Fundamentals and Applications of Dielectric Ceramics

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Lecture - 14
Brower’s Diagram

So welcome again to the new lecture of this course fundamentals and applications of dielectric ceramics. So, we will briefly recap what we did in the last lecture.

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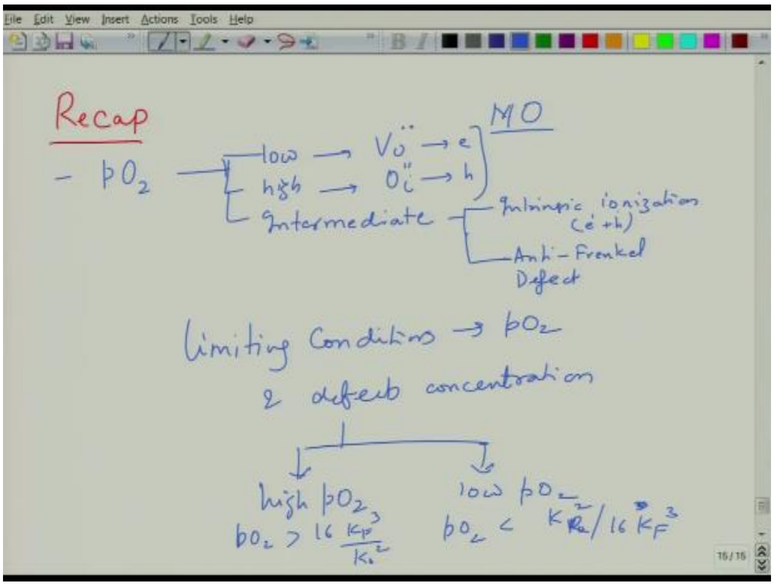

So in the last lecture, we started our work on deriving defect concentrations under various ambient conditions. So, we took 3 regimes of low *pO2*, high *pO2*, and intermediate *pO2* and we took an example of oxide MO. So, under low partial pressure of oxygen conditions, we consider oxygen vacancy as a dominant defect and high partial pressure of oxygen, we considered oxygen interstitials as dominant defects and oxygen vacancies give rise to electrons and oxygen interstitial give rise to holes.

Under intermediate conditions, we considered either intrinsic ionization which is nothing but formation of electrons and holes or anti-Frenkel defect formation and this anti-Frenkel defect goes together with a kind of defect that we form. So, under low partial pressure of oxygen, we have electrons as a result of electronic compensation, at high *pO2* we have holes as a result of electronic compensation due to formation of oxygen interstitials and anti-Frenkel defects will form because we have V_O and O_i combination.

If you had metal vacancies at high pO_2, then we will have Schottky defects. So, accordingly we worked out under limiting conditions of partial pressure of oxygen as well as defect concentrations under so what we worked out was high pO_2 and low pO_2. So, we saw that under low pO_2 condition, the partial pressure of oxygen

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

and in the high pO_2 condition, we determined

$$pO_2 \gg 16K_F^3 / K_O^2$$

So, you can see that is just inverted and that makes sense you know.

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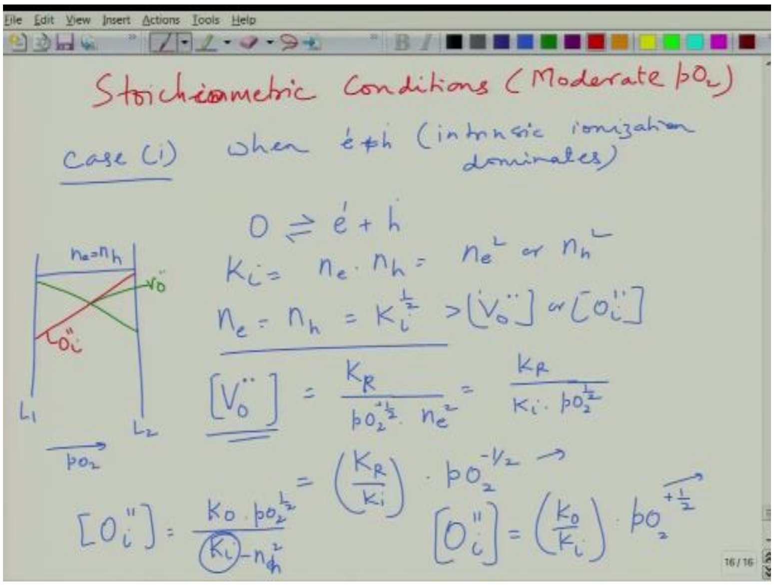

Stoichiometric Conditions (Moderate pO_2)

Case (i) when $e' + h^{\cdot}$ (intrinsic ionization dominates)

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

$$K_i = n_e \cdot n_h = n_e^2 \text{ or } n_h^2$$

$$n_e = n_h = K_i^{1/2} > [V_O^{\cdot\cdot}] \text{ or } [O_i'']$$

$$[V_O^{\cdot\cdot}] = \frac{K_R}{pO_2^{+1/2} \cdot n_e^2} = \frac{K_R}{K_i \cdot pO_2^{1/2}}$$

$$= \left(\frac{K_R}{K_i}\right) \cdot pO_2^{-1/2} \rightarrow$$

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

$$[O_i''] = \left(\frac{K_O}{K_i}\right) \cdot pO_2^{+1/2}$$

Now, we need to determine the same thing in the stoichiometric condition. So, let us first consider stoichiometric conditions, that is moderate pO_2 okay. So, we consider the case 1 when $e' + h^{\cdot}$ formation that is intrinsic ionization dominates okay. So, the defect reaction is nothing but this okay, we knew that this

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

under these conditions, that is an intermediate pO_2. So, basically you can say that

$$n_e = n_h = K_i^{1/2} > [V_O^{\cdot\cdot}] \; or \; [O_i'']$$

Basically, what we are saying is intrinsic ionization dominates, it means there could be Frenkel defect formation, but it is just that concentration of electrons and holes is significantly larger than the concentration of oxygen interstitial or oxygen vacancies formed as a result of anti-Frenkel forming defects. So, this is n_e this thing and from the previous reaction, we know that,

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

So, now, we are not saying that n_e is equal to $2V_O$, we are saying that n_e and V_O are independent under intermediate pO_2 conditions, because n_e is forming through intrinsic ionization, V_O is forming through Frenkel defect formation, so they are independent, but this is the relation between the two, how they are related to each other. So, now, what you do is that you substitute this expression for n_e, that is K_R divided by n_e square which so n_e square is equal to nothing but K_i into pO_2 to the power half.

$$[V_O^{\cdot\cdot}] = \frac{K_R}{pO_2^{1/2} \cdot n_e^2} = \frac{K_R}{K_i \cdot pO_2^{1/2}}$$

So, basically your V_O will become in this case oxygen dependent and this will be,

$$[V_O^{\cdot\cdot}] = \left(\frac{K_R}{K_i}\right) \cdot pO_2^{-1/2}$$

it still has minus sign but the number has changed, instead of having -1/6 dependence, it has -1/2 dependence. So, this is the expression for V_O. Similarly, you can also find the expression dependence of, so just like we have expression for V_O, we had expression for O_i. The expression for O_i was, so we had in the previous.

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

, it would remain the same except that because $K_i = n_h^2$, so you know the reaction was from the previous reactions you can see

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

K_i is nothing but n_h^2 okay, so K_o was

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

So, from this, we have worked out Oi,

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

, n_h^2 replaced by K_i.

So, basically

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

So, in case of oxygen vacancies, the relationship goes as minus half, in case of oxygen interstitial, it goes as plus half. So, instead of +1/6, we have a case of +1/2. So, between the two limiting regions, this is how the variation will occur. So, this is in the stoichiometric region. So, within the stoichiometric region, so this is one limiting condition, let us say L1, this is the L2 as a function of pO_2.

Within this region, $n_e = n_h$ okay, how will the concentration of oxygen will vary? So, it will cut at some point. So, essentially it will go as minus half in this regime, so this is V_O, and plus half in for O_i and then it has to follow the continuity in the next regime and that we will see when we got them together.

