Advanced Ceramics for Strategic Applications
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Lecture - 16
Electrical Conduction in Ceramics (Contd.)

In the all there class we were discussing about the valence controlled semiconductors, primarily the impurity effect in controlling the conductivity of some of the oxides and the non-stoichiometric oxides in particular. We has seen the conductivity is closely controlled or in strongly controlled by the non-stoichiometric, and that non-stoichiometric relates to the defect concentration. However, the defect concentration can be fixed by addition of impurities and those are called valence controlled semiconductors. And, we have given two examples of NiO nickel oxide and Fe2O3.

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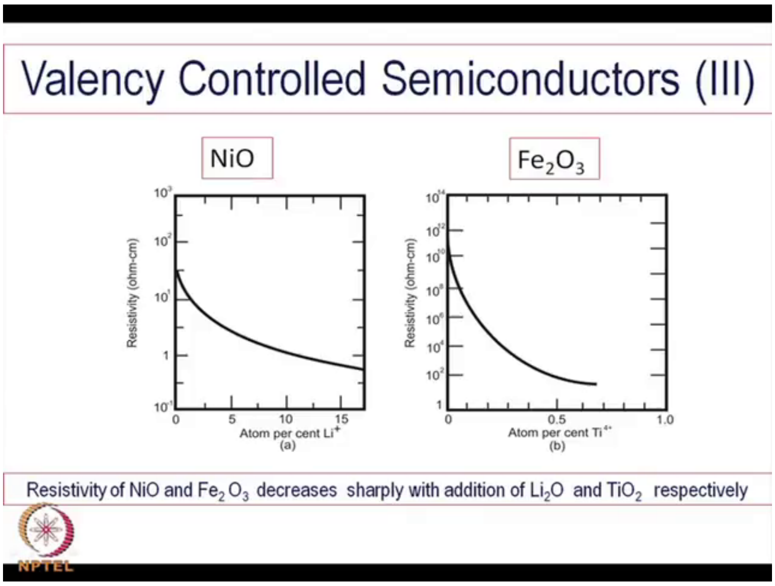
Valency Controlled Semiconductors (III)

Resistivity of NiO and Fe_2O_3 decreases sharply with addition of Li_2O and TiO_2 respectively

I have also seen that the conductivity in such oxides decreases or increases quite significantly; in this case plots as been made for resistivity as a function of broken concentration. So, in case of NiO it is lithium concentration, in case of Fe2O3 it is TiO2 concentration which decrease of the resistivity quite significantly. I also mention that these are independent of the TiO2 and also one temperature.

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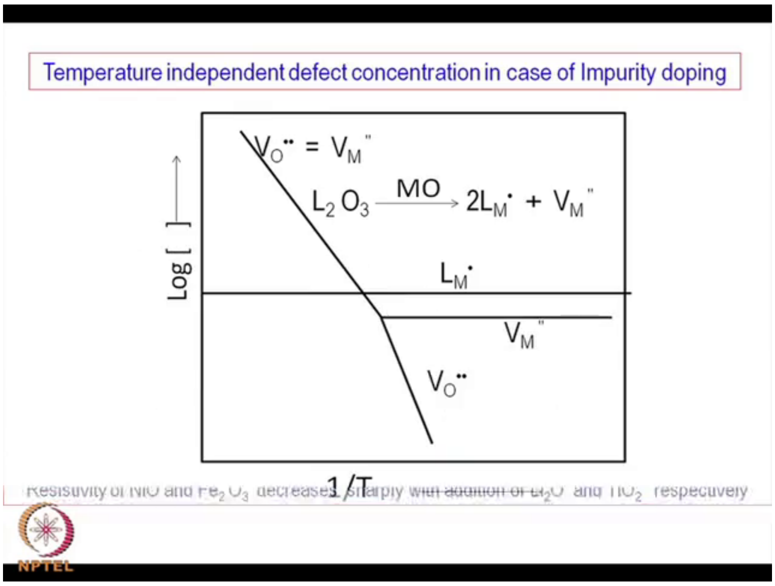

Temperature independent defect concentration in case of Impurity doping

Resisuvity of NiO and Fe_2O_3 decreases sharply ~~with addition of Li_2O~~ and TiO_2 respecuvely

So, there is a illustration here, how the defect concentration changes as a function of temperature as a function of temperature of course, is 1 by T it been plotted as a defect concentration. And, we will see L is impurity here, L2O3 has been added to MO the original host oxide is MO. And, to that L2O3 has been added that means the trivalent, this is trivalent. So, this is a effectively possible charge of the defect concentration at that remains constant. The defect concentration remains constant as a function of independent of temperature.

