Defects

- Caused by deviations from perfect atomic arrangement or strichiometry
- Point defects are electrically neutral in metals

Oxides → charged

So these are the two books that you can look at, ceramics will fulfil the criteria for this course, this Physical Ceramics book, but if you wanted to get into details, you can go through this Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides by Per Kofstad. Now, let us begin our discussion with what these defects are. So we first begin with what we call as point defects. And these point defects are basically caused by deviations from perfect atomic, you can say arrangement or stoichiometry, okay.

So, these could be, you know, missing ions, these could be interstitial ions, these could be substitutional atoms and these could be presence of extra electrons or holes, these kind of things. Usually, these point defects are electrically neutral in metals, but in oxides, they are charged and they change the electrical properties quite significantly.

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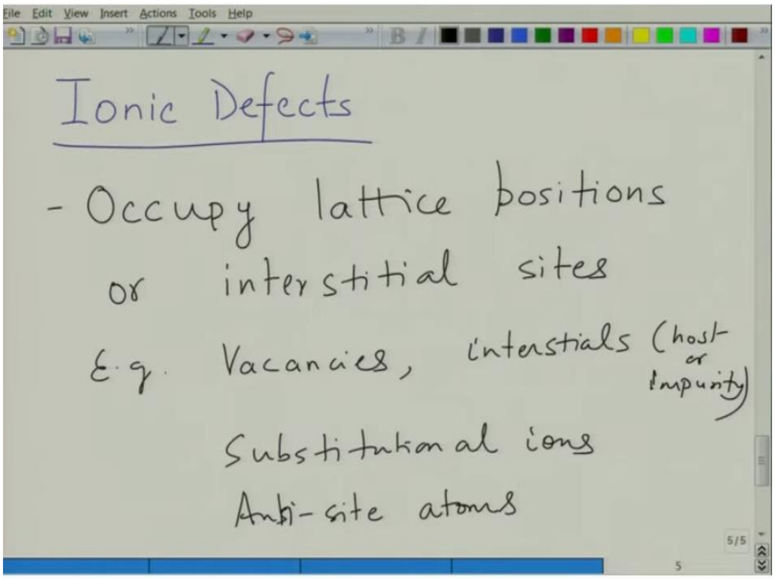

Ionic Defects

- Occupy lattice positions or interstitial sites

E.g. Vacancies, interstials (host or impurity)

Substitutional ions

Anti-site atoms

So, what are these, so some of these defects are basically subcategorized into ionic defects, ionic defects are basically the defects, which occupy lattice positions or interstitial sites. These could be, so examples are, vacancies, interstitials; both host or impurity. Substitutional ions. So, these are again substitutional ions can be basically impurity atoms or and it could be anti-site defects, anti-site atoms or ions, okay. So these are some examples of ionic defects.

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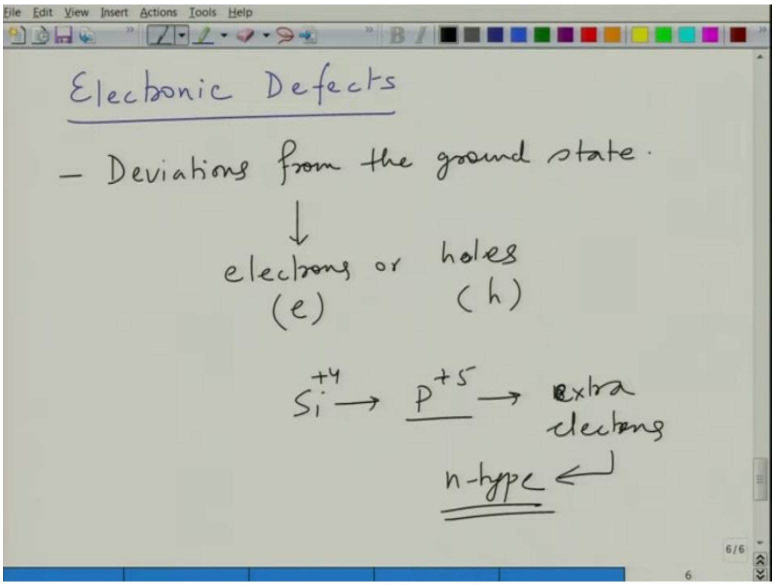

Electronic Defects

– Deviations from the ground state.

