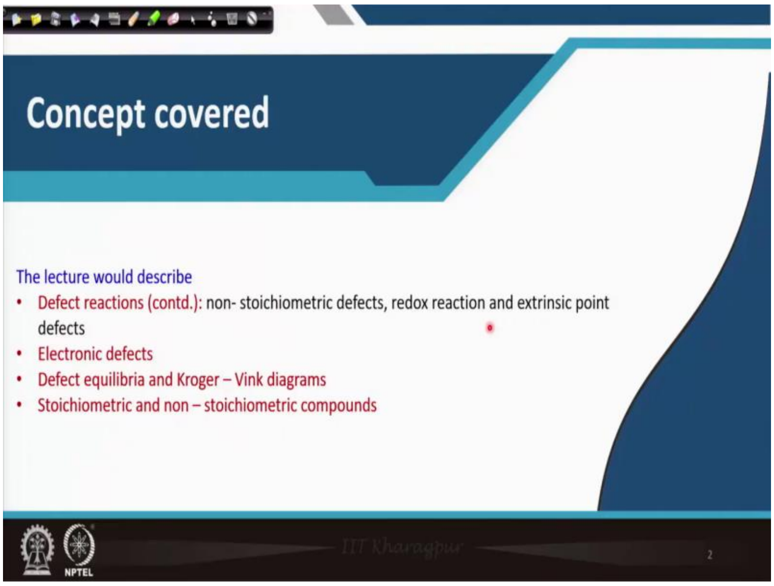
Non-Metallic Materials
Prof. Subhasish Basu Majumder
Department of Materials Science Centre
Indian Institute of Technology, Kharagpur

Module - 02
Defects, and reaction kinetics of non - metallic materials
Lecture - 07
Non-stoichiometry in non-metallic materials

Welcome to the course Non-Metallic Materials. And this is part of module 2, Defects and reaction kinetics of non-metallic materials. And in module 2, today I will be discussing the Non-stoichiometry in non-metallic materials.

In the last class, we talked about the stoichiometric defect and we derive the relation of a normal defect followed by Frankel and Schottky type defects. And also antisite defects, they are also considered to be stoichiometric defect.

(Refer Slide Time: 01:10)



Concept covered

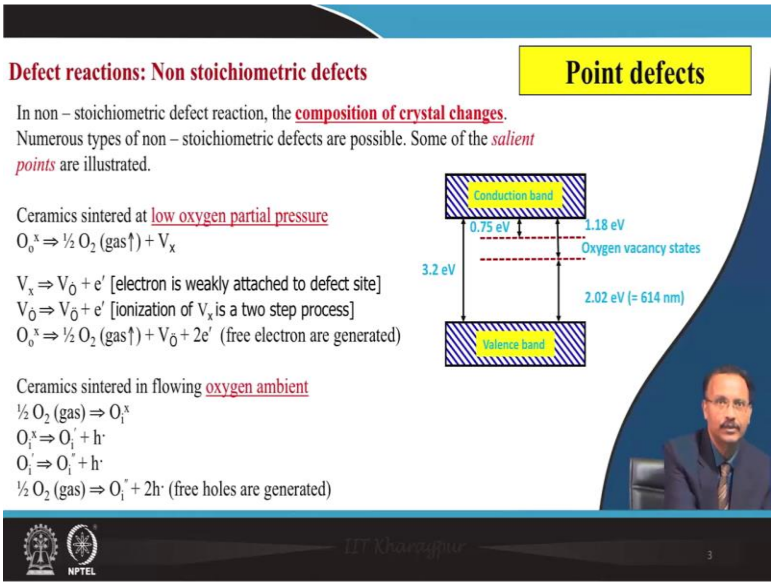
The lecture would describe

- Defect reactions (contd.): non- stoichiometric defects, redox reaction and extrinsic point defects
- Electronic defects
- Defect equilibria and Kroger – Vink diagrams
- Stoichiometric and non – stoichiometric compounds

But today’s chapter is quite interesting because this talks about non-stoichiometry where the chemical composition is changing and we will introduce the concept of the redox reaction. And more importantly the extrinsic point defect effect we call it is aliovalent doping, and this aliovalent doping is very important for the field of ceramic materials.

We will briefly introduce about electronic defects in this type of material, and defect equilibria we will be talking about and how to construct the Kroger and Vink diagram we will learn that. And finally, we will briefly introduce the stoichiometric and non-stoichiometric compounds.

(Refer Slide Time: 01:57)



Defect reactions: Non stoichiometric defects

Point defects

In non – stoichiometric defect reaction, the **composition of crystal changes**. Numerous types of non – stoichiometric defects are possible. Some of the *salient points* are illustrated.

Ceramics sintered at low oxygen partial pressure

$O_o^x \Rightarrow \frac{1}{2} O_2 (gas\uparrow) + V_x$

$V_x \Rightarrow V_{\dot{O}} + e'$ [electron is weakly attached to defect site]

$V_{\dot{O}} \Rightarrow V_{\ddot{O}} + e'$ [ionization of V_x is a two step process]

$O_o^x \Rightarrow \frac{1}{2} O_2 (gas\uparrow) + V_{\ddot{O}} + 2e'$ (free electron are generated)

Ceramics sintered in flowing oxygen ambient

$\frac{1}{2} O_2 (gas) \Rightarrow O_i^x$

$O_i^x \Rightarrow O_i' + h^{\cdot}$

$O_i' \Rightarrow O_i'' + h^{\cdot}$

$\frac{1}{2} O_2 (gas) \Rightarrow O_i'' + 2h^{\cdot}$ (free holes are generated)

So, to start with you see that now the thing is a bit different. And the difference is that the composition of the crystal changes. In the earlier time we talked about Frankel defect and Schottky defect, one cation vacancy, one anion vacancy or one interstitial defect, one vacancy in terms of the Frankel the stoichiometry remains unchanged.

But many of the ceramic material the composition of the crystal changes and there are numerous types of non-stoichiometric defect. And it is almost impossible to all club together in a single lecture, but only the salient point which is important to be understood we will discuss that.

First you consider that you are annealing or sintering a ceramic material at low oxygen partial pressure. So, you have applied a vacuum pump and then you are sintering at lower oxygen partial pressure. So, oxygen will be lost from the crystal lattice and the vacancy will be created. So, initially the vacancy is not ionized, but progressively it will ionize, we call it is a single ionize.

So, it will have a single ionized oxygen vacancy. And suddenly it will trap electron because oxygen vacancy is positively charged. So, it will trap electron. Followed by again ionization of the oxygen vacancy again it will trap one electron, so two electrons will be trapped. So, basically this reaction will be oxygen is going out from your lattice and creation of oxygen vacancy and two trap electron.