So, these are the intrinsic region of course are very high temperature. The concentration of the intrinsic defect that is vacancy or the metal constant is controlled by this. And, however the oxygen vacancy changes at the lower temperature is much lower than the impurity concentration, but the higher temperature it over takes over. Then, therefore the intrinsic defect concentration predominates over the impurity concentration. So, impurity concentration is controlled or the constant over the temperature remains. So, at lower temperature predominates whereas; higher temperature in intrinsic conductivity comes in.

So, if you plot the log conductivity versus 1/T like in earlier other semiconductor. Here also you have an extrinsic region; and an intrinsic region and the slope blue change this is the activation, there is no activation here. Whereas, there is activation energy for high-temperature. So, this becomes the intrinsic region and this becomes a extrinsic region of course it is only the concentration has been plotted here. If you plot log the other term also will come in that is the mobility term. So, mobility may change; and therefore there will be slight slope here.

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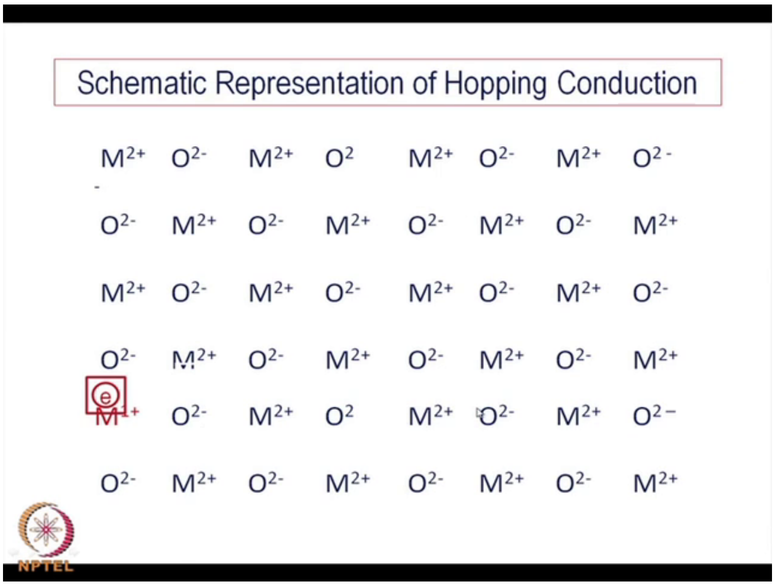

Schematic Representation of Hopping Conduction

M^{2+} O^{2-} M^{2+} O^{2} M^{2+} O^{2-} M^{2+} O^{2-}

O^{2-} M^{2+} O^{2-} M^{2+} O^{2-} M^{2+} O^{2-} M^{2+}

M^{2+} O^{2-} M^{2+} O^{2-} M^{2+} O^{2-} M^{2+} O^{2-}

O^{2-} M^{2+} O^{2-} M^{2+} O^{2-} M^{2+} O^{2-} M^{2+}

$\boxed{e}$ M^{+} O^{2-} M^{2+} O^{2} M^{2+} O^{2-} M^{2+} O^{2-}

O^{2-} M^{2+} O^{2-} M^{2+} O^{2-} M^{2+} O^{2-} M^{2+}

Well, we have discussed these mechanisms and the nature of different conductivity in different oxides. We have been referring that there is basically electronic conduction either they will electrons or the whole conduction. So, either the electrons and holes or the basic charge carriers here. Only different of course compare to the elemental semiconductors or in metals. In metals or semiconductor as we have mentioned earlier that relatively more free. Whereas, in a oxide semiconductor the chargers are much more strongly attached to the ion of course.

And, therefore the charge carrier here is really not a free hole or free electron they are called polar ions. We will see what is that polar ion means but before that what is the mechanism by which is actually moves? And, this is a animated view of what exactly happens, when in an electrons we will we have seen even in valence control semiconductor and so on or any other semiconductor or semiconductor metal oxides.