↓

electrons or holes

(e) (h)

$Si^{+4} \rightarrow \underline{P^{+5}} \rightarrow$ extra electrons

n-type ←

The electronic defects on the other hand, electronic defects are basically they are because of deviations from the ground state. So, basically when you have excitation of electrons or holes, so you form extra electrons or holes in the system, okay. And these are depicted as ‘e’ or ‘h’, okay. So, basically when you have deviation from the ground state, you have excitations. For example, if you excite an electron from the valence to conduction band, this leads to creation of electron and a hole.

You can also possibly, if you put an impurity, if the impurity is different charge, so for example, we know in the case of silicon, right. In the case of silicon, when we put phosphorus in it, the silicon is +4, phosphorus is +5. What phosphorus does is, it creates extra electrons in the, and this makes silicon n-type. And those n-type are extra electrons, extra charge that is created. These are electronic defects, similarly when you put in a 3+ like boron, boronType equation here. is 3+ right, it creates holes. So, these are basically electronic defects as we call them.

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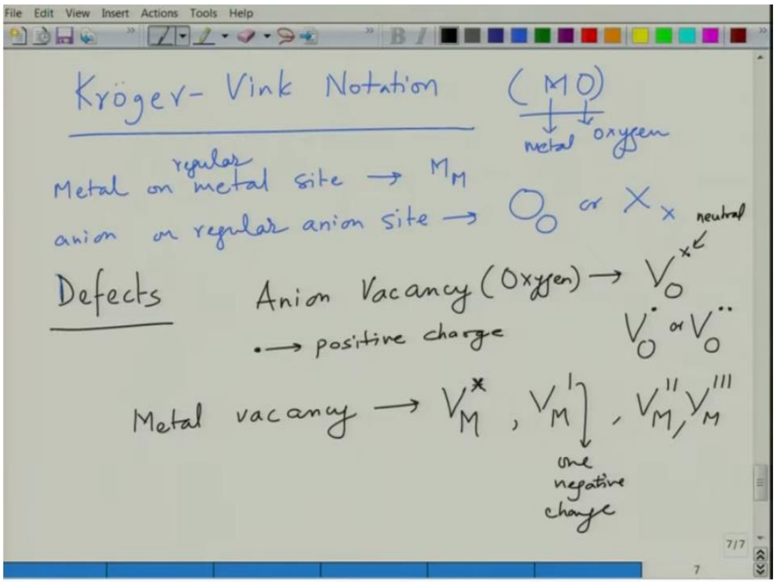
Kröger- Vink Notation (MO)

metal oxygen

Metal on regular metal site → M_M

anion on regular anion site → O_O or X_X

Defects

Anion Vacancy (Oxygen) → V_O^{x} ← neutral

• → positive charge $V_O^{\bullet}$ or $V_O^{\bullet\bullet}$

Metal vacancy → V_M^{x} , $V_M^{'}$, $V_M^{''}$, $V_M^{'''}$

one negative charge

So, before we go into details of this defect chemistry, let us first look at the notation, the notation is called as Kroger-Vink notation. So, Kroger-Vink notation generally, in this case, let us say you have a metal oxide as MO. So, M is the metal and O is the oxygen atom, okay. So, if you have metal on metal site, it is going to be M_M, this is regular metal site, okay. Similarly, if you have anion on regular anion site, it is going to be O_O or X_X, okay. The defects are depicted little differently.

So, if you have anion vacancy which is basically oxygen vacancy in this case, in most cases, then this is going to be V_O, okay. And this could be a neutral vacancy, it could be a charged vacancy. So, if it is a neutral vacancy, you write it as V_O^X, if it is charged vacancy then you write it as $V_O^{\bullet}$ or $V_O^{\bullet\bullet}$. It can carry one positive charge or two positive charges, the oxygen vacancy is positively charged. So, dot represents in this case positive charge, okay. So it could be V_O^X, X will be neutral.

$V_O^{\bullet}$ will mean single positive charge and $V_O^{\bullet\bullet}$ will mean it is a double positive charge. Similarly a metal vacancy will be V_M, again neutral would be V_O^X, if it is charged, then it would be $V_M^{'}$, this will be one negative charge. And if it is doubly charged, it is $V_M^{'''}$, if it is triply charged, it is $V_M^{'''}$. So for example for Al^{3+} you can have up to $V_M^{'''}$, for zirconium, you can have $V_M^{''''}$, for niobium you may have $V_M^{'''''}$, because their valences are +3, +4, and +5.

So that is how it will change depending upon the.

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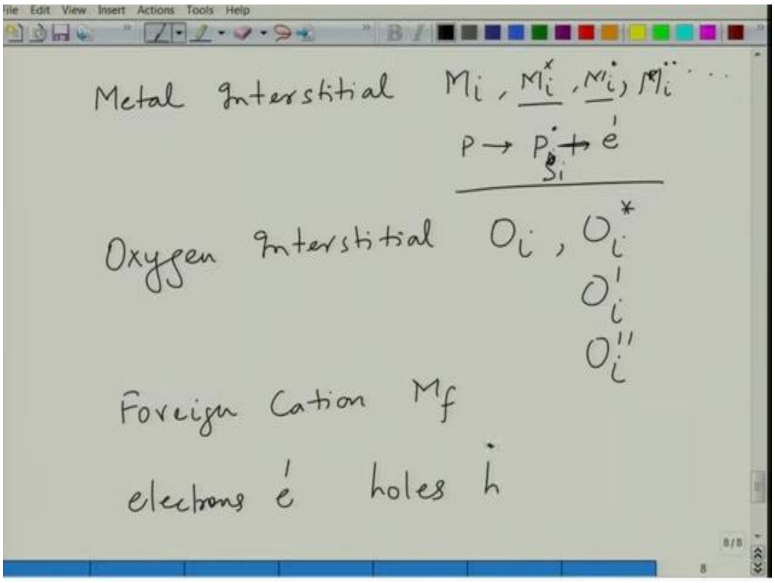

Metal Interstitial M_i, $\underline{M_i^{x}}$, $\underline{M_i^{\cdot}}$, $M_i^{\cdot\cdot}$ . . .

$P \to P^{\cdot}_{Si} + e'$

Oxygen Interstitial O_i, O_i^{*}, O_i', O_i''

Foreign Cation M_f

electrons e' holes $h^{\cdot}$

So, and if you have metal interstitial, it will be M_i, again it could be M_i^X, it could be $M_i^{\bullet}$, it could be $M_i^{\bullet\bullet}$ and so on and so forth depending upon the valence of the metal, whether it is completely ionized, whether it is partially ionized or whether it is un-ionized. Un-ionized will mean, it is M_i^X, it does not lead to any extra charges, $M_i^{\bullet}$ will mean it leads to extra charges. So, if for example phosphorus and silicon, so it would be P_i or it would be $P^{\bullet}$.

Because it gives rise basically phosphorous atom is giving rise to one positive charge on the silicon site, plus an extra electron, okay.

$$P \to P_{Si}^{\bullet} + e^{-}$$

So, this is how it becomes charged neutral, right. So, if you put a metal for example inside a metal, so, it may give rise to charges or it may not give it to charges depending upon its ionization energy. So, this reaction whether it will take place or not, it depends upon the ionization energy of the impurity. Similarly, you can have oxygen interstitial, this will be O_i, and this O_i can again be O_i^X, it can O_i'.

It could be O_i''. In case of oxygen, it can maximum have O_i'' because of oxygen has valence of -2. If you have a foreign cation, foreign cation is generally M_f and this M_f can also take positive and negative charges depending upon where and how it goes, okay. And there are some other conventions that we will see, as we continue in the in the course, okay. And generally electrons and holes are written as, electron are depicted as $e'$and holes are depicted as $h^{\bullet}$.