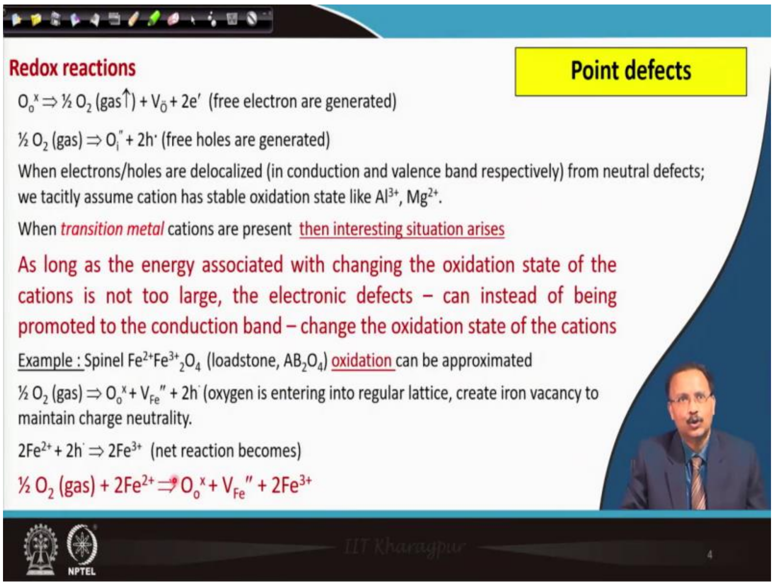
If you see the otherwise insulating material it is having a large band gap, but you are creating this defect level inside the band gap. So, this will trap electron. So, it is not band to band transition that will take place. The electron will get de trapped from this defect level and go to the conduction band and eventually the electronic conductivity of this material maybe improved maybe increased. So, that is one implication.

Similarly, you can consider that you sinter it in flowing oxygen. So, lot of oxygen is there. So, oxygen will be pumped in inside the material. So, it will go to the interstitial and it all depends on the crystal structure. You should have space, in the interstitial to accommodate oxygen ion.

So, not all types of crystal structure will allow you to do that, but certain crystal structure will allow.

So, if it allows, then it will form interstitial oxygen, first it will ionize an oxygen this will carry a negative charge, so it will trap hole. So, it will be near to the valence band this kind of defect level. So, similar to that you have oxygen ion in interstitial for ceramics which are fired in flowing oxygen ambient and free holes will be generated which also eventually will increase the conductivity of this material.

(Refer Slide Time: 05:06)



Redox reactions

Point defects

$O_O^x \Rightarrow \frac{1}{2} O_2 (gas\uparrow) + V_O^{\bullet\bullet} + 2e'$ (free electron are generated)

$\frac{1}{2} O_2 (gas) \Rightarrow O_i'' + 2h^{\bullet}$ (free holes are generated)

When electrons/holes are delocalized (in conduction and valence band respectively) from neutral defects; we tacitly assume cation has stable oxidation state like Al^{3+}, Mg^{2+}.

When *transition metal* cations are present then interesting situation arises

As long as the energy associated with changing the oxidation state of the cations is not too large, the electronic defects – can instead of being promoted to the conduction band – change the oxidation state of the cations

Example : Spinel $Fe^{2+}Fe^{3+}{}_2O_4$ (loadstone, AB_2O_4) oxidation can be approximated

$\frac{1}{2} O_2 (gas) \Rightarrow O_O^x + V_{Fe}'' + 2h^{\bullet}$ (oxygen is entering into regular lattice, create iron vacancy to maintain charge neutrality.

$2Fe^{2+} + 2h^{\bullet} \Rightarrow 2Fe^{3+}$ (net reaction becomes)

$\frac{1}{2} O_2 (gas) + 2Fe^{2+} \Rightarrow O_O^x + V_{Fe}'' + 2Fe^{3+}$

So, another interesting thing can happen, I mean it is not always true that it will go to the conduction band and start to increase the conductivity. So, eventually free electrons are generated, eventually free holes are generated depending on the fact whether you are annealing it in the oxygen, less environment or oxygen affluent environment.

Now, this electron and hole they are delocalized, if they are delocalized in the conduction and valence band from the so called neutral defect. So, that is possible to improve the electronic conductivity.

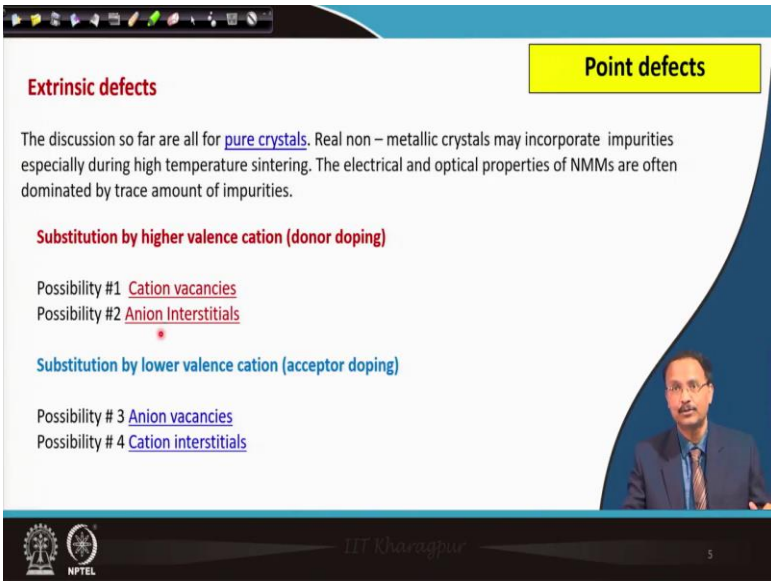
In guessing that we are tacitly assume that the cations that is present they are very stubborn, they will not change its valence state. But consider that you have a transition metal cation where the valence state is not very stubborn like alumina or magnesium oxide or zirconium plus 4 ion. And it is not that kind of stable.

So, as long as the energy which is associated with changing the oxidation state of the cations is not too large then instead of promoting it to the conduction band. Then it is possible to either oxidize or reduce your transition metal cation.

One example I have cited in case of spinel structure, AB_2O_4, it has iron in plus 2 valence state iron in plus 3 valence state. So, here you can see that plus 2 valence state iron, this is actually reacting with the hole which is being generated because of pumping of oxygen and it is oxidized to iron 3 plus. So, you can just add it up, so the reaction relevant is this.

So, this is one implication that whenever you create this electrons and holes in the lattice. Not always it is delocalized in the conduction or valence band, but sometimes it can also change the redox of the constituent transition metal cations.