The electrons are basically getting attached to one of the cations; and that is how the valence of that get change a 2 plus. For example, if this charge carrier which is basically polar ion or a form of quasi particle, electron plus polarization discussed little bit later.

So, this is the charge carrier here from the timing being we considered as an electron. And, that is sitting on this site of the M plus or M2 plus going in a lattice of a M2 plus and O2 minus. We have an additional electron here which is sitting at the site of the M or the metal and it changes the valency from 2 plus to 1 plus. So, that is what happens then these electrons actually what they call hopping mechanism. It hopes from one metal site to another and then goes to another and then goes to other in this manner; this is for as been animated here. The electron goes there it is over the top of another metal. In the process this becomes M2 plus and these becomes M1 M plus. And, then again it goes to another metal site and also makes the other one M plus. And, then goes to another one these becomes M2 plus these goes to become M plus and in this way it goes on.

Finally, from this site it is move through the lattice were a kind of hopping mechanism; and finally, it has gone through the other end of the solid. So, this is what we call the schematic representation of hopping conduction. So, the electrons or charge carriers in this case is actually moving from the lattice point to the lattice point. So, the resident time in between the lattice is very low; either it is residing very close to the one of cationic sites or it is moving into the material. It is really not staying any other anyplace in between so that is known as the hopping mechanism.

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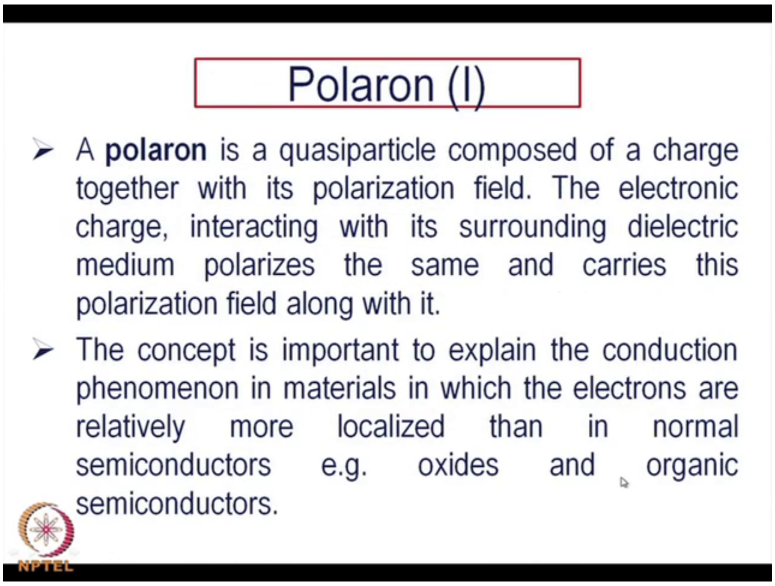

Polaron (I)

- A **polaron** is a quasiparticle composed of a charge together with its polarization field. The electronic charge, interacting with its surrounding dielectric medium polarizes the same and carries this polarization field along with it.
- The concept is important to explain the conduction phenomenon in materials in which the electrons are relatively more localized than in normal semiconductors e.g. oxides and organic semiconductors.

And, then we come to the so called concepts of polarons because these are tightly bound be electrons. And, this tightly electrons have different characteristics than the free electrons which we have in metals or elemental semiconductors. So, as per definition or as per understanding, a polaron is a quasi particle composed of charge which is in electronic charge obviously, either electronic charge or a hole charge or positive charge to whether it is polarize the field. The electronic charge interacting with the surroundings dielectric medium because there are relatively less conducting; polarizes the same; carries this polarization field along with it.

So, it is basically a combination of a charge along with polarization field so interact. Because interaction of the phonons there is an electron characteristics of free electron is slightly different. In fact is effective mass is also different and as it has a larger their size. So, it carries that polarization field along with this and that is why it is called polaron. The concept is important to explain to conduction phenomenon in materials in which; electrons are relatively more localized that is what was mentioned than the normal semiconductor examples are oxides and organic semiconductors.