Wherever you have x, it means neutral wherever you have dot or dash, it means charged, okay.

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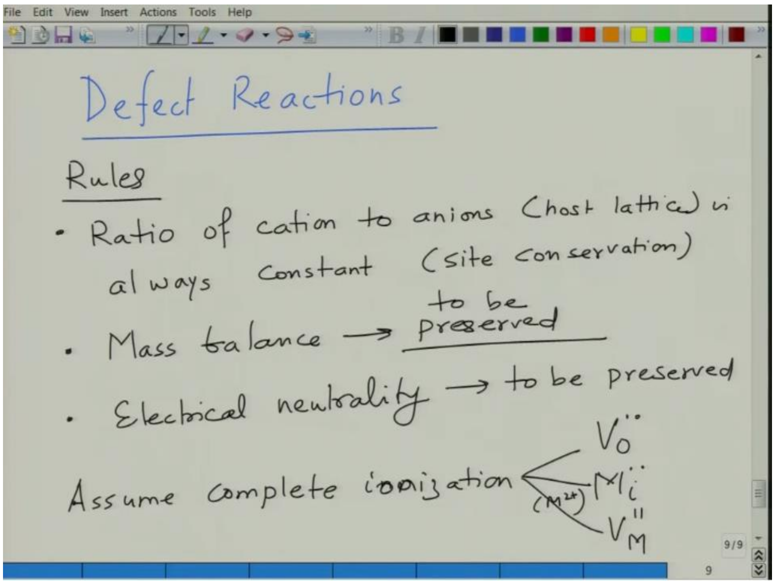

Defect Reactions

Rules

- Ratio of cation to anions (host lattice) is always constant (site conservation)
- Mass balance → to be preserved
- Electrical neutrality → to be preserved

Assume complete ionization $V_O^{\bullet\bullet}$, $M_i^{\bullet\bullet}$ (M^{2+}), V_M''

So, this is basically the Kroger-Vink notation. So, defects are usually represented by writing what we call as defect reactions, okay. They are sort of chemical reactions. But we need to follow certain rules and the rules are; first one is, that the ratio of cation to anion sites or the host lattice right as per the host lattice, is always constant. So, which is basically it is the law of site conservation, okay. So, if it is AO lattice, which means number of A sites is equal to number O sites, you cannot change that ratio.

You cannot make it A_2O_3 or you cannot make it A_2O, AO is the host lattice. Then, mass balance. So, mass balance has to be preserved you have to have mass balance whatever goes in has to be accommodated and accounted for. You cannot have disturbance in the masses, you cannot have inequality in the masses, you have to account for each and everything that comes in and goes out. And then we have electrical neutrality, in the end, to be preserved.

So, mass balance has to be preserved, electrical neutrality has to be preserved, solid has to be always electrically neutral, you cannot have imbalance of charges. So, all the positive charges have to satisfy all the negative charges. So, that is why it is always electrically neutral. So, when you write defect reaction, these three rules are holy grail, you have to have site conservation, you have to have mass conservation, you have to have electrical neutrality, condition to be fulfilled.

And that is how we write and when we write defect reactions and generally from the perspective of teaching, we will assume complete ionization. So, in case of oxygen vacancies, it will be

$V_O^{\bullet\bullet}$ in case of metal interstitial, let us say if it is 2+ metal, then it will be $M_i^{\bullet\bullet}$, in case of metal vacancy, it will be V_M''. So, we are taking complete ionization instead of, there are possibilities you can have incomplete ionization in practice, but for the sake of teaching this module, we will consider complete ionization of all the defects.

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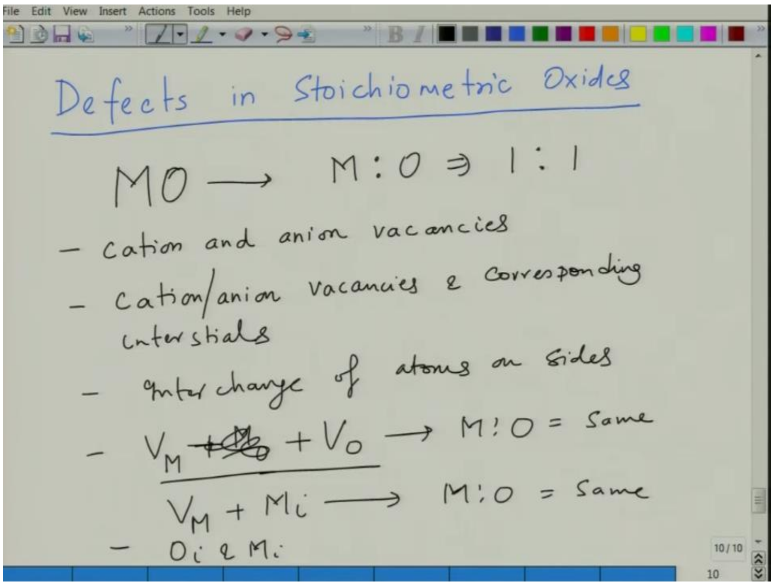

Defects in Stoichiometric Oxides

$MO \longrightarrow M:O \Rightarrow 1:1$

- cation and anion vacancies
- cation/anion vacancies & corresponding interstials
- interchange of atoms on sides
- $V_M + V_O \longrightarrow M:O = \text{Same}$

$V_M + M_i \longrightarrow M:O = \text{Same}$

- O_i & M_i

So, let us first consider defects in stoichiometric oxides. So, stoichiometric oxides are basically, when the defects form, they do not change the stoichiometry, okay. So, if you have oxide MO, the stoichiometry remains as M:O as 1:1. So, no matter what the defect forms, ratio of number of metal ions to number of oxygen ions remain always similar. So, the defects which form in such scenarios, you can have cation and anion vacancies. You can also form cation/anion vacancies and corresponding interstitials, okay.

You can have interchange of atoms, basically anti-site defects, you can have vacancies and misplaced atom of same kind of, so, you can have for example, combination of metal vacancy and then you have metal sitting on oxygen site, there is a possibility, so you have oxygen missing as well as. So, there are various possibilities, so you will have $V_M + V_O$ does not change the ratio. So, you have M:O, which is the same, okay as parent. You can have $V_M + M_i$.

So, metal has left metal site and gone to interstitial site, which means M:O remains the, we have done nothing to oxygen and we have done nothing to metal, because metal ions are same in number. So, these are various possibilities and we will see there is a possibility that you can form interstitials also. So, you might have O_i and Mi without forming any vacancies you bring in extra oxygen and extra metal, both of them sit in the interstitial side without changing the stoichiometry.

So, many combinations are possible, let us see few of them how they exist.

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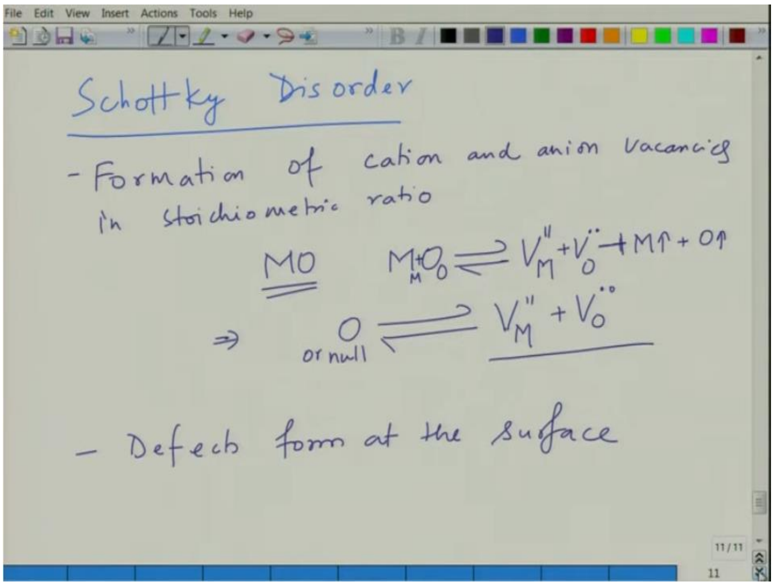

Schottky Disorder

- Formation of cation and anion vacancies in stoichiometric ratio

MO $\quad M_M + O_O \rightleftharpoons V_M'' + V_O^{\bullet\bullet} + M\uparrow + O\uparrow$

$\Rightarrow \quad 0 \rightleftharpoons V_M'' + V_O^{\bullet\bullet}$

or null

- Defects form at the surface

So, first of these stoichiometric defect is called as Schottky defect. So, the Schottky disorder is basically you have, this defects is basically formation of cation and anion vacancies in stoichiometric ratio, okay. So, if you have oxide MO, for MO basically you can write this reaction as you have 1 M and 1 O, so you can say you had M at M site and O at O site, okay. They go out of the system. You can say that this M and this O, M goes out and O go out, they create vacancies at oxygen and metal site, right.

$$M_M + O_O \leftrightarrow V_M'' + V_O^{\bullet\bullet} + M\uparrow + O\uparrow$$

V_O and V_M and these vacancies will be negatively and these we vacancies will be positively charged. So this is basically, alternatively you can write this reaction as, so you have seen that this has not changed their stoichiometry. For each molecule of MO, one molecule has gone out, it has created one vacancy, so you can write this reaction as

$$0 \leftrightarrow V_M'' + V_O^{\bullet\bullet}$$

,okay. So, what this means is that both metal and oxygen have to leave the system.

So, this generally does not happen in the interior of the system it happens at the surface, that is why these defects are usually found, because the metals and oxygen have to diffuse out of the system and this diffusion takes energy and it is more plausible at the surface than the interior. So these defects generally form at the surface.

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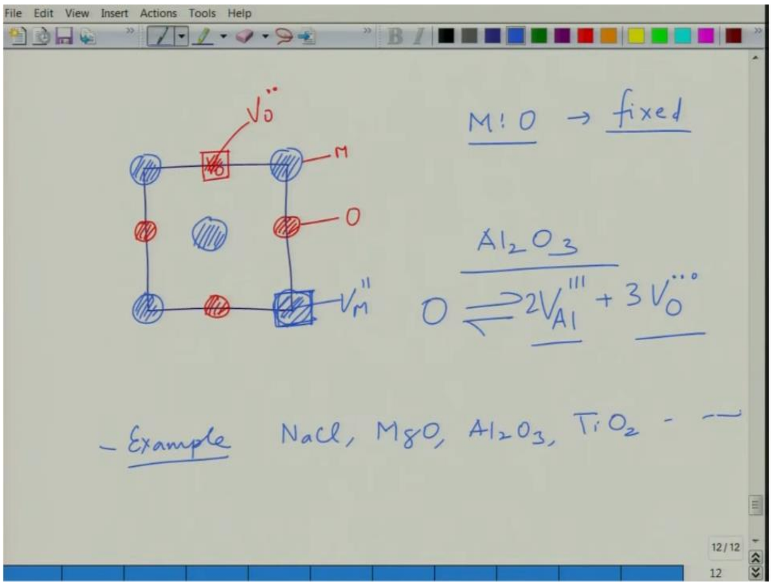

So basically, if you look at a structure, it looks like, so you have let us say, this is a lattice, let's say you have these as oxygen ions and let's say you have these as metal ions, okay. So, right now, this is all stoichiometric, right. Now, in the Schottky defect, what will happen is that this will become a vacancy. So, this will become, you can denote a vacancy like, so let us say this becomes a vacancy, this becomes V. So, this was metal, this was oxygen, let's say, okay.
So, this becomes V_O and similarly, this metal here, it will become V_M. So, you have pair of vacancies without changing the, so M:O is fixed, okay. So, this is called as Schottky reaction and this reaction generally happens at the outer or inner surfaces or at dislocations wherever energetics permits it and generally these metals and oxygen they are diffuse out of the system until you reach equilibrium. So, this is equilibrium defect, you will have some of these defects always present thermodynamically in a system, we will do the thermodynamics later on.

And these defects are generally preferred when anion and cation are of equal sizes or comparable sizes. So, this is for MO, suppose you wanted to do it for Al_2O_3. For Al_2O_3, you can write a reaction as

$$0 \leftrightarrow 2V_{Al}''' + 3V_O^{\bullet\bullet}$$

,so here you can see the stoichiometry is 2:3, so which means you will have two vacancies of aluminum plus three vacancies of oxygen. So you can see, you have site neutrality, you have mass neutrality, mass conservation, you have charge conservation, you have six of negative and six of positive charges.

So you can write this reaction for, so this is called as stoichiometric defect, it does not change the stoichiometry of the system. And the materials which show this kind of defects are, things like sodium chloride, magnesium oxide, Al_2O_3, TiO_2, many of these materials show this kind of Schottky defects.

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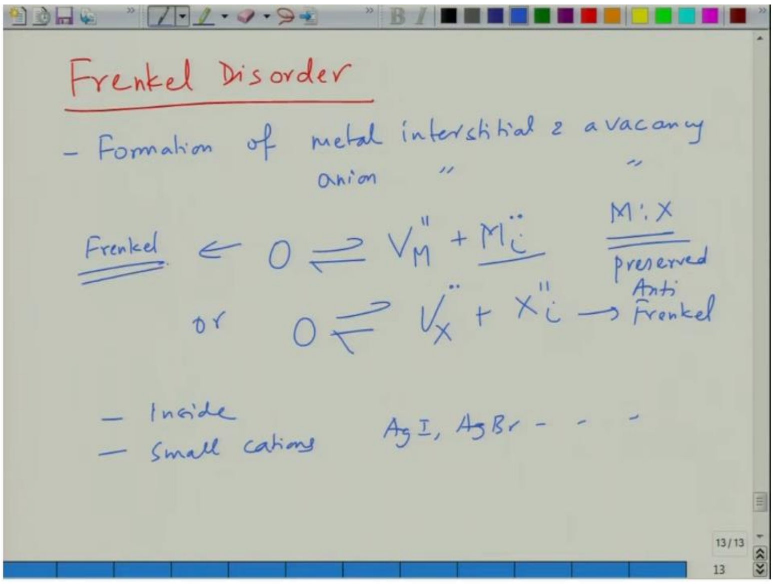

Frenkel Disorder

- Formation of metal interstitial & a vacancy
  anion " "

Frenkel $\Leftarrow$ $0 \rightleftharpoons V_M'' + M_i^{\bullet\bullet}$ M:X preserved

or $0 \rightleftharpoons V_X^{\bullet\bullet} + X_i'' \rightarrow$ Anti Frenkel

- Inside
- Small cations AgI, AgBr - - -

Second defect in the series is called a Frenkel disorder. Frenkel disorder is basically about formation of, it is about formation of metal interstitial and vacancy, so either metal or anion interstitial and vacancy. So, the way this reaction is written as, you have

$$0 \leftrightarrow V_M'' + 3M_i^{\bullet\bullet}$$

or

$$0 \leftrightarrow 3V_X^{\bullet\bullet} + X_i''$$

, so let us say if x is doubly charged as well, then you will have V_x and X_i. So, you will form either metal interstitial or vacancy of metal and vacancy of metal or you will form vacancy of anion and anion interstitial.

In both cases, either this or that, in both cases, stoichiometry is not disturbed, because metal has not gone out of system, it has remained inside the system, so M:X is same, it is preserved, okay. So mass is preserved. You can see there is a site preservation, you have not created any extra site, because it has gone to interstitial site, interstitial sites cannot be created or destroyed and vacancy has been created on the metal site itself.

So, this happens inside the crystal because nothing has to leave and it happens only when cations, so inside the crystal and then it happens in systems with the smaller cations. So, things like AgI, AgBr many halides show this kind of system where this kind of reaction, okay. So this is Frenkel or anti-Frenkel; anti-Frenkel in case of anion and Frenkel in case of cation. So we will stop here today. Remaining defect chemistry will take up in the next lecture. Thank you.