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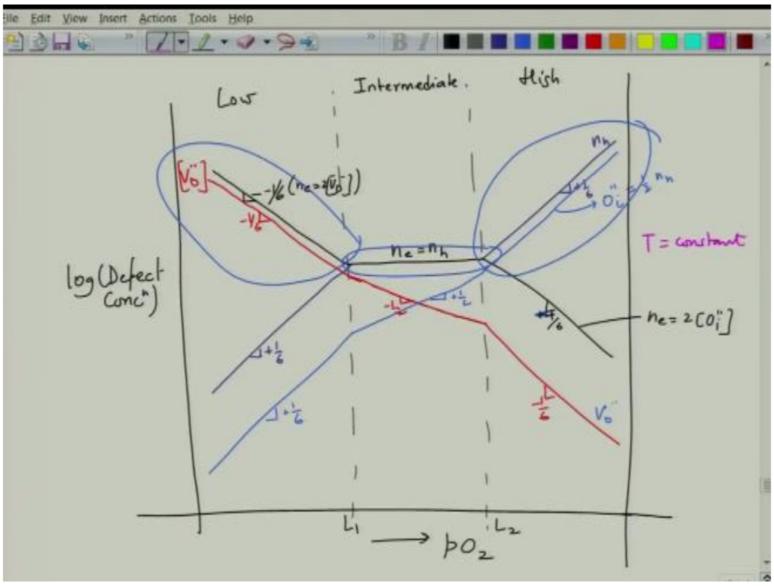

So, now you can see what we are going to do using this framework, second situation, so in the first case if this is the scenario, when this happens, then we can make a plot of, sorry let me use the black color, log of defect concentration as a function of pO_2 okay. I made 3 regimes. This is intermediate, this is high, and this is low. So, this is oxidizing condition on the right, in the middle you have intermediate condition, on the left we have reducing conditions.

So, now let us begin with $n_e = n_h$. This is $n_e = n_h$ in this regime. Now, since the defect concentrations have to be continuous, the n_e follows this particular sequence with a slope minus 1 over and n_e was equal to $2V_O$ right, and in this case, n_e follows this particular line which is +1/6 and n_e being equal to $2O_i$ and these are the limiting conditions Ll, L2 of partial pressure of oxygen. Now, let us make other lines. What about oxygen line? Oxygen line is just half of this.

This is V_O, oxygen vacancy concentration, sorry not oxygen line, oxygen vacancy concentration. So, this is -1/6 here. How does it follow in this case? It will go as half. So, half means the slope will, it will be something like this right. So, this is -1/2 and then again it comes down to -1/6, right. How about the hole now, so hole concentrations on the other hand, this is the hole line. The hole concentration in this regime goes as +1/6, this is for n_e.

Similarly, hole concentration in this regime also goes as +1/6. What about the oxygen interstitial concentration? Oxygen interstitial in this regime will go half of what we have here. So, this is O_i, which is half of n_h. In this regime, the slope decreases, it goes as plus half, and then again in this regime it will go as +1/6. So, this is how the variations of pO_2, the variations of defects will occur under different conditions.

So, under this condition when the intrinsic ionization dominates, under reducing conditions the dominant defects are these, oxygen vacancies and electrons. Under oxidizing condition, the dominant defects are oxygen interstitials and holes. Under stoichiometric conditions, you are likely to have $n_e = n_h$ with lower concentration of O_i and V_O. **"Professor - student conversation starts"** Sir if V_O concentration **(( )) (12:39)** is -1/2. Sorry for V_O, I will see. The V_O in third region for V_O concentration. Yeah, this is minus 1 over 6. Written plus is no, no this is V_O, this is V_O, n_e. Sorry n_e, ha this is minus, this is for n_e okay, this should be minus. **"Professor - student conversation ends."** So, is that clear how to construct this diagram?

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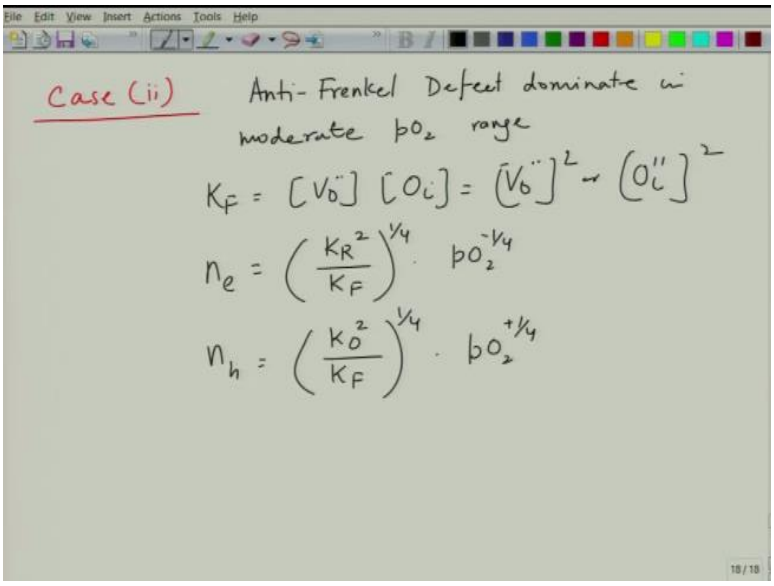

Case (ii) Anti-Frenkel Defect dominate in moderate pO_2 range

$$K_F = [V_O^{\bullet\bullet}][O_i] = [V_O^{\bullet\bullet}]^2 \rightarrow [O_i'']^2$$

$$n_e = \left(\frac{K_R^2}{K_F}\right)^{1/4} \cdot pO_2^{-1/4}$$

$$n_h = \left(\frac{K_O^2}{K_F}\right)^{1/4} \cdot pO_2^{+1/4}$$

Now, let us say the second scenario is instead of having intrinsic ionization, we make case 2 as we can say that is anti-Frenkel defects dominate in moderate pO_2 right. If that happens and again in the similar fashion, we know that

$$K_F = [V_O^{\cdot\cdot}][O_i''] = [V_O^{\cdot\cdot}]^2 or [O_i'']^2$$

and using the same relation between oxygen interstitial and holes and oxygen vacancy and electrons that we used in previous case, we can determine what is n_e.

$$n_e = \left(\frac{K_R^2}{K_F}\right)^{1/4} \cdot pO_2^{-1/4}$$

and,

$$n_h = \left(\frac{K_O^2}{K_F}\right)^{1/4} \cdot pO_2^{+1/4}$$

If this is the case, then what we will get is a slightly different situation. In the first case, we saw that the slopes were of some type, in this case we will have slopes of other types.

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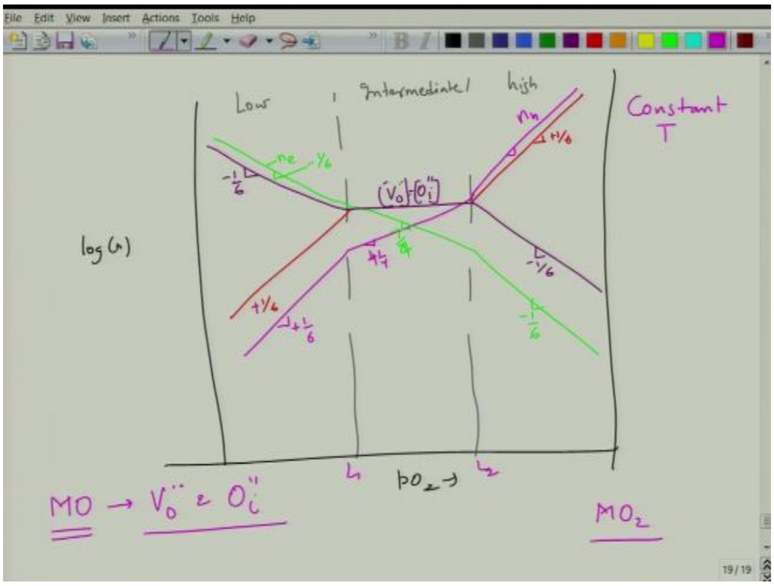

So, again we make this line log of defect concentration, pO_2, again we make 3 regimes. So this is high, intermediate, low. In the intermediate regime, we can say now instead of ne being equal to oh, we have V_O being equal to O_i. So, Vo will follow the same line. So, V_O will follow this line with a slope -1/6 and this will go as -1/6 in this region, this is V_O. For O_i, it will follow this line +1/6 and -1/6, n_e and n_h on the other hand will be no different.

So, for n_e, so this is n_e and slope is -1/6. From the previous equation, you see that now it has to follow a slope of -1/4. So, it will follow a slope of -1/4 and then again it will follow a slope of -1/6. Similarly, holes, this will be for holes n_h, same slope, and now it will reduce its slope to +1/4 and before it takes a slope, this is +1/6. So, they will have slopes of + and - as per the character, but now the behavior has changed thus okay.

So, this is basically the way in which you construct what we call as a Brower's diagram. The diagram which provides you a plot of defect concentrations of all types as a function of partial pressure of oxygen at a constant, so this is a constant temperature okay, constant temperature and this is also at T is equal to constant and mind you this is also valid for a given oxide MO considering that defects are V_O and O_i.

If you have MO_2, what will happen, the slopes will change, the partial pressure of oxygen dependencies will change and the boundary conditions L1, L2 will also change okay. So, when you change the type of defect, when you change the type of oxide, the slopes will change, the limiting conditions will change, but the procedure will remain the same okay.

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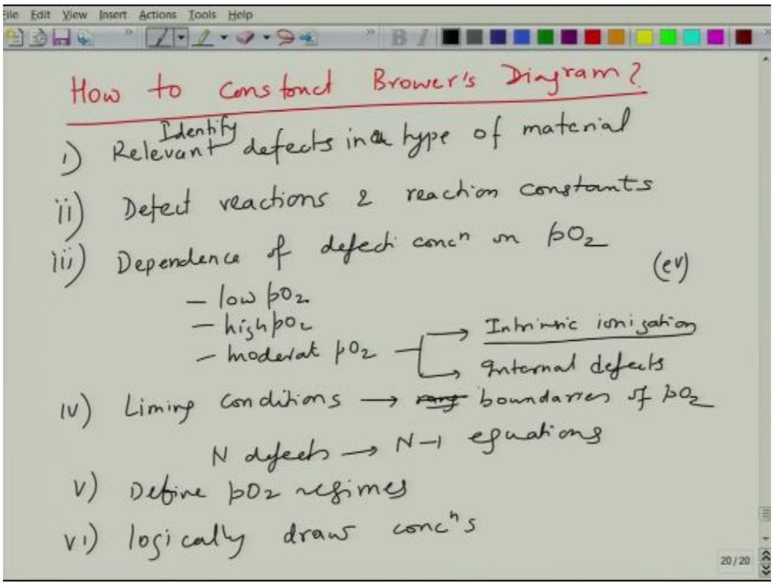

How to construct Brower's Diagram?

i) Identify Relevant defects in a type of material

ii) Defect reactions & reaction constants

iii) Dependence of defect concn on pO_2 (ev)

- low pO_2
- high pO_2
- moderate pO_2 → Intrinsic ionisation / Internal defects

iv) Limiting conditions → ~~rang~~ boundaries of pO_2

N defects → N−1 equations

v) Define pO_2 regimes

vi) logically draw concn's

So, procedure to calculate this is basically first, so when you want to know how to construct a Brower's diagram. So, what are the steps? First you need to see the relevant defects and type of material right. So, you need to see what kind of defects can be present in the material. Basically, there are 4 possible defects which are possible, you can have oxygen interstitials, oxygen vacancies, metal interstitials, metal vacancies. You need to know the defect formation energy, and depending upon the type of oxide, those with the lower defect formation energy are more likely to form.

So, when you identify the type of defects, so identify relevant defects in a type of material okay and then write the defect reactions okay. So, generally for a close packed structure, you know one can neglect interstitial. If the structure is very heavily close packed, then interstitial are not possible to occur because they are smaller and generally oxygen interstitials are bigger, so as a result anti-Frenkel will not be possible. So, for such kind of materials which are close packed structured material, you will mainly consider what we call as Schottky disorder, not anti-Frenkel or Frenkel disorder.

So, that judgment has to be made by you as a scientist, and then once you identify the defects and type of defects, intrinsic defects, etc., you write the defect reactions. So, once you write the defect reactions, you work out the dependence of defect reactions and reaction constants okay and workout the dependence of defect concentration on pO_2. So, you do it for low pO_2, do it for high pO_2 and do it for moderate pO_2. When you do it for moderate pO_2, then you also have a situation whether you may have intrinsic ionization dominant cases or you may have internal defects such as Schottky or Frenkel okay.

This depends generally on the band gap. If band gap is low, then intrinsic ionization is favored. So, you have to consider the energies in terms of eV per defect or whatever, which ones are lower. So, if a defect can be formed easily, then internal ionization will occur less, and if your internal ionization can occur at lower band gap, then defects will be difficult to form. So, once you do that, then you basically find out what is the limiting conditions right. Limiting conditions will give you boundaries of pO_2 right.

So, basically if you have N defects, you will have (N-1) equations that you may have in the system okay. So, you define these regions of pO_2, define pO_2 regimes, and then you have to use your logic, then logically draw concentrations making sure they are continuous, they do not become discontinuous as you switch from one to another regions. So, as we saw in previous figures, you look at electron concentration or hole concentration or you look at oxygen vacancy concentration or you look at oxygen interstitial concentration, no matter what the situation is, the defect concentration remain continuous.

It is just that their slope changes as a function of partial pressure of oxygen. So, these diagrams are very useful and these diagrams allow you to understand what kind of defects can be present in different systems as a partial pressure of oxygen.

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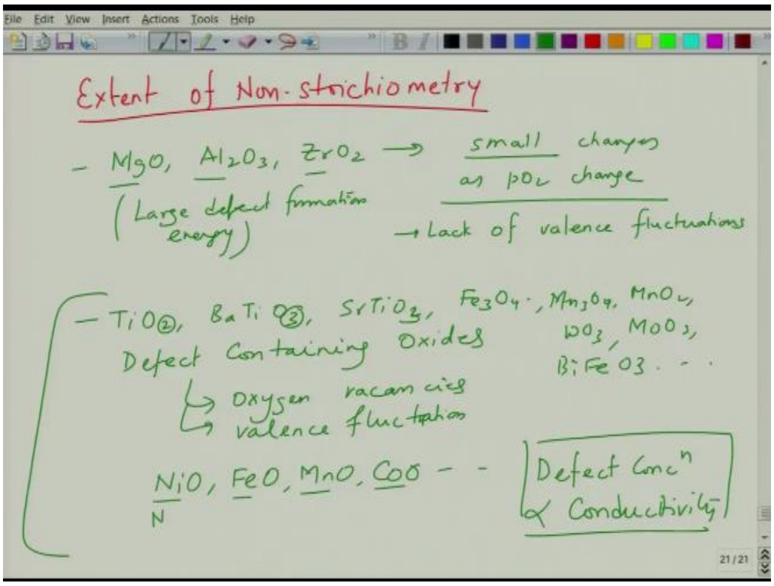

Extent of Non-stoichiometry

- MgO, Al_2O_3, ZrO_2 → small changes as pO_2 change
  (Large defect formation energy)
  → Lack of valence fluctuations

- TiO②, BaTiO③, $SrTiO_3$, Fe_3O_4, Mn_3O_4, MnO_2, WO_3, MoO_3, $BiFeO_3$ . . .
  Defect Containing Oxides
  ↳ Oxygen vacancies
  ↳ valence fluctuations

  NiO, FeO, MnO, CoO - -
  N

$\boxed{\text{Defect Conc}^n \propto \text{Conductivity}}$

Now, I can just briefly tell you about how much is the when we work out that extent of non-stoichiometry in these oxides. So, the question is oxide can be non-stoichiometric, so how much non-stoichiometry can be. So, let us see a brief discussion on non-stoichiometry extent. So, in materials like MgO or alumina or even zirconium oxide, the extent of non-stoichiometry is small. They are generally very stoichiometric oxides because the energy which is required for oxidation or reduction is very large.

So as a result, the defect formation energy is very large and as a result change in partial pressure of oxygen has little effect on the defect chemistry. So, small changes occur as pO_2 change. So, these are very robust systems, they have large defect formation energy and the cations also they are generally of, so magnesium generally occurs in only +2, aluminum is most stable at +3, zirconium is also very stable as +4, they do not valence fluctuations. So, lack of valence fluctuations, makes them very stable oxides.

So, extent of stoichiometry is very small in the systems. So, basically you can say they have large defect formation energy. So, energetics does not permit them to be non-stoichiometric. On the other hand, elements such as you know TiO_2 or barium titanate or even strontium titanate, iron oxide, these are defect containing oxides because the defect formation energy in these oxides is very small, relatively smaller. So, you can form in these systems oxygen vacancies, you can also form valence fluctuations, and so on and so forth.

So, as a result, these systems where you have transition elements, especially Fe_3O_4 you can have, Mn_3O_4 you can have, MnO_2, things like tungsten oxide, molybdenum oxides, bismuth ferrite, all these systems they are prone to having valence fluctuations and oxygen vacancies especially in the system and hence, titanium can occur in Ti^{+3} state for example okay. If you have Ti^{+3}, then oxygen content will go down. Similarly, in this oxygen content will go down. Similarly, in strontium titanate, oxygen content may go down.

So, because of valence fluctuations, you may have non-stoichiometry. So, similarly if you look at oxides such as Nio, FeO, MnO, cobalt oxide all of them are prone to having reasonably large defect concentration because Ni is a transition metal ion, Fe is transition metal, Mn is transition metal, cobalt is transition metal. So, Ni can occur in different valences, Fe can occur in different valences, manganese can. So, this brings non-stoichiometry in the system.

So, they can again have a non-stoichiometry of about 0.05%, 0.05% is very large okay, 0.05% it sounds a small number, but when you have about 20 something atoms in a system, 0.05% is a very large number and here their stoichiometry is of the order of few ppm. So, you know a few ppm non-stoichiometry is good enough to give you large defect concentration. So, stoichiometries occur. So, these are non-stoichiometry prone materials, whereas on top we have materials which are stoichiometry, they are generally resistant.

So, this is what it is and so we have seen how the defect concentration varies as a function of partial pressure of oxygen. So, this sort of gives you have an idea what you can do with oxides. If you want to make them oxygen rich, then you can use conditions to annihilate or calcine in such a condition so that they become like oxygen vacancy rich or metal vacancy rich and you can dope them with certain impurities to tailor their defect concentration.

So, if you wanted to make something lower in let us say $BaTiO_3$, if it is oxygen deficient to begin with due to titanium oxygen valence fluctuation, you can dope it with something like niobium which brings in extra oxygen into the system. So, this is how you make oxides conducting or non-conducting by using the defect chemistry. So, this knowledge is very important to engineer, because the defect concentration is directly proportional to conductivity. So, defect concentration is proportional to conductivity.

So, as defect concentration goes up generally, the conductivity also goes up, and for dielectrics, we need to reduce the conductivity. So, we need to reduce the defect concentration either by calcining them in conditions or sintering them in conditions which reduces their defect concentration or if you cannot achieve that, then you need to dope it with appropriate dopants so that it would reduce the defect concentration which has been prevailing in that material okay.

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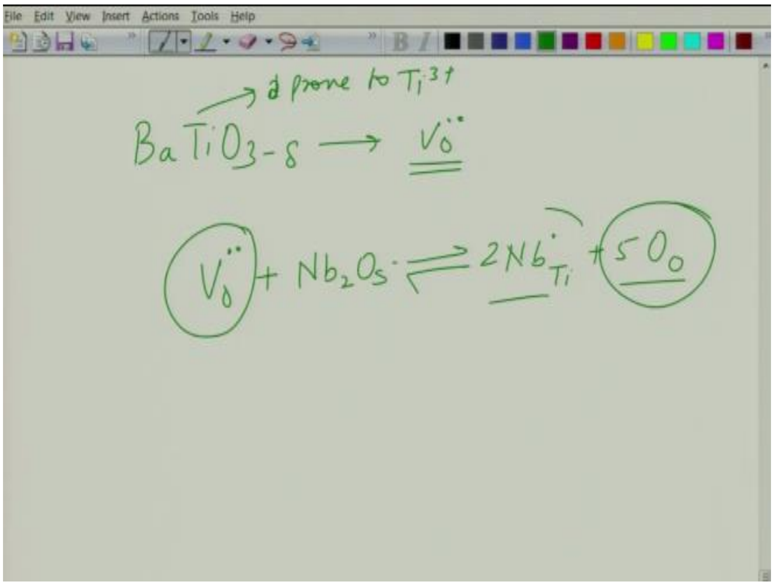

$\rightarrow \delta$ prone to Ti^{3+}

$$BaTiO_{3-\delta} \rightarrow \underline{\underline{V_O^{\bullet\bullet}}}$$

$$V_O^{\bullet\bullet} + Nb_2O_5 \rightleftharpoons \underline{2Nb_{Ti}^{\bullet}} + \underline{5O_O}$$

So, for example, as I said Barium titanate. Titanium is prone to Ti^{3+} formation. So as a result, it becomes $BaTiO_{3-\delta}$, which means it will have oxygen vacancies in the system. So, if it has oxygen vacancies in the system, then I bring in niobium oxide. If I bring in niobium oxide, the niobium goes to titanium site. So, 2 niobium go to titanium site, 5 oxygen go to oxygen site. So, 4 of them are related to titanium and one of them is related to V_O.

So, as a result, they sort of compensate, so in charge compensation is done by like this. So, your oxygen vacancies are compensated by these extra oxygen brought in by the +5 valence. So, that is how you make it resistant to conduction and this is very important in the context of dielectric materials, dielectric should be insulating, that is why you need to control their defect chemistry very accurately and this knowledge hopefully will enable you to do that okay.

So, let us stop there. So, this completes our discussion on defect chemistry. From the next lecture, we will start discussion on dielectric ceramics starting with linear dielectric materials. Thank you.