So, if you want to understand the conduction mechanism; the charge transport mechanism in particularly oxide which are more ionic in character or organic semiconductor which are in more covalent in character. In those situation the concepts of the polaron or more useful. And, one is to understand how exactly this charge carriers of course what I am talking about is more simplified manner, simplistic manner.

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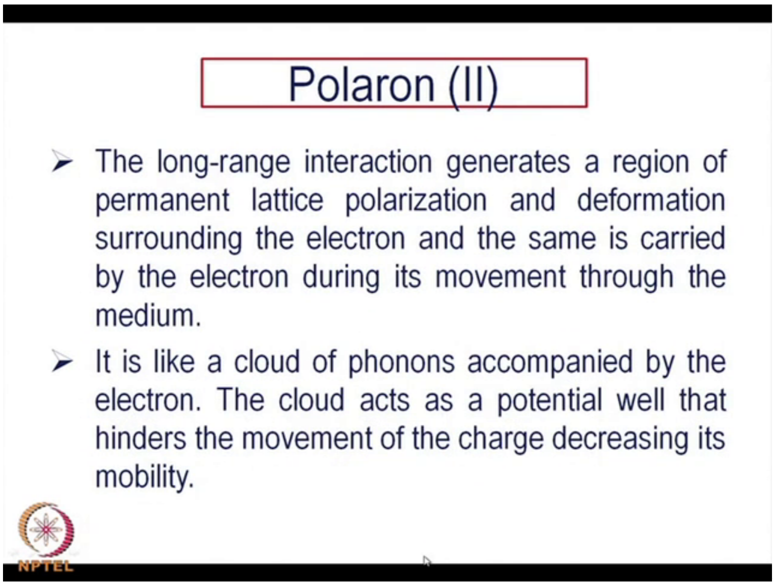

Polaron (II)

- The long-range interaction generates a region of permanent lattice polarization and deformation surrounding the electron and the same is carried by the electron during its movement through the medium.
- It is like a cloud of phonons accompanied by the electron. The cloud acts as a potential well that hinders the movement of the charge decreasing its mobility.

There are more complex theories to this. The long-range interaction generates region of permanent of lattice polarization and deformation surrounding the electron. And, the same is carried by the electron during its movement through the medium; is more early the same thing talked about. It is like a cloud of phonons accompanied by the electrons. Now, we were talking about the cloud of phonons will talk of cloud of electrons. So, the electron is a sea of phonons that is why they are sometimes called as sea of phonons. And, that is a lattice vibration and the cloud, acts as a potential well that hinders the movement of the charge decreasing its mobility.

So, the mobility obviously the mobility because we have been talking primarily of the concentration of the defects, concentration of the charge carriers is certainly one of the important components, who is determines conductivity of the resistivity. But in additional there is another important term is the mobility term. So, it is also the mobility who is determines the overall conductivity and the polarons, because of their polarization as associated to it as if a much larger molecule larger species is moving within the medium. And, therefore its mobility is much less and it is different interrelations, different characteristics for the mobility concern. So, this is all about polar ions will not go when much more details to it.

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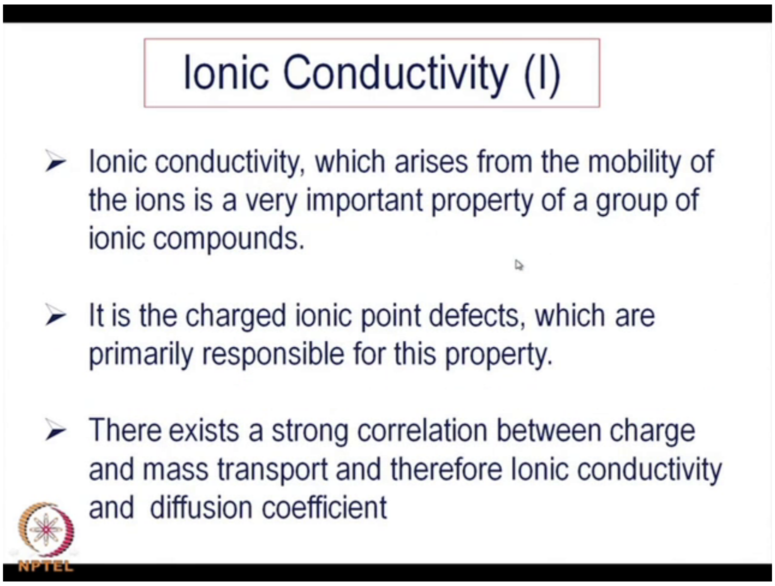

Ionic Conductivity (I)

- Ionic conductivity, which arises from the mobility of the ions is a very important property of a group of ionic compounds.
- It is the charged ionic point defects, which are primarily responsible for this property.
- There exists a strong correlation between charge and mass transport and therefore Ionic conductivity and diffusion coefficient

So, that really completes our discussion on the semi-conductivity in oxides. How it is determine by the partial pressure? How it is determine by the impurity content? And, how it is determine towards extent? It is determines by the temperature and all these things can be explain once, you understand the back diagram of the semiconducting or insulating the oxides. There is another important phenomenon in oxides particularly, while we are talking about conductivity, the actual conductivity and that is ionic conductivity. We have also seen that non-stoichiometric oxide where the defect compensation is primarily because of the ions or change of the concentration of ionic defects.

They are we are not talking about the electronic charge carriers; either the negative charge carriers or the positive charge carriers, electrons or holes. Their conductivity is primarily controlled by the concentration ions and they give rise to so called ionic conductivity by deficient mechanism. So, that there is not only charge transport, but there is a mass transport as well and both of them are interlinked. So, one as a inter-relationship to the other. So, let us talk little bit about the ionic conductivity. The ionic conductivity which arises from the mobility of the ions is a very important property of group of ionic compounds. There are many technological applications or industrial applications for the ionic conductors. Since, most of these oxides or solids; ionic conductivity is the major requirement of an electronical system, electrolyte of an electrochemical system.

So, these oxides on this compound are also known as solid electrolytes. So, the electrolytes in the solid-state and one can make electrochemical sales out of it. And, that sales have a tremendous importance, particularly in the current contacts of energy crisis and the energy technology. So, we will discuss them at a later stage, but now for the time being let us try to understand what is this ionic conductivity and what are their its characteristics? As I have mentioned the ionic conductivity which arises from the mobility of the ions is a very important property of the group of ionic compounds, it will be discharge ionic point defects, charge ionic point defects. We have talked about ionic point defects as well as electronic point defects here it is the charged ionic point defects which are primarily responsible for this property.

So, once again it is related to the points defects no doubt but they are the defect compensation is by ionic defects as they are more predominant defects in the oxides than the electronic defects. And, the stoichiometric with an extent of stoichiometric is very limited is extremely limited there exist a strong correlation between the charge and mass transport; and therefore ionic conductivity and diffusion coefficient. So, that is also another point of our interest.

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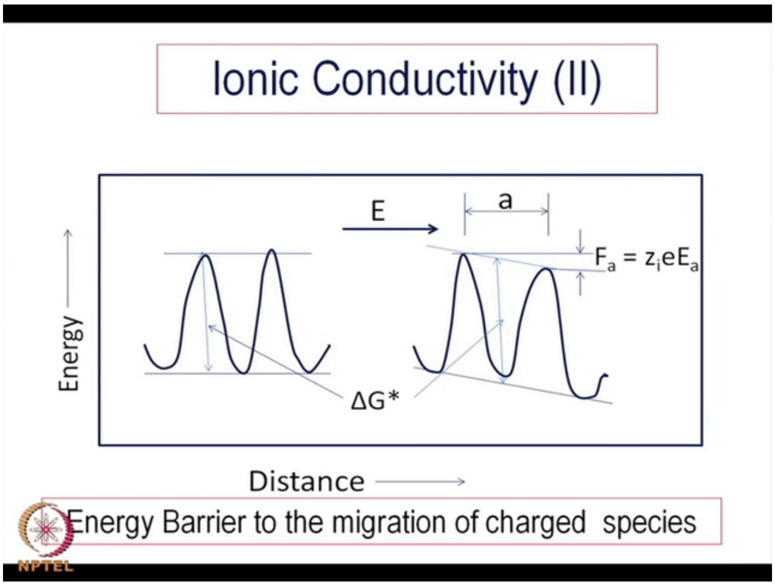

Ionic Conductivity (II)

Energy Barrier to the migration of charged species

Now, if the ion is moving a in a through a lattice. You can consider a kind of energy or the variation of energy based on its particular site where it is located. So, as a function of distance, one can plot this kind of potential wells or potential barriers. So, these are basically, inter atomic spacing and the ions is moving through the surroundings of another set of ions; so as in any other deficient mechanism so on. It as to go through a barrier it as to go though barrier; and then come to down low-energy sites and high-energy sites. So, periodically it moves like that.

Now, this is what happens? They are basically symmetrical, wherever there is no electrical field. If there is an electrical field of let us say E; and at a distance of inter-particular distance of a. So, the force experienced by particular in this ionic charge of course the ionic species the application in the electric field is applied; a forces is getting experience. And, that force is actually this one and this is depression and the depression of the energy in this direction.

So, there is a less potential on this side and the higher potential on the side. Naturally there is a dragon force which will drive these ions towards the application of electric field. So, this is the basic thing and the energy barrier here is both in this case, as well as in this case. So, this is only be depressed in this direction; the energy barrier to the migration of charged species that is what have considered. If the situation is like that you can considered the migration of the ion coming back to that migration of the ion in the forward direction, and there is a finite possibility ions can also move back. So, which is considered the two equations Arrhenius types of equations?

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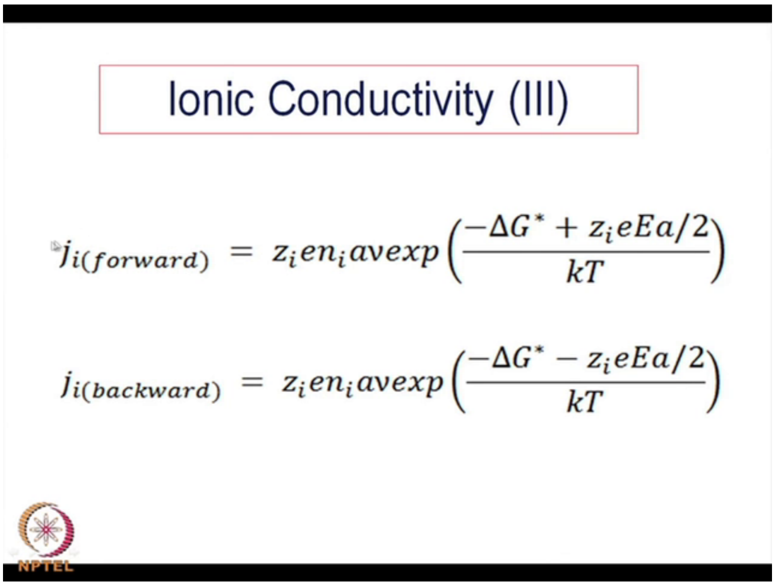

Ionic Conductivity (III)

$$j_{i(forward)} = z_i e n_i a v exp\left(\frac{-\Delta G^* + z_i eEa/2}{kT}\right)$$

$$j_{i(backward)} = z_i e n_i a v exp\left(\frac{-\Delta G^* - z_i eEa/2}{kT}\right)$$

So, the flux the (( )) number of ions moving forward per unit area for the that is forward detection of flux and that is can be expressed as zi. These expression has already been considered earlier number of charges per each charge carrier; e is the electronic charge, ni concentration of that charge of this charge species, a is the distance, that is (( )) spacing mu is frequency natural vibration frequency of vibration of the atoms and exponential term what is the minus delta G star is without field then plus this is the additional energy change. So, we are talking about this value and compare to this value and of course by KT; so it is a normal Arrhenius kind of equation. And, if it is in the backward direction so this is reduced, this increase actually the total these are less value delta G and this is the higher value this activation barrier is higher of the delta G. So, less number of ions will be backward then the forward; so they will be forward movement of that.

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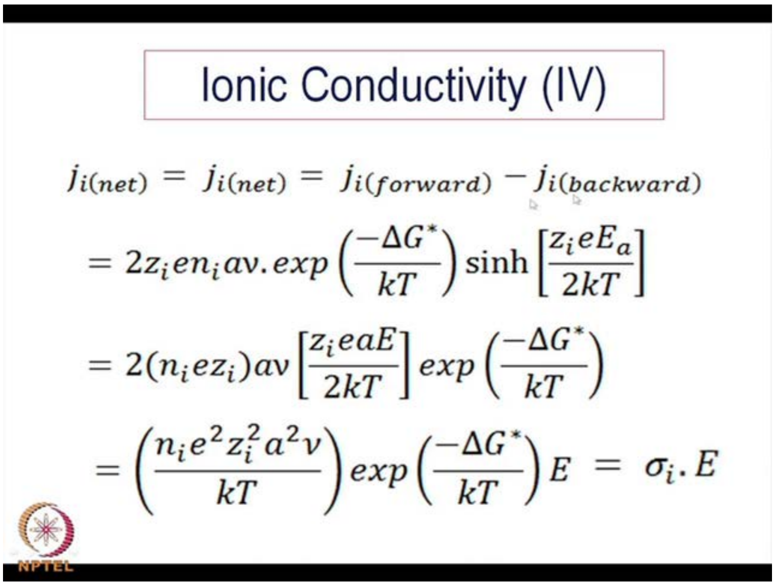

Ionic Conductivity (IV)

$$j_{i(net)} = j_{i(net)} = j_{i(forward)} - j_{i(backward)}$$

$$= 2z_i e n_i a v . exp\left(\frac{-\Delta G^*}{kT}\right) \sinh\left[\frac{z_i e E_a}{2kT}\right]$$

$$= 2(n_i e z_i) a v \left[\frac{z_i e a E}{2kT}\right] exp\left(\frac{-\Delta G^*}{kT}\right)$$

$$= \left(\frac{n_i e^2 z_i^2 a^2 v}{kT}\right) exp\left(\frac{-\Delta G^*}{kT}\right) E \; = \; \sigma_i . E$$

So, the ji net; the net flux will be forward minus backward; and if you do that sin hyper hyperbolic this and this is almost equal to 1. So, the ultimately this ji net will be simplified in this form 2(niezi) avzieaE by 2KT exponential. So, this is a constant term dependent on temperature; inversely proportional temperature and there is exponential term here. Ultimately this can be written as this is actually sigma i by e. According to the definition of the flux density this is actually sigma i e and the e term is already there; from the earlier consideration the e; e is already there so there is a e here. So, this can be written e can be separated out and this will be actually the sigma in case that is ionic conductivity because you have considered the movement of the charge species. This is the flux density of the charge or the charged density charge moving per unit time by a unit cross-section.

So, that becomes the charge current density and this becomes your sigma ohms law the current density is proportional to the applied field. So, if you take the proportional the constant that becomes sigma. That is what has been written i means the i species particularly the higher species for which the current density has been at the flux density has been calculated.

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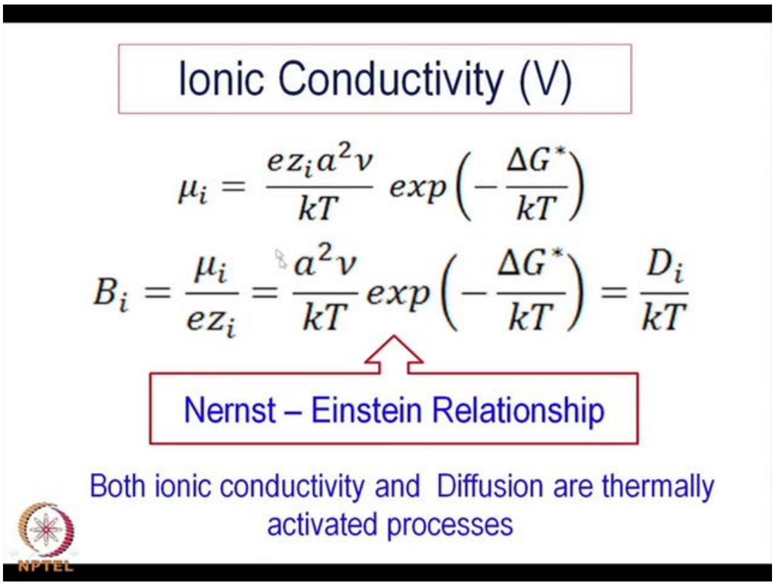

Ionic Conductivity (V)

$$\mu_i = \frac{ez_i a^2 \nu}{kT} \, exp\left(-\frac{\Delta G^*}{kT}\right)$$

$$B_i = \frac{\mu_i}{ez_i} = \frac{a^2 \nu}{kT} exp\left(-\frac{\Delta G^*}{kT}\right) = \frac{D_i}{kT}$$

Nernst – Einstein Relationship

Both ionic conductivity and Diffusion are thermally activated processes

Now, this also gives you another relationship because sigma is actually (( )) the concentration, the charge and the multiplied by the mobility term. So, one can write nhu i again the mobility of the charge species is also a exponential term; mobility of the charge species the sigma is an exponential term and the mobility is also and exponential term which is actually delta g star by kT, and this is a pre exponential constant where e is there, zi is there, a is also there. And, the mu the vibration of frequency. Now, this gives a relationship that mu i by ezi mu i by ezi is actually Bi a mobility of the diffusion coefficient or the mass transport mobility.

So, that becomes this one and ultimately one can write Di by kT. So, this is mobility and and this is Di. So, the mobility actually the mobility of the charge carrier is proportional to the Di the diffusion coefficient which can be measured maybe independent. Because diffusion coefficients also have a very similar mechanism by which the mass transport is taking place. Here the mass as well as charge, only thing the mass is having a charge. The diffusion coefficients when you measure it may have a species may have the charge, may not have the charge, but even then we will have a deficient coefficient. For example, in metals there is no charge, but the diffusion coefficients is their because of the concentration gradient.

So, in diffusion coefficient it is the concentration gradient which is basically the driving forces whereas, in ionic conductivity it is the impressed EMF, impressed voltage or the impressed field electric field which is the driving force. Because the species are here charged and therefore they respond to the electric field as well. So, but since the species are itself have contents of some mass. So, the concentration gradient also places a important role.

So, there is coordination between the impressed field and the concentration gradient. So, both of them actually drive a charge species into the lattice with the through the lattice. And, this relationship between the movement of the charge species and the diffusion coefficients is known as the Nernst- Einstein relationship is an important relationship in ionic conductivity and diffusion of course. Both ionic conductivity and diffusion are thermally activated processes and they are related by this relationship.

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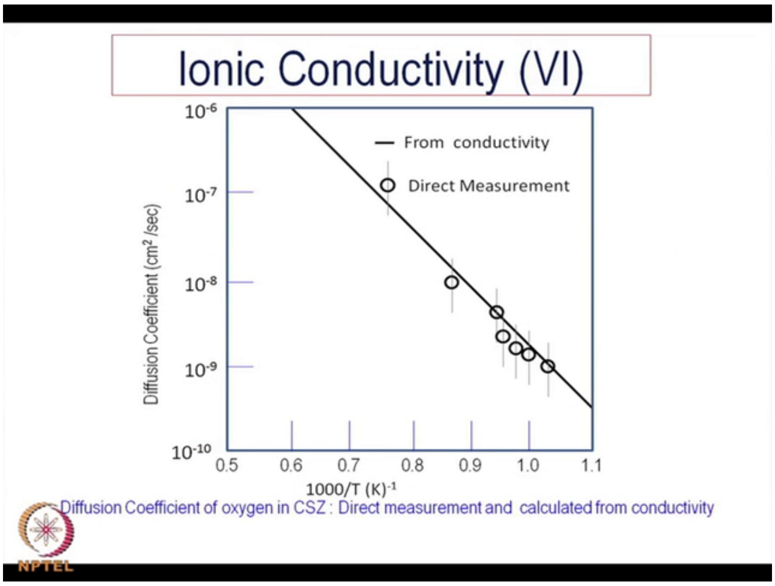

Ionic Conductivity (VI)

Diffusion Coefficient of oxygen in CSZ : Direct measurement and calculated from conductivity

Now, this is a basically justification or of this relationship that means in reality actually we do get a co-relationship between the ionic conductivity and diffusion. This is in case of a CSZ that is (( )) the diffusion coefficient of oxygen. Particularly in this case we have seen earlier that addition of calcium oxide to zirconia reacts considerable amount of oxygen vacancy. And, that oxygen vacancy favors the movement of the oxygen ions in this lattice and impