Fundamentals and Applications of Dielectric Ceramics

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Lecture - 13
Intrinsic Ionization in Metal Oxide

So, welcome again to this new lecture of the course fundamentals and applications of dielectric ceramics. So, let us just briefly recap what we were doing earlier.

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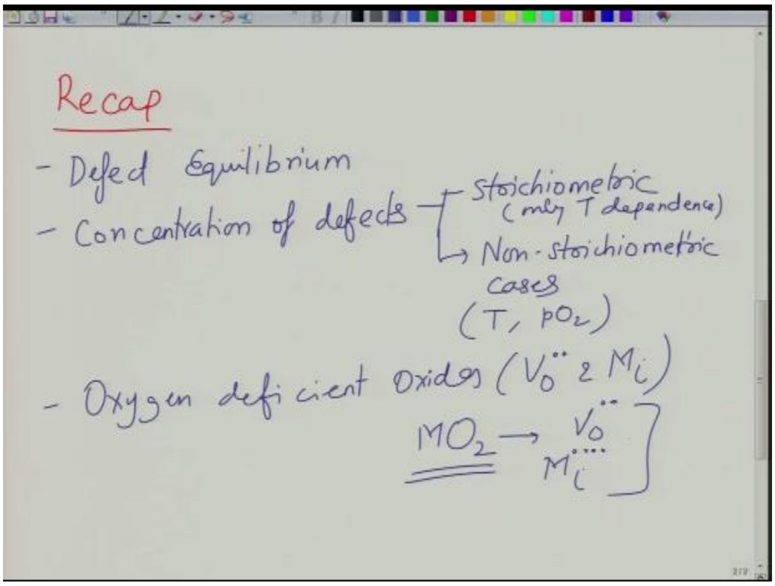

Recap

- Defect Equilibrium
- Concentration of defects
  - Stoichiometric (only T dependence)
  - → Non-stoichiometric cases (T, pO_2)
- Oxygen deficient oxides ($V_O^{\bullet\bullet}$ & M_i)

$MO_2 \rightarrow V_O^{\bullet\bullet}$, $M_i^{\bullet\bullet\bullet\bullet}$

So, in the previous few lectures, we looked at the defect equilibrium. So, basically, we estimated the concentration of defects for stoichiometric cases in which there is only temperature dependence is there for all the concentrations and then we looked at non-stoichiometric cases, where you have temperature as well as partial pressure of oxygen dependence. So, we looked at the case for oxygen deficient oxides in which you can have vacancy of oxygen as well as metal interstitial and we looked at the case of MO_2.

So MO_2 will have Vo as well as Mi as dominant defects. So, we looked at the cases when vacancy of oxygen dominates, we looked at the case when metal interstitial dominates, and we looked at the case when both of them coexist. So, as a result, you have a mixed kind of plot that you get.

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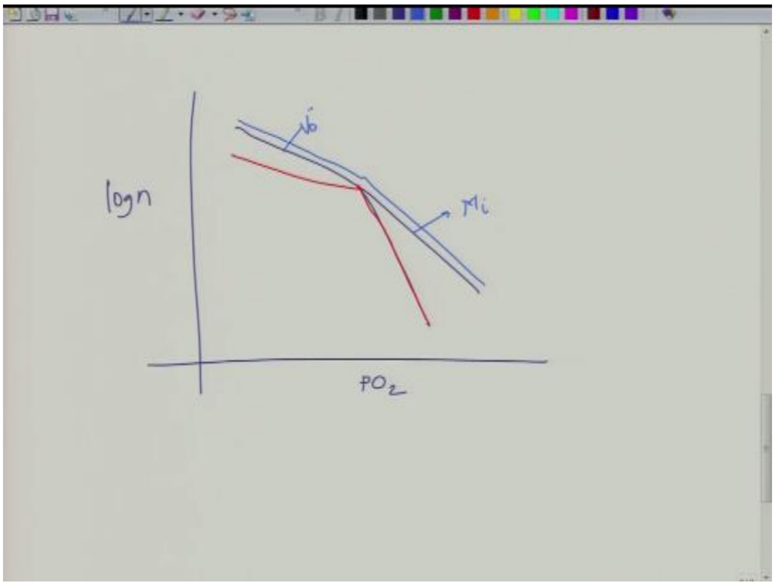

So, if you recall then we plotted this $\log n$ *vs* pO$_2$, you had dependence, which was something like this and other defect went like this okay. So, in one case, alright, so, it is little bit steep actually. So, it could be little bit something like that okay and then electron concentration will go on top like this. So, in one case, you have vacancies dominating, in the other case, you have metal interstitials domination as a function of partial pressure of oxygen and they will all have different dependence on partial pressure of oxygen.

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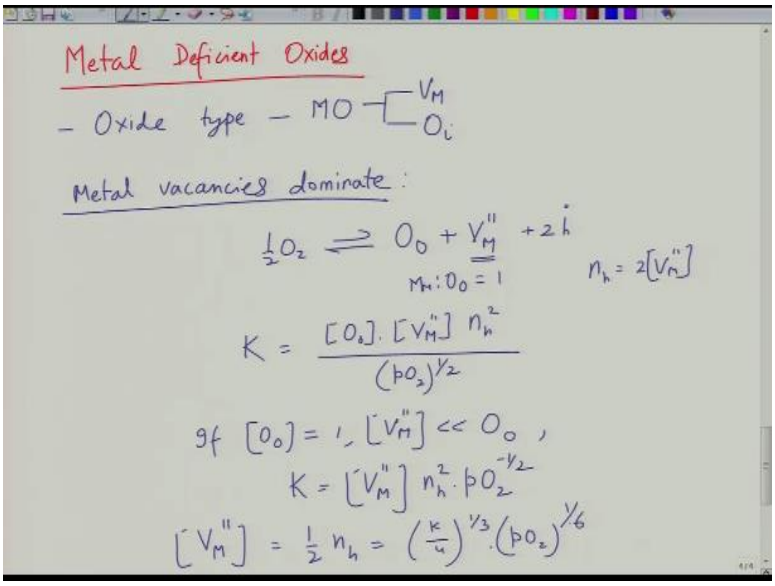

Metal Deficient Oxides

- Oxide type – MO – V_M, O_i

Metal vacancies dominate:

$$\frac{1}{2}O_2 \rightleftharpoons O_O + \underline{\underline{V_M''}} + 2h^{\bullet}$$

$M_M : O_O = 1$ $\qquad n_h = 2[V_M'']$

$$K = \frac{[O_O].[V_M'']\,n_h^2}{(pO_2)^{1/2}}$$

If $[O_O] = 1$, $[V_M''] << O_O$,

$$K = [V_M'']\,n_h^2 \cdot pO_2^{-1/2}$$

$$[V_M''] = \frac{1}{2}n_h = \left(\frac{K}{4}\right)^{1/3} \cdot (pO_2)^{1/6}$$

So, now, let us look at the cases of metal deficient oxides. So, let us look at the example of so oxide type is MO. So, MO can have either vacancy of metal or oxygen interstitial, these are 2 possible defects that you can have. So, in this case, we will just proceed with the metal vacancies. So, if metal vacancies dominate, then you can do for MO kind of oxide, the oxygen in the system enters from outside.

$$\frac{1}{2}O_2 \leftrightarrow O_O + V_M'' + 2h^{\cdot}$$

So, oxygen goes to oxygen site, for maintaining the site of stoichiometry, you will form a metal vacancy so that you have M_M/O_O ratio is 1.

So, you create this site which is vacant and as a result it gives rise to 2 holes to maintain the charge neutrality. So, equilibrium constant for this action can be written as

$$K = \frac{[O_O] \cdot [V_M''] \cdot n_n^2}{(pO_2)^{1/2}}$$

If, $[O_O] = 1, [V_M''] \ll O_O$

Then, $K = [V_M''] \cdot n_n^2 \cdot (pO_2)^{-1/2}$

So what is the electrical neutrality condition, the electrical neutrality condition says that n_h is equal to twice of V_M, you create 2 holes for every oxygen metal vacancy and as a result, you can now substitute this to calculate what is

$$[V_M''] = \frac{1}{2}n_h = \left(\frac{K}{4}\right)^{1/3} \cdot (pO_2)^{1/6}$$

So, in this case, you can see that concentration is proportional to partial pressure of oxygen, but it is other way round.

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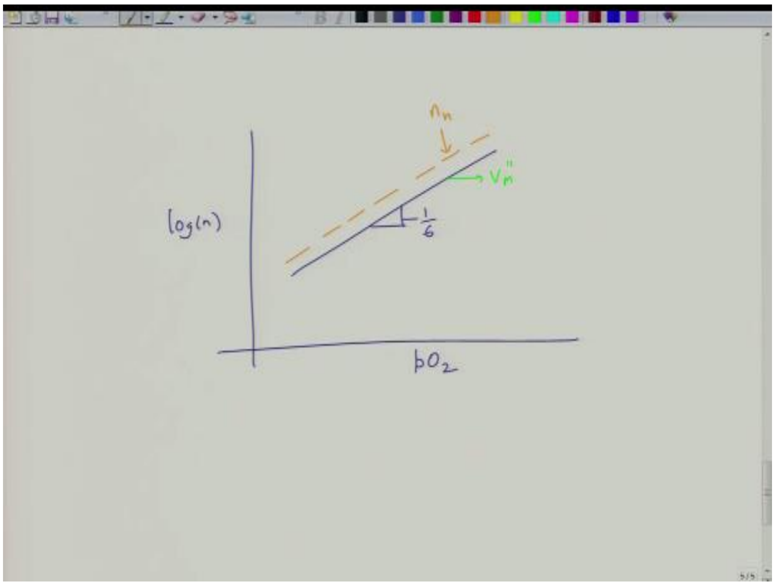

So, if you plot log n as a function of pO_2, now, the defect concentration increases. So basically, this is 1/6. So, this is for V_M and you can plot a similar line for, this would be n_h okay. So, you can do the similar exercise for oxygen interstitial as well, which we will not do.

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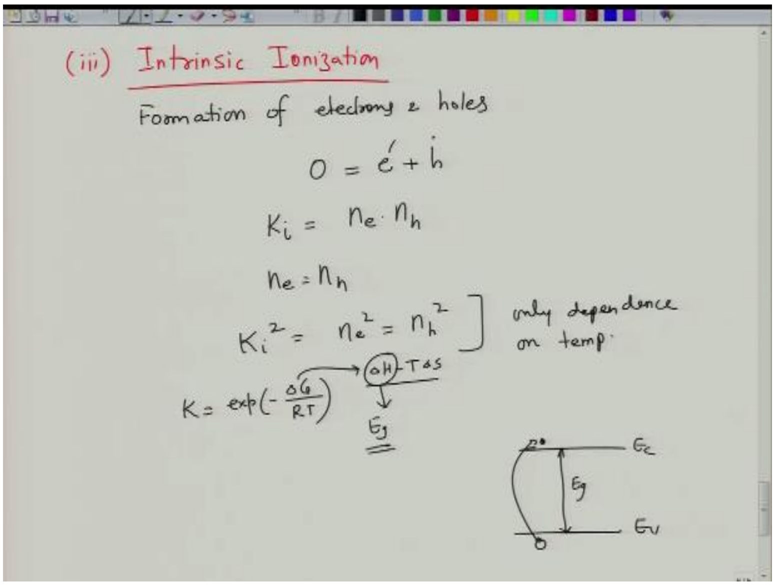

(iii) Intrinsic Ionization

Formation of electrons & holes

$$0 = e' + \dot{h}$$

$$K_i = n_e \cdot n_h$$

$$n_e = n_h$$

$$K_i^2 = n_e^2 = n_h^2$$ only dependence on temp.

$$K = exp\left(-\frac{\Delta G}{RT}\right) \rightarrow \boxed{\Delta H} - T\Delta S, \quad \Delta H \downarrow E_g$$

The third case could be the case when intrinsic ionization is strong. So, we looked at the case of oxygen deficiency, we looked at the case of metal deficiency, and then we look at the case of third case as intrinsic ionization and this is something that can happen in any system. So, what it would mean is basically formation of electrons and holes,

$$0 = e' + h^{\cdot}$$

and again this is stoichiometric, it does not change the stoichiometric. So, in this case, let us say K_i is the reaction constant.

$$K_i = n_e \cdot n_h$$

Then this will become

$$n_e = n_h$$

you can write

$$K_i^2 = n_e^2 = n_h^2$$

this is for intrinsic ionization in case when, so again this is similar to stoichiometric defects okay. So, in this only dependence on because

$$K = exp\left(-\frac{\Delta G}{RT}\right)$$

and $\Delta G = \Delta H - T\Delta S$, $\Delta H = E_g$ = enthalpy of formation of defects.

In this case, its intrinsic ionization, what is the intrinsic ionization enthalpy, it is nothing but band gap right.

So, if you have a system like this where you have E_c, E_v, so to create the electron whole pair, you need to excite an electron, make it go here, and you form a hole here and the energy that you need to overcome is the band gap. So, in this case, it is defect formation energy, in this case is nothing but the band gap of material okay. So, this will be nothing but similar to band gap of the material and again it is independent of temperature, sorry, it is independent of partial pressure of oxygen, it is only dependent upon.

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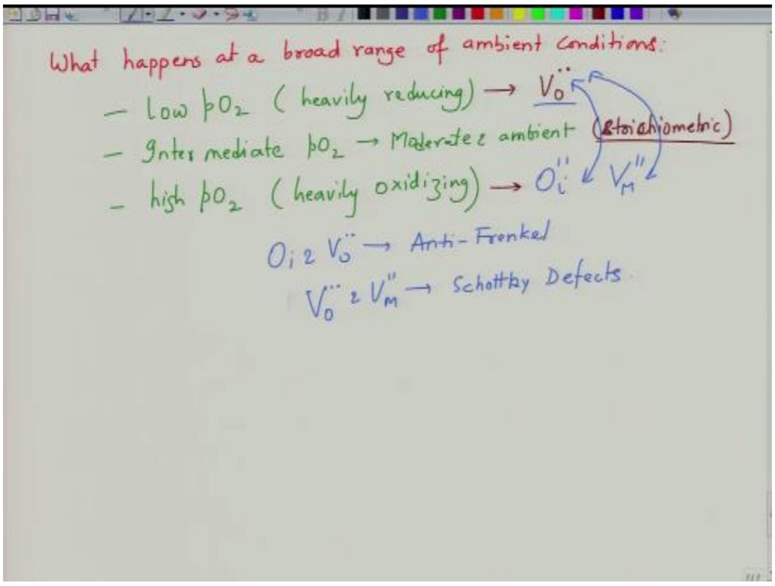

What happens at a broad range of ambient conditions:

- low pO_2 (heavily reducing) → $V_O^{\cdot\cdot}$
- Intermediate pO_2 → Moderate & ambient (stoichiometric)
- high pO_2 (heavily oxidizing) → O_i'' & V_M''

O_i & $V_O^{\cdot\cdot}$ → Anti-Frenkel

$V_O^{\cdot\cdot}$ & V_M'' → Schottky Defects

So now, let us make a broader picture. So, suppose you have oxide, dielectric oxide. So, basically, what happens at a broad range of ambient conditions? So, how can you define them? Now, first condition can be low partial pressure of oxygen, which means heavily reducing conditions right, so heavily reducing conditions, then you can have intermediate pO_2 which means it is moderate or we can say ambient sort of conditions, right. It can depend upon oxide to oxide, but let us say it is ambient for the case that we have and then we have high pO_2, which is heavily oxidizing.

Now, from the previous analysis, you can see low partial pressure of oxygen leads to what kind of defects, basically when you reduce the oxygen concentration in a material, you create more and more vacancies of oxygen. So, under this condition, V_O let us say is the dominant defect. Let us not consider metal interstitial, let us just consider V_O. What will happen at high pO_2? You will have metal vacancies at high partial pressure of oxygen and then we have intermediate range we have oxide as stoichiometric, the stoichiometry does not change.

So, you form stoichiometric defects, those documented defects could be Schottky defects or Frenkel defects or it could be an electron whole pairs, but there is no change in not defect chemistry at intermediate pressures of oxygen. So, let us say, so in this case let us consider instead of V_M, let us consider O_i okay. So, we consider O_i and V_O. So, the dominant effects are oxygen vacancies and metal interstitial and when you have this kind of oxygen interstitial plus vacancy of oxygen for them to go in tandem across various ranges of oxygen pressures.

The combination of O_i and V_O gives rise to what kind of defect? We have anti-Frenkel defects okay. If it was V_M, it would have been, if it was V_O and V_M, what would it have been? Okay, so accordingly you will have the defects formation at stoichiometric condition. So, if you consider V_O and O_i, then the defect that will form, that is likely to form under stoichiometric condition is anti-Frenkel, and if your combination of defects is V_O and V_M, then you are likely to form Schottky defects. So, let us say we first considered low partial pressure of oxygen situation.

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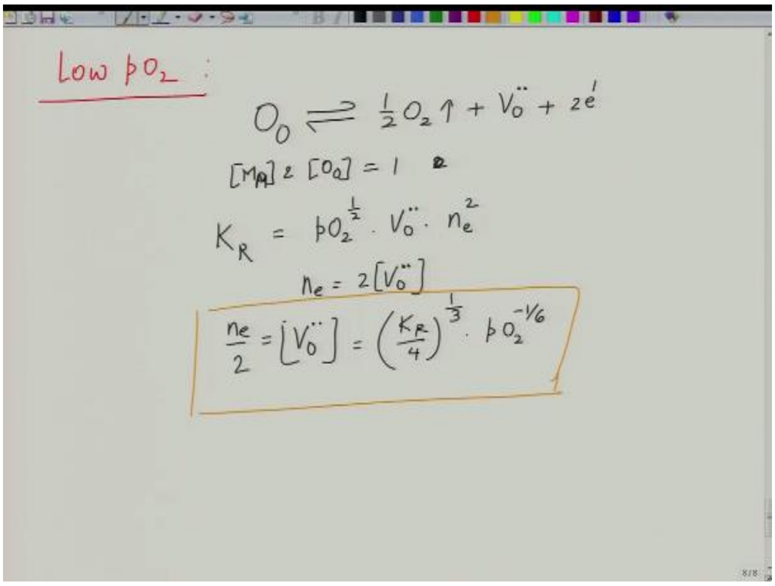

Low pO_2 :

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

$$[M_A] = [O_O] = 1$$

$$K_R = pO_2^{\frac{1}{2}} \cdot V_O^{\cdot\cdot} \cdot n_e^2$$

$$n_e = 2[V_O^{\cdot\cdot}]$$

$$\boxed{\frac{n_e}{2} = [V_O^{\cdot\cdot}] = \left(\frac{K_R}{4}\right)^{\frac{1}{3}} \cdot pO_2^{-1/6}}$$

So, let us say we first considered low pO2. If we consider low pO2, then the defect reaction can be

$$O_O \leftrightarrow \frac{1}{2}O_2 \uparrow + V_O^{\cdot\cdot} + 2e'$$

oxygen at oxygen site goes out okay. It gives rise to formation of oxygen vacancy and then this is compensated by a formation of 2 electrons. So, we consider only electronic compensation, let us not worry about ionic composition, otherwise you can do in terms of ionic composition and let us assume that activities

$$[M_A] = [O_O] = 1$$

Then we can write this reaction as the reaction constant for this is let us say, so this is a reducing reaction, we can write this as,

$$K_R = pO_2^{1/2} \cdot V_O^{\cdot\cdot} \cdot n_e^2$$

and

$$n_e = 2[V_O^{\cdot\cdot}]$$

we can write this as

$$\frac{n_e}{2} = [V_O^{\cdot\cdot}] = \left(\frac{K_R}{4}\right)^{1/3} . pO_2^{-1/6}$$

This will be my first expression for carrier concentration for the low pO_2 condition.

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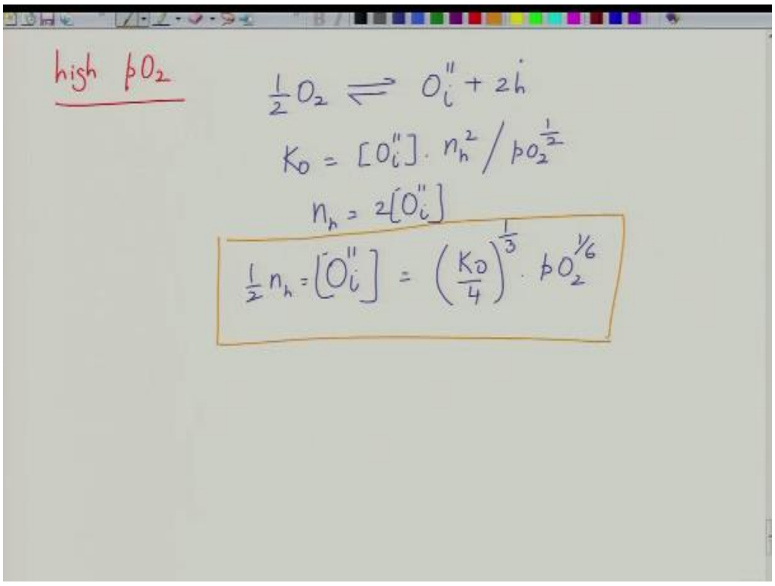

high pO_2

$$\frac{1}{2}O_2 \rightleftharpoons O_i'' + 2h^{\cdot}$$

$$K_O = [O_i''] . n_h^2 / pO_2^{\frac{1}{2}}$$

$$n_h = 2[O_i'']$$

$$\boxed{\frac{1}{2}n_h = [O_i''] = \left(\frac{K_O}{4}\right)^{\frac{1}{3}} . pO_2^{1/6}}$$

Now, let us look at what will happen at high pO2 condition? At high pO2, we know that we have more oxygen in ambient, as a result oxygen gets into the system. So let us say oxygen goes to interstitial site and then it forms 2 holes right.

$$\frac{1}{2}O_2 \leftrightarrow O_i'' + 2h^{\cdot}$$

There is no site conservation problem because oxygen goes to interstitial site, does not go to lattice sites, as a result, we do not need to create or destroyer a site.

So now, this is oxidizing reaction, then for this accordingly you can write reaction constant

$$K_O = [O_i''] \cdot {n_h^2}\big/{pO_2^{1/6}}$$

, n_h being equal to two of O_i, you can write

$$\frac{n_h}{2} = [O_i''] = \left(\frac{K_O}{4}\right)^{1/3} . pO_2^{1/6}$$

So, this is my second concentration of careers.

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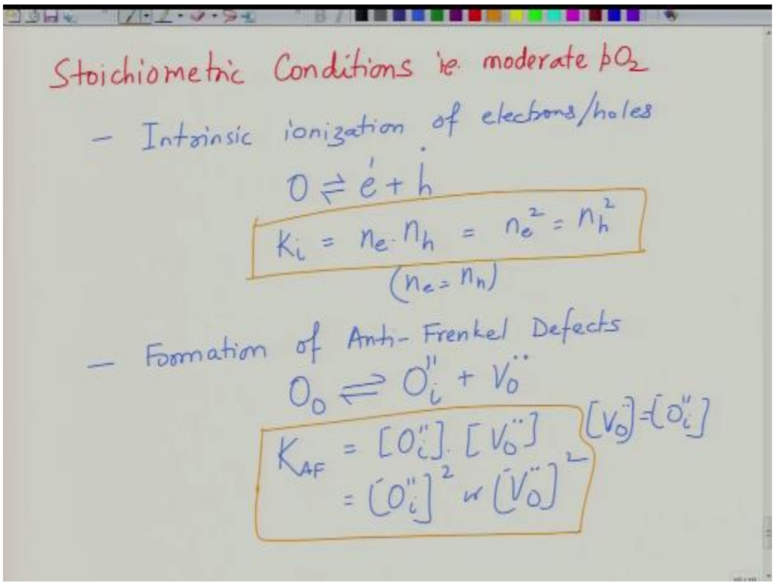

Stoichiometric Conditions i.e. moderate pO_2

- Intrinsic ionization of electrons/holes

$$0 \rightleftharpoons e' + h^{\cdot}$$

$$\boxed{K_i = n_e \cdot n_h = n_e^2 = n_h^2}$$

$(n_e = n_h)$

- Formation of Anti-Frenkel Defects

$$O_O \rightleftharpoons O_i'' + V_O^{\cdot\cdot}$$

$[V_O^{\cdot\cdot}] = [O_i'']$

$$\boxed{\begin{aligned} K_{AF} &= [O_i''] \cdot [V_O^{\cdot\cdot}] \\ &= [O_i'']^2 \text{ or } [V_O^{\cdot\cdot}]^2 \end{aligned}}$$

Now what will happen at stoichiometric conditions? Now third is that is moderate pO_2 okay, partial pressure of oxygen. So, under these 2 scenarios might happen, the first scenario is intrinsic ionization of electrons and holes. So, if the band gap of material is small, then there is a possibility you might form intrinsic ionized defects. So, in such a scenario, your defects that will form is

$$0 = e' + h^{\cdot}$$

and in this case Ki would be

$$K_i = n_e \cdot n_h = n_e^2 = n_h^2$$

because of electrical neutrality,

$$n_e = n_h$$

So, this is third one and the second scenario that might happen is formation of anti-Frenkel defects okay, so which means oxygen and oxygen site goes to interstitial and as a result it forms vacant sites of oxygen.

$$O_O \leftrightarrow O_i'' + V_O^{\cdot\cdot}$$

So, I can write this

$$K_{AF} = [O_i''] \cdot [V_O^{\cdot\cdot}]$$

and this is equal to

$$K_{AF} = [O_i'']^2 \; or \; [V_O^{\cdot\cdot}]^2$$

because of electrical neutrality

$$[V_O^{\cdot\cdot}] = [O_i'']$$

So, this is another reaction, I can write this as K_{AF} okay.

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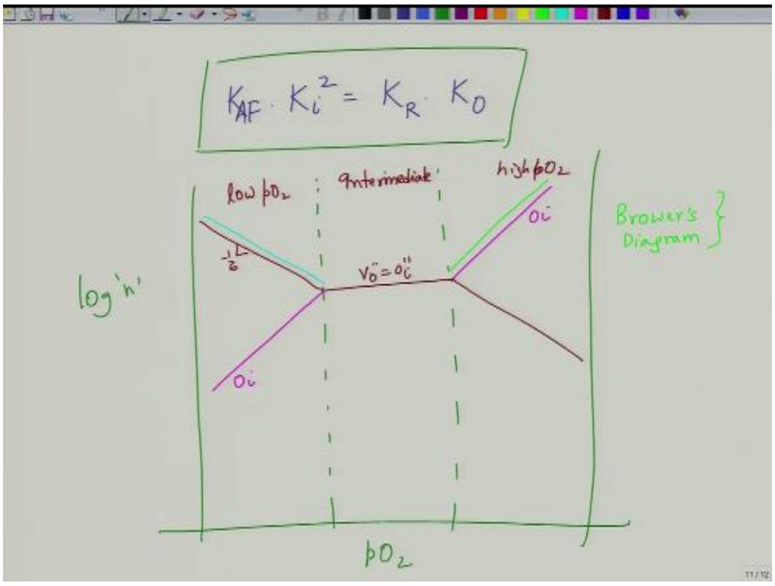

If you consider these 4 reactions, so I will leave that for you to prove, but you can write K_{AF} as,

$$K_i^2 = K_R \cdot K_O$$

, this is a relation that you can write between the all 4 reaction constants. So if you now do the similar analysis, okay, so you have regime of high pO_2, so when you plot this as a function of let us say, so, this is log of certain kind of defect okay, n means defect, and as a function of partial pressure of oxygen. So, you might have multiple scenarios, right?

So, you can distinctly draw 3 regions. So, this is a region of let us say intermediate pO2, this is high pO_2, and this is low pO_2 okay. So, let us say if the anti-Frenkel defect dominated, if anti-Frenkel defect dominated, then in this region your V_O will be equal to O_i and there will be certain concentration okay. The thing is these defect concentrations must remain continuous as they go across partial pressure of oxygen.

So, at lower pressures of oxygen, we saw that the dependence is minus 6, so if you just keep continuing it in the lower region, it will be minus 6 dependence of Vo and if you do the same analysis as we did in the last class, you can form, so in the high pO_2 region we have found oxygen interstitials, but then again combining all 4 equations, you can find expression for V_O as well. The Vo will go something like that in this region and O_i on the other hand, now V_O is equal to O_i, the O_i follows this pattern in this.

So, this is for O_i and it will follow something like this in this region okay and the electrons and holes, so in this case, the electron will be like this and the electron will follow something else in the other region and the holes will follow this kind of thing, you need to follow what their behavior will be in the intermediate regions. So, let us see how do we do that? We want to make a plot of these defects which is called as Brower's diagram which allows us to determine the defect concentrations at various pressures in given dielectric or oxide ceramic okay. So, for that, we need to consider limiting conditions okay.

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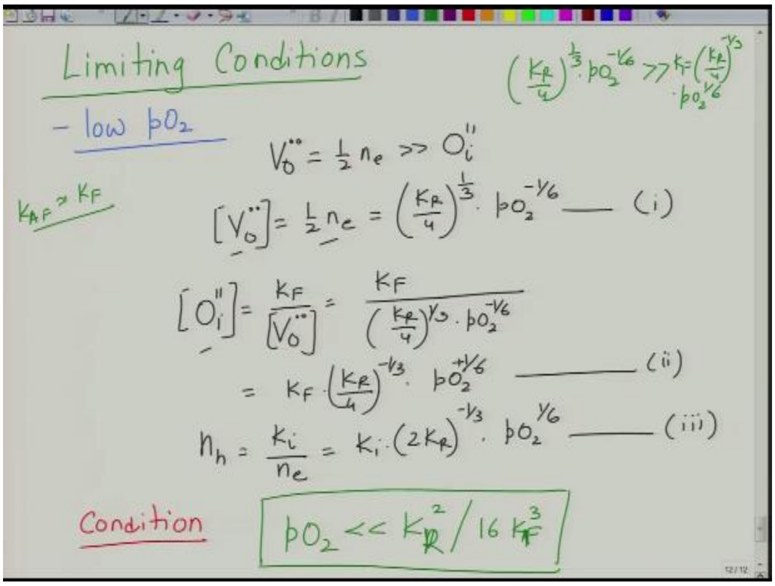

Limiting Conditions

$$\left(\frac{K_R}{4}\right)^{\frac{1}{3}} \cdot pO_2^{-1/6} >> K_F \left(\frac{K_R}{4}\right)^{-1/3} \cdot pO_2^{1/6}$$

- low pO_2

$K_{AF} \gg K_F$

$$V_O^{\bullet\bullet} = \frac{1}{2} n_e >> O_i''$$

$$[V_O^{\bullet\bullet}] = \frac{1}{2} n_e = \left(\frac{K_R}{4}\right)^{\frac{1}{3}} \cdot pO_2^{-1/6} \text{ —— } (i)$$

$$[O_i''] = \frac{K_F}{[V_O^{\bullet\bullet}]} = \frac{K_F}{\left(\frac{K_R}{4}\right)^{1/3} \cdot pO_2^{-1/6}}$$

$$= K_F \cdot \left(\frac{K_R}{4}\right)^{-1/3} \cdot pO_2^{+1/6} \text{ —— } (ii)$$

$$n_h = \frac{K_i}{n_e} = K_i \cdot (2K_R)^{-1/3} \cdot pO_2^{1/6} \text{ —— } (iii)$$

Condition $\boxed{pO_2 << K_R^2 / 16 K_F^3}$

So, limiting conditions first, so we need to determine what are the limiting conditions. So, basically how will these transitions occur, where will you put the boundaries, and how will the electron and whole concentration will take place, let us say the intrinsic if the anti-Frenkel defects dominate. So, let us say first condition is low pO_2 which means oxygen deficit okay. So, this is the case, then we can assume that

$$V_{O}^{\cdot\cdot} = \frac{1}{2} n_e \gg O_i''$$

So, we can write

$$[V_{O}^{\cdot\cdot}] = \frac{1}{2} n_e = \left(\frac{K_R}{4}\right)^{1/3} \cdot pO_2^{-1/6}$$

This is how we determined. Now Oi is nothing but

$$[O_i''] = \frac{K_F}{[V_O^{\cdot\cdot}]} = \frac{K_F}{\left(\frac{K_R}{4}\right)^{1/3} \cdot pO_2^{-1/6}}$$

$$[O_i''] = K_F \cdot \left(\frac{K_R}{4}\right)^{-1/3} \cdot pO_2^{1/6}$$

So, we can see that this is +1 over 6.

So, we have determined V_O, we have determined n_e, we have determined O_i and we now need to determine what is n_h,

$$n_h = \frac{K_i}{n_e} = K_i \cdot (2K_R)^{-1/3} \cdot pO_2^{1/6}$$

So, we have determined the 4 expressions. The first for V_O and n_e, second for O_i, and this for n_h and what is the limiting condition. Limiting condition is V_O is a lot greater than O_i.

So now we know the expression for V_O, we know the expression for O_i, from this you can get what should be the pO_2. The pO_2 will work out if you combine these equations, the limiting condition will be, so you just write basically

$$\left(\frac{K_R}{4}\right)^{1/3} \cdot pO_2^{-1/6} \gg K_F \left(\frac{K_R}{4}\right)^{-1/3} \cdot pO_2^{1/6}$$

and just manipulate the terms and what we will get is basically, so you have only 3 terms here, one is K_R, second is K_F and third is pO_2. So, we will get

$$pO_2 \ll K_R^2 / 16K_F^3$$

This is the relation that you will get. So, this is the limiting oxygen partial pressure, that pO_2 must be smaller than K_R^2 divided by $16K_F^3$ and what is K_R and K_F,

$$K_R = exp\left(-\frac{\Delta H_F}{kT}\right)$$

and

$$K_R = exp\left(-\frac{\Delta H_{AF}}{kT}\right)$$

sorry, this is AF, not anti-Frenkel but that is okay I mean, so we can write K_{AF} similar to K_F okay, Frenkel and anti-Frenkel just can be interchanged okay.

So, this is the limiting pressure for low pO_2 two conditions. Now, let us see what is the limiting condition for high pressure condition. So, for the high-pressure condition, the situation was O_i was equal to half of n_h which should be greater than V_O.

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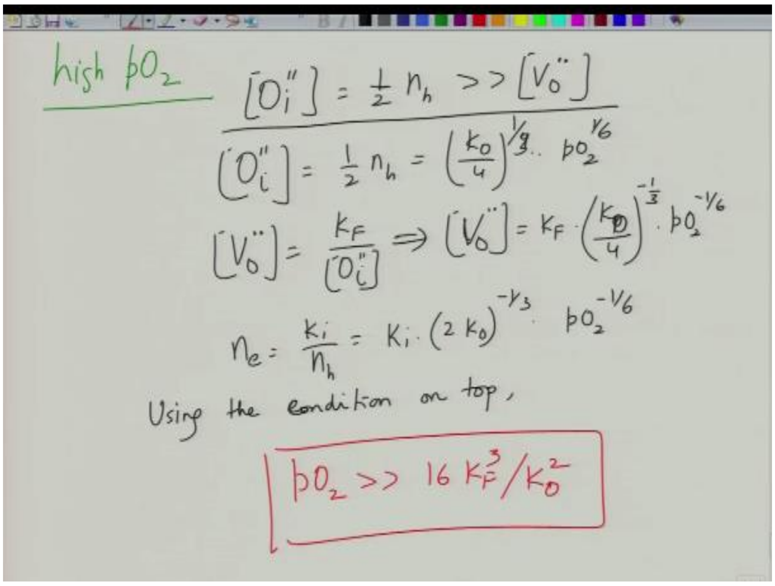

high pO_2

$$[O_i''] = \frac{1}{2} n_h >> [V_O^{\cdot\cdot}]$$

$$[O_i''] = \frac{1}{2} n_h = \left(\frac{K_O}{4}\right)^{1/3} \cdot pO_2^{1/6}$$

$$[V_O^{\cdot\cdot}] = \frac{K_F}{[O_i'']} \Rightarrow [V_O^{\cdot\cdot}] = K_F \cdot \left(\frac{K_O}{4}\right)^{-\frac{1}{3}} \cdot pO_2^{-1/6}$$

$$n_e = \frac{K_i}{n_h} = K_i \cdot (2K_O)^{-1/3} \cdot pO_2^{-1/6}$$

Using the condition on top,

$$\boxed{pO_2 >> 16 K_F^3 / K_O^2}$$

So now, the limiting condition for high pO_2. So, for high pO2, we can write

$$[O_i''] = \frac{1}{2} n_h \gg [V_O^{\cdot\cdot}]$$

$$[O_i''] = \frac{1}{2} n_h = \left(\frac{K_O}{4}\right)^{1/3} \cdot pO_2^{1/6}$$

So, we know that

$$[V_O^{\cdot\cdot}] = \frac{K_F}{[O_i'']} \Rightarrow [V_O^{\cdot\cdot}] = K_F \cdot \left(\frac{K_O}{4}\right)^{-1/3} \cdot pO_2^{-1/6}$$

,that is how it will vary.

Similarly, we know

$$n_e = \frac{K_i}{n_h} = K_i \cdot (2K_O)^{-1/3} \cdot pO_2^{-1/6}$$

One thing you can see that no matter what the situation is, V_O and ne always go as pO_2 to the power minus something and V_O, O_i, and n_h always go as pO_2 to power plus something. So, basically what it says is that as you increase the partial pressure of oxygen and that makes sense.

As you increase the partial pressure of oxygen, the oxygen can just come down, the electron come down in number, but holes and oxygen interstitial will increase in number. So again, using this equality which is written on top, using the condition on top and concentrations of O_i and V_O, we can determine that in this case

$$pO_2 \gg {}^{16K_F^3}\!/_{K_O^2}$$

So, partial pressure of oxygen must be greater than this number, in between the two, we will have stoichiometric condition.

So, we will stop here, we have run out of time today. So, in the next lecture, we will finish this stoichiometric part and build a whole diagram to see how the variation of defects concentration as a function of pO_2 looks like okay.