(Refer Slide Time: 07:15)



Point defects

Extrinsic defects

The discussion so far are all for pure crystals. Real non – metallic crystals may incorporate impurities especially during high temperature sintering. The electrical and optical properties of NMMs are often dominated by trace amount of impurities.

Substitution by higher valence cation (donor doping)

Possibility #1 Cation vacancies
Possibility #2 Anion Interstitials

Substitution by lower valence cation (acceptor doping)

Possibility # 3 Anion vacancies
Possibility # 4 Cation interstitials

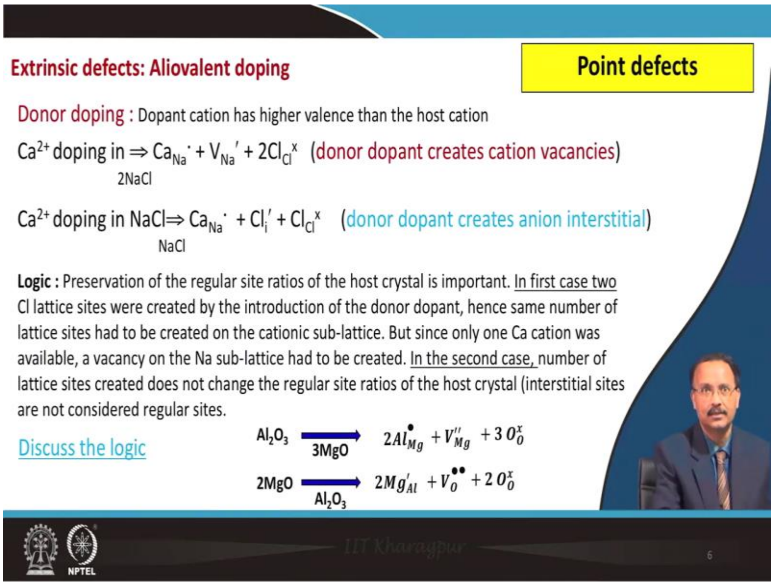
Next we will talk about the extrinsic defect. And extrinsic defect is something some guest ion which can replace the host ion and this guest ion is either having higher valence state or lower valence state than the guest state, guest ion.

So, several possibilities are there, but I have tried to make a generalized statement that if you take a higher valence cation we call it is a donor doping. Then there is one possibility cation vacancy can be created and that is related to the maintaining of electrical charge neutrality.

Remember, in the last class also I talked about it that the charge neutrality must be maintained irrespective of whether it is a stoichiometric defect or non-stoichiometric defect. The site ratio should also be maintained. And third important parameter is that mass will not be destroyed and mass will not be generated. So, these 3 principles are valid for all these cases.

So, two possibility when you are doing donor doping, either cation vacancy will be created or anion interstitial will be created. When you are doing acceptor doping then either anion vacancy will be created or cation interstitial will be created. This is very apparent I mean if you think on it then you will be able to understand the logic. But to start with let us remember these things.

(Refer Slide Time: 08:52)



Extrinsic defects: Aliovalent doping

Point defects

Donor doping : Dopant cation has higher valence than the host cation

Ca^{2+} doping in $\underset{2NaCl}{\Rightarrow} Ca_{Na}^{\cdot} + V_{Na}' + 2Cl_{Cl}^{x}$ (donor dopant creates cation vacancies)

Ca^{2+} doping in NaCl$\underset{NaCl}{\Rightarrow} Ca_{Na}^{\cdot} + Cl_i' + Cl_{Cl}^{x}$ (donor dopant creates anion interstitial)

Logic : Preservation of the regular site ratios of the host crystal is important. In first case two Cl lattice sites were created by the introduction of the donor dopant, hence same number of lattice sites had to be created on the cationic sub-lattice. But since only one Ca cation was available, a vacancy on the Na sub-lattice had to be created. In the second case, number of lattice sites created does not change the regular site ratios of the host crystal (interstitial sites are not considered regular sites.

Discuss the logic

$$Al_2O_3 \xrightarrow[3MgO]{} 2Al_{Mg}^{\bullet} + V_{Mg}'' + 3\,O_O^{x}$$

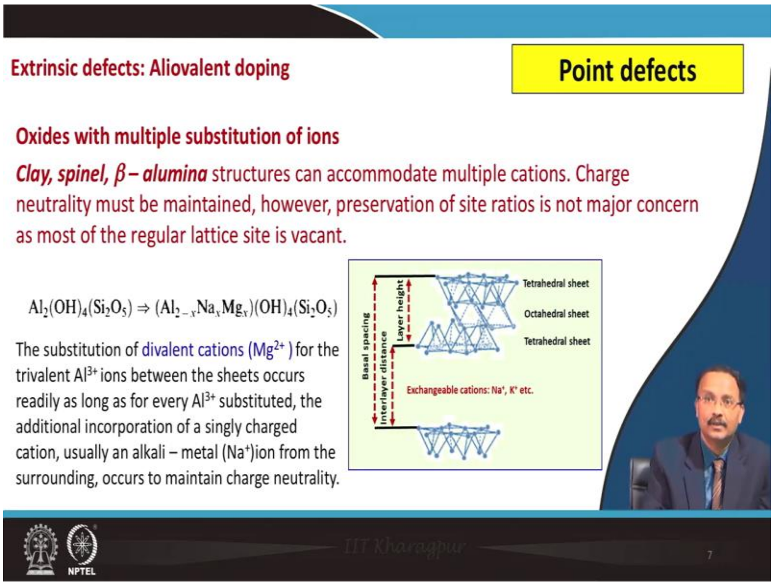
$$2MgO \xrightarrow[Al_2O_3]{} 2Mg_{Al}' + V_O^{\bullet\bullet} + 2\,O_O^{x}$$

So, the example of donor doping, for example, I have taken sodium chloride crystal and I am doping it with calcium oxide. So, calcium 2 plus is there, it is replacing sodium, so it is bringing one positive charge. So, one possibility is that that it creates anion interstitial chloride ion is minus and this plus, so charge neutrality is maintained.

Other possibility what I told that it will create vacancy. So, it is going to the sodium site, it is creating vacancy in the sodium site which is negatively charged. So, somewhere the positive charge will be there and this is the site calcium in sodium lattice positively charged electrical neutrality is maintained. So, this logic will have to be formal, I mean well understand. And for you to do the practice you can do that take magnesium oxide lattice and dope it with alumina. This is one important ceramic system.

Here magnesium is plus 2, alumina is plus 3, aluminum in alumina is plus 3, so it is a donor doping. So, in case of donor doping cation vacancy is being created. If you just reverse it take aluminium oxide dope it with magnesia, so this is plus 3, this is plus 2. So, here acceptor vacancy, I mean acceptor anion vacancy is being created since this is the acceptor doping.

(Refer Slide Time: 10:24)



Extrinsic defects: Aliovalent doping

Point defects

Oxides with multiple substitution of ions

Clay, spinel, β – alumina structures can accommodate multiple cations. Charge neutrality must be maintained, however, preservation of site ratios is not major concern as most of the regular lattice site is vacant.

$$Al_2(OH)_4(Si_2O_5) \Rightarrow (Al_{2-x}Na_xMg_x)(OH)_4(Si_2O_5)$$

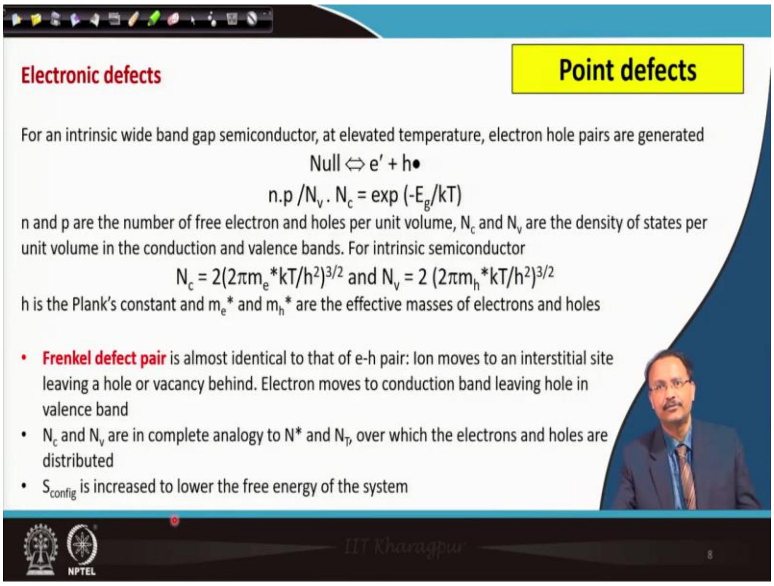
The substitution of divalent cations (Mg^{2+}) for the trivalent Al^{3+} ions between the sheets occurs readily as long as for every Al^{3+} substituted, the additional incorporation of a singly charged cation, usually an alkali – metal (Na^+)ion from the surrounding, occurs to maintain charge neutrality.

Now, it is also possible for you to do multiple kind of aliovalent doping, not only one single cation in a host lattice. And for this type of material clay based material or spinel ceramics or beta alumina that is very much important.

I have sited one example for the clay. You know the clay is having intercalated structure, so the basic formula is having an alumina octahydra and silica base tetra hydra. And here as you can see it replaces part of alumina by magnesia, so this is plus 2 valent. So, in order to maintain the charge neutrality no other defect is formed, but another alkali ion from the neighborhood it can accept to maintain the charge neutrality.

And in fact, the clay is basically it is characterized by this base exchange capacity, how much sodium it can accommodate for certain application, application point of view. So, this is another example of aliovalent doping.

(Refer Slide Time: 11:33)



Point defects

Electronic defects

For an intrinsic wide band gap semiconductor, at elevated temperature, electron hole pairs are generated

$$\text{Null} \Leftrightarrow e' + h^{\bullet}$$

$$n.p / N_v . N_c = \exp(-E_g/kT)$$

n and p are the number of free electron and holes per unit volume, N_c and N_v are the density of states per unit volume in the conduction and valence bands. For intrinsic semiconductor

$$N_c = 2(2\pi m_e^* kT/h^2)^{3/2} \text{ and } N_v = 2\,(2\pi m_h^* kT/h^2)^{3/2}$$

h is the Plank's constant and m_e^* and m_h^* are the effective masses of electrons and holes

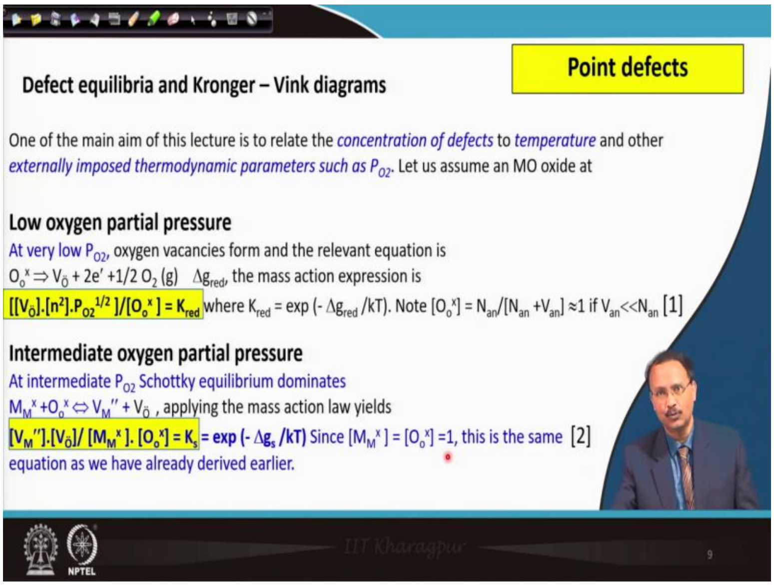
- **Frenkel defect pair** is almost identical to that of e-h pair: Ion moves to an interstitial site leaving a hole or vacancy behind. Electron moves to conduction band leaving hole in valence band
- N_c and N_v are in complete analogy to N^* and N_T, over which the electrons and holes are distributed
- S_{config} is increased to lower the free energy of the system

Apart from that normal electronic defects whatever you know from the semi conducting material that is also prevalent here. So, electron and hole, this two will be constant. So, the concentration of n and p and this is actually the N_v is the density state of the valence band and density state for the conduction band. And which is basically defined by this relations and this is a constant, n and p will always be constant.

And somewhere it is more or less similar to your Frankel defect because you know that here an electron hole pair is generated. There ions move to an interstitial site leaving a hole behind. So, in that respect these two are identical. N_c and N_v which are the density state of conduction band and valence band, they are somewhere related to the interstitial site and the total number of sites whichever is there in the crystal which is showing this Frankel defect.

And eventually the configurational entropy increase to lower the free energy of the system. So, in that way that is also quite straightforward.

(Refer Slide Time: 13:00)



Point defects

Defect equilibria and Kronger – Vink diagrams

One of the main aim of this lecture is to relate the *concentration of defects* to *temperature* and other *externally imposed thermodynamic parameters such as P_{O2}*. Let us assume an MO oxide at

Low oxygen partial pressure

At very low P_{O2}, oxygen vacancies form and the relevant equation is

$O_o^x \Rightarrow V_{\ddot{O}} + 2e' + 1/2\ O_2\ (g)$ Δg_{red}, the mass action expression is

$[[V_{\ddot{O}}].[n^2].P_{O2}^{1/2}]/[O_o^x] = K_{red}$ where $K_{red} = \exp(-\Delta g_{red}/kT)$. Note $[O_o^x] = N_{an}/[N_{an} + V_{an}] \approx 1$ if $V_{an} << N_{an}$ [1]

Intermediate oxygen partial pressure

At intermediate P_{O2} Schottky equilibrium dominates

$M_M^x + O_o^x \Leftrightarrow V_M'' + V_{\ddot{O}}$, applying the mass action law yields

$[V_M''].[V_{\ddot{O}}]/[M_M^x].[O_o^x] = K_s = \exp(-\Delta g_s/kT)$ Since $[M_M^x] = [O_o^x] = 1$, this is the same [2] equation as we have already derived earlier.

Now, we will have to write a defect equilibria and based on that we will have to formulate a Kroger-Vink diagram which will tell me that how the defect concentration changes. For example, with an external factor like oxygen vacancies. So, what I am aiming to do that to correlate the concentration of the defect to temperature and other external stimuli imposed thermal parameters also it is coupled there in terms of its oxygen partial pressure.

So, we have taken a simple metal oxide. So, if you do it do the annealing at low oxygen partial pressure, applying a vacuum pump or something like that. This relation already I have described oxygen vacancy will be created it will trap electron and the energy I free energy change, I am assuming it is a reduction type, so del g rate.

Then, I will write a mass action reaction, so product concentration divided by the reactant concentration and that is related with this equilibrium constant and equilibrium constant is related to this free energy change.

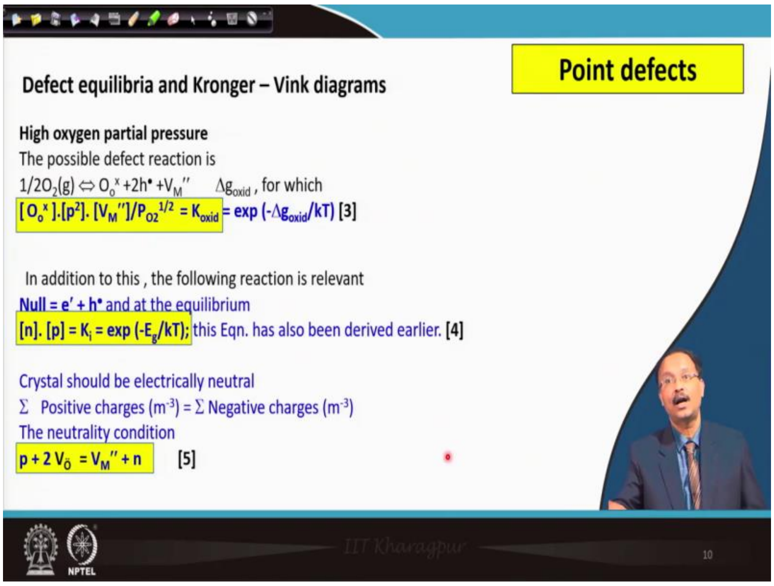
So, this thing I will suggest you follow my lectures and then whatever equation I have written you try to work it out. You just try to work it out whatever is written whether it makes sense because from a class it is impossible for me to make you understand line by line of all the equations. So, I will suggest that after the class you do a homework you just do write this equation and see whatever has been proposed how far it is correct.

So, we will find this is ok and here this oxygen concentration you see this is nothing, but number of anion divided by total site including regular anion site and the vacancy anion site, right. So, this is very small anion vacancy is very small. So, eventually this is 1. So, if this number of vacancy is very small as compared to the regular lattice site then this concentration of oxygen we can take 1.

Similar equation I have written for intermediate oxygen partial pressure. So, here not only oxygen vacancy, but your metal vacancy is also possible. So, this is a typical example of the Schottky defect.

And you write the relation here. And also mass action law you apply you come up with the following relation which is marked yellow marked here, right. So, you create the metal vacancy, oxygen vacancy divided by concentration of metal and concentration of oxygen. And here also the concentration of metal and oxygen this is same and equal to 1 because it is a Schottky defect.

(Refer Slide Time: 16:11)



Defect equilibria and Kronger – Vink diagrams

Point defects

High oxygen partial pressure

The possible defect reaction is

$1/2O_2(g) \Leftrightarrow O_o^x + 2h^\bullet + V_M''$ Δg_{oxid}, for which

$[O_o^x].[p^2].[V_M'']/P_{O2}^{1/2} = K_{oxid} = \exp(-\Delta g_{oxid}/kT)$ [3]

In addition to this , the following reaction is relevant

Null = $e' + h^\bullet$ and at the equilibrium

$[n].[p] = K_i = \exp(-E_g/kT)$; this Eqn. has also been derived earlier. [4]

Crystal should be electrically neutral

Σ Positive charges (m^{-3}) = Σ Negative charges (m^{-3})

The neutrality condition

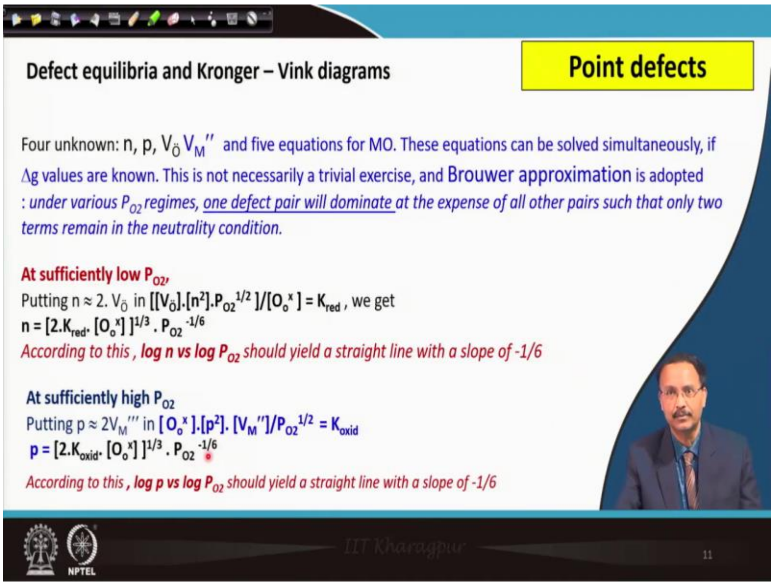
$p + 2V_{\ddot{o}} = V_M'' + n$ [5]

Then you go to high oxygen partial pressure, what will happen? That oxygen will come into the lattice and it will create hole into the lattice. So, oxygen is coming into the lattice creation of hole is there and eventually in order to maintain the charge neutrality vacancy in the cation site will be there. So, this is nothing but superoxide.

You see that ZnO and then put lot of oxygen eventually if it is ZnO_2; that means, your cation vacancy is taking place. So, I have written this relation and this is my relation for the third equation, I mean the third case where high oxygen partial pressure is there.

Fourth one is simple like wide band gap semiconductor you have electron and hole, the law of mass action tells you that it is related to the band gap. And finally, the material or the crystal should be electrically neutral. So, all your positive charge, so your positive charge is in terms of hole p type conductor in terms of oxygen vacancy, which is positively charged and negative is cation vacancy and electron. So, they should equate. So, electrically the material should be completely neutral.

(Refer Slide Time: 17:32)



Defect equilibria and Kronger – Vink diagrams

Point defects

Four unknown: n, p, $V_{\ddot{O}}$ V_M'' and five equations for MO. These equations can be solved simultaneously, if Δg values are known. This is not necessarily a trivial exercise, and **Brouwer approximation** is adopted *: under various P_{O2} regimes, one defect pair will dominate at the expense of all other pairs such that only two terms remain in the neutrality condition.*

At sufficiently low P_{O2},

Putting $n \approx 2.V_{\ddot{O}}$ in $[[V_{\ddot{O}}].[n^2].P_{O2}^{1/2}]/[O_o^x] = K_{red}$, we get

$n = [2.K_{red}.[O_o^x]]^{1/3}.P_{O2}^{-1/6}$

*According to this, **log n vs log P_{O2}** should yield a straight line with a slope of -1/6*

At sufficiently high P_{O2}

Putting $p \approx 2V_M'''$ in $[O_o^x].[p^2].[V_M'']/P_{O2}^{1/2} = K_{oxid}$

$p = [2.K_{oxid}.[O_o^x]]^{1/3}.P_{O2}^{-1/6}$

*According to this, **log p vs log P_{O2}** should yield a straight line with a slope of -1/6*

Now, eventually you have this four variables, right concentration of electron, concentration of hole, oxygen vacancy and metal vacancy. And you have five equations. So, usually you will be able to easily estimate the defect concentration because you have five equation four unknown. But actually this is done by a famous approximation that is known as Brouwer approximation.

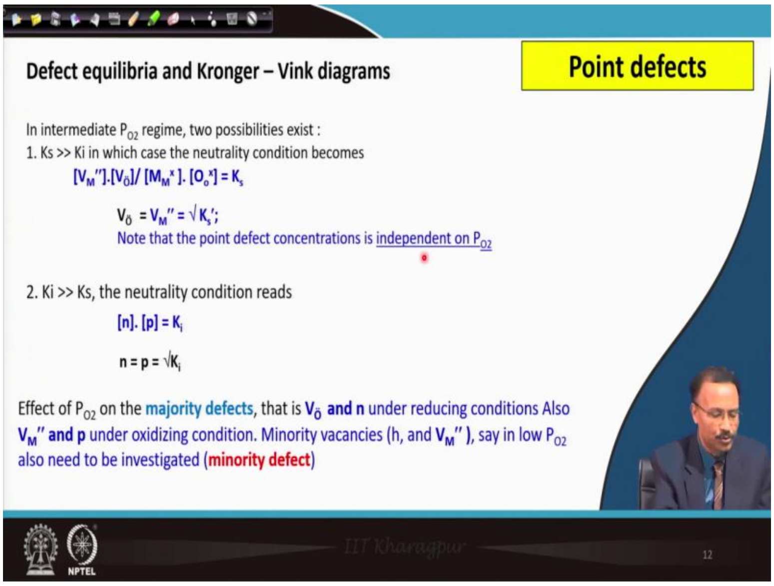
And what this Brouwer approximation tells? That one defect pair will dominate the process. So, if it is sufficiently low pressure partial pressure of oxygen, then what is happening? Oxygen vacancy is being created and that is the dominant defect. So, I can put the number of electron is twice of oxygen vacancy, one single oxygen vacancy one single oxygen forms one oxygen vacancy. So actually it is a di-molecular gas so two oxygen vacancy will form.

So, I will write instead of the vacancy concentration in my last equation, equation number 1, I will just replace this one with two vacancy of oxygen. So, it will be n divided by 2. And once you do that then you can estimate the concentration of n that is given by this relation and it actually has a minus one-sixth power with the oxygen partial pressure, right?

Its significance I will let you know. So, what you are doing? You are correlating the defect concentration with oxygen partial pressure at a particular temperature.

At sufficiently high oxygen partial pressure, again the concentration of hole the p type of carrier concentration that will be related with the metal cation vacancies, right. And here also the p, the log of this p will be a straight line here from this relation and the slope because if we are plotting with l n of partial pressure of oxygen it will be minus 1 by 6 from this relations.

(Refer Slide Time: 19:58)



Defect equilibria and Kronger – Vink diagrams

Point defects

In intermediate P_{O2} regime, two possibilities exist :

1. Ks >> Ki in which case the neutrality condition becomes

$$[V_M''].[V_{\ddot{O}}]/ [M_M^x]. [O_o^x] = K_s$$

$$V_{\ddot{O}} = V_M'' = \sqrt{K_s'};$$

Note that the point defect concentrations is independent on P_{O2}

2. Ki >> Ks, the neutrality condition reads

$$[n]. [p] = K_i$$

$$n = p = \sqrt{K_i}$$

Effect of P_{O2} on the **majority defects**, that is **$V_{\ddot{O}}$ and n** under reducing conditions Also **V_M'' and p** under oxidizing condition. Minority vacancies (h, and **V_M''**), say in low P_{O2} also need to be investigated (**minority defect**)

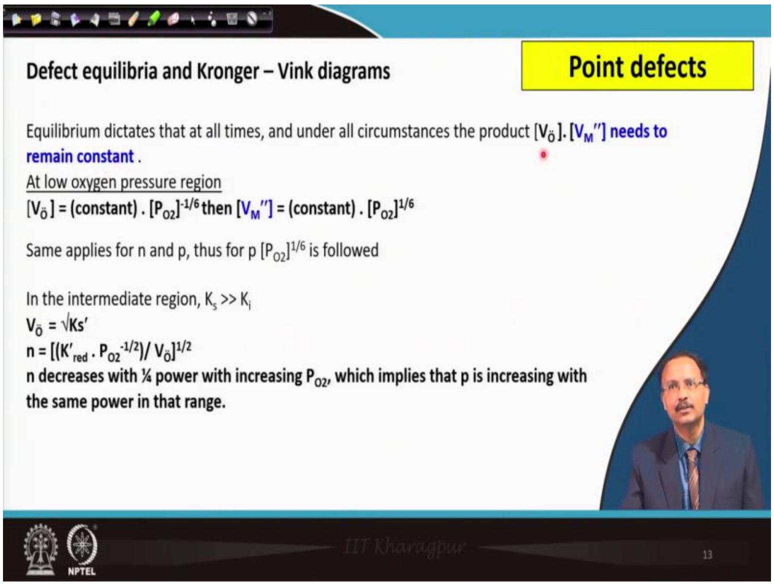
When the Schottky defect is happening there are two possibilities, either the Schottky equilibrium coefficient this K_s value is much larger than your intrinsic K value that is K_i or the vice versa. So, in the first case it is the Schottky defect which will be prevalent.

In the second case, your electron and hole concentration will be prevalent. So, here also you can do the same kind of formulism one can do. And you will come up with oxygen vacancy concentration and metal vacancy concentration they are almost similar and this is nothing, but root over of the value of K_S. So, this tells me that this is independent of the partial pressure of oxygen.

In the last class, both the gases, low oxygen partial pressure, high oxygen partial pressure, it was dependent with partial pressure to the power the power was minus one-sixth. Here it is independent of this. So, this is the way to determine various types of major defects. In this case, the major defects are oxygen vacancy, number of electron and so on and so forth.

So, the majority defects oxygen vacancy and n the number of electron, under reducing condition also under oxidizing condition it is metal vacancy and concentration of hole they are important. But side by side the minority defects are also there because in the former case hole and metal vacancies are the minority defect and this also you will have to understand.

(Refer Slide Time: 22:03)



Defect equilibria and Kronger – Vink diagrams

Point defects

Equilibrium dictates that at all times, and under all circumstances the product $[V_{\ddot{O}}]$. $[V_M'']$ **needs to remain constant**.

At low oxygen pressure region

$[V_{\ddot{O}}] = (\text{constant}) . [P_{O2}]^{-1/6}$ then $[V_M''] = (\text{constant}) . [P_{O2}]^{1/6}$

Same applies for n and p, thus for p $[P_{O2}]^{1/6}$ is followed

In the intermediate region, $K_s >> K_i$

$V_{\ddot{O}} = \sqrt{Ks'}$

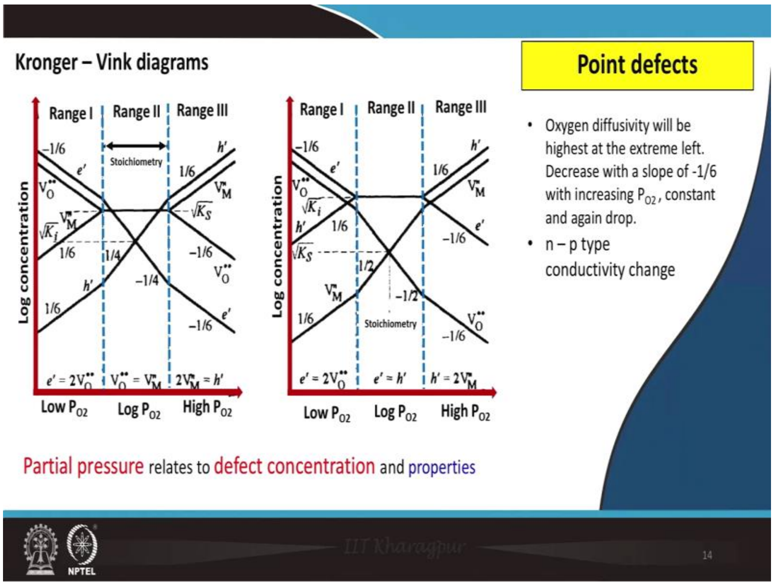
$n = [(K'_{red} . P_{O2}^{-1/2})/ V_{\ddot{O}}]^{1/2}$

n decreases with ¼ power with increasing P_{O2}, which implies that p is increasing with the same power in that range.

So, that is pretty straight forward because you know that this relation is always valid. So, concentration of the oxygen vacancy and concentration of this metal, this will remain constant. In semiconductor also you know that the concentration of n and p they are constant. So, this same thing is applied here, and then I do I write a expression for oxygen vacancy and I write an expression for metal vacancy, and it will see that if needs to be constant then this two powers should cancel. So, if 1 is minus 1 by 6, another has to be plus 1 by 6.

And the intermediate region, as I showed that the oxygen vacancy that goes with root over of K_i. So, if you just replace this value for the Schottky defect then the number of n actually it is the vacancy you are replacing it with this the value of K_s, so the power dependence will be one-forth, power dependence will be one-forth in this region.

(Refer Slide Time: 23:16)



Kronger – Vink diagrams

Point defects

- Oxygen diffusivity will be highest at the extreme left. Decrease with a slope of -1/6 with increasing P_{O2}, constant and again drop.
- n – p type conductivity change

Partial pressure relates to defect concentration and properties

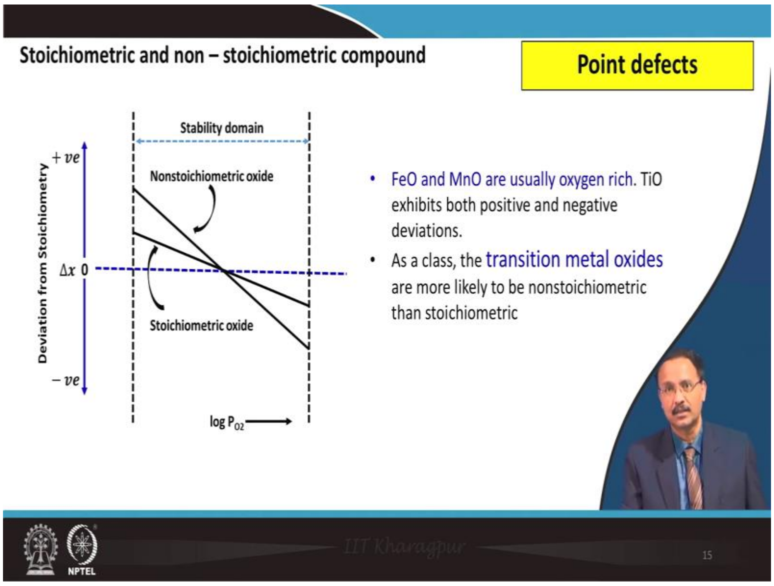
So, all this calculation, particularly we have done here a very simple calculation we try to understand the vacancy concentration, various types of defect, point defects, but the variable is only oxygen partial pressure. We have not completed it by aliovalent doping or by some other means, right. So, it is only simple oxygen vacancy in your annealing ambient I have just demonstrated.

The first case is in one case where the Schottky defect is prevalent and the second one where the electronic defect is prevalent. So, here you just draw the straight line according to the slope. Initial case you see it this is minus 1 by 6, this is also minus 1 by 6 at high oxygen partial pressure and low oxygen partial pressure.

Now, in between the slope changes to minus 1 by 4 that also I have shown. But if you see the metal vacancy concentration it is one-sixth which is just reverse than your oxygen vacancy concentration. And here in this region the intermediate region where the Schottky defect is prevailing then it is independent of the partial pressure. So, this partial pressure that relates to the defect concentration and property.

So, this has immense influence in terms of understanding of the material property. For example the oxygen diffusivity will be highest where at the extreme left where the oxygen diffusion is possible decrease the slope to minus 1 by 6 with increase in partial pressure and then it again drops down. In case of electronic defect, you can see n type is being converted to p type. So, the conductivity changes into p transition that can be predicted from this kind of Kroger and Vink diagrams.

(Refer Slide Time: 25:19)



Stoichiometric and non – stoichiometric compound

Point defects

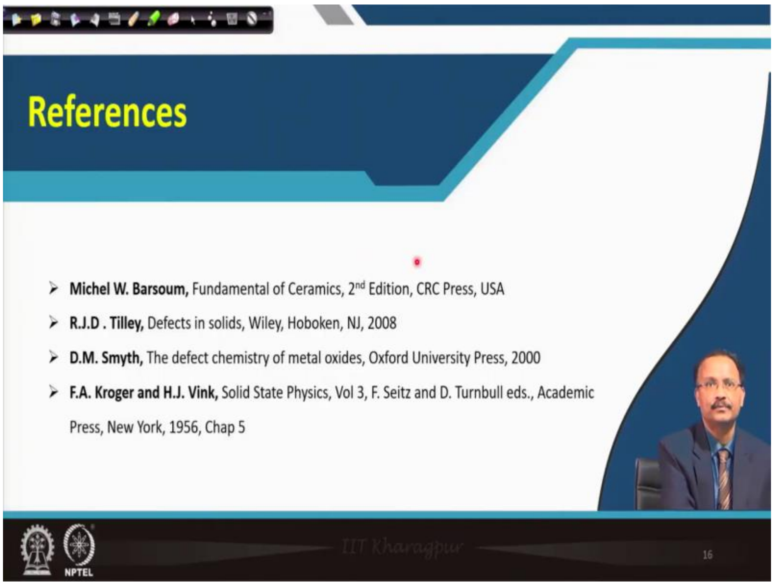
- FeO and MnO are usually oxygen rich. TiO exhibits both positive and negative deviations.
- As a class, the transition metal oxides are more likely to be nonstoichiometric than stoichiometric

So, based on that you can always construct a stoichiometric and non-stoichiometric compound. So, non-stoichiometric compound as you can see that when you anneal it at lower oxygen partial pressure or higher oxygen partial pressure, then this deviation of its composition is too much.

If you are starting with titanium oxide, then if it is non-stoichiometric like lead oxide then at low oxygen partial pressure lot of oxygen vacancy will be created. At high oxygen partial pressure superoxide will form, so they are not stable.

But the so called stoichiometric oxide you will find that this deviation of the oxide content or the metal vacancy the way you interpret it, they are much more stable. So, in fact, there is only one partial pressure where the deviation is actually 0, but that will not allow you only to use this partial pressure to process your ceramic material. But usually if you are working with transition metal cation where the valence states are changed then the non-stoichiometry is very prominent. So, transition metal if we are working with the transition metal oxide type of ceramic non-metallic materials then you will have to be careful.

(Refer Slide Time: 26:43)

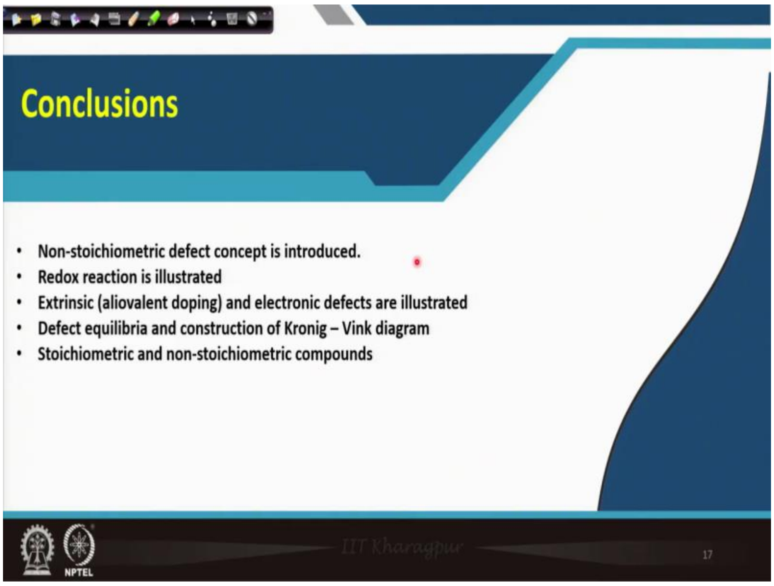


References

- **Michel W. Barsoum,** Fundamental of Ceramics, 2nd Edition, CRC Press, USA
- **R.J.D . Tilley,** Defects in solids, Wiley, Hoboken, NJ, 2008
- **D.M. Smyth,** The defect chemistry of metal oxides, Oxford University Press, 2000
- **F.A. Kroger and H.J. Vink,** Solid State Physics, Vol 3, F. Seitz and D. Turnbull eds., Academic Press, New York, 1956, Chap 5

So, this is the reference. One of the best references of non-stoichiometric material.

(Refer Slide Time: 26:52)



Conclusions

- Non-stoichiometric defect concept is introduced.
- Redox reaction is illustrated
- Extrinsic (aliovalent doping) and electronic defects are illustrated
- Defect equilibria and construction of Kronig – Vink diagram
- Stoichiometric and non-stoichiometric compounds

And I can conclude that I have make I mean try to make you understand about the non-stoichiometric defect concept, then the redox reaction also we have introduced. Then extrinsic doping we have touched upon aliovalent doping, and defect equilibria, and concentric construction of a Kroger and Vink diagram. And finally, stoichiometric non-stoichiometric compound we have touched up on.

Thank you so much, for your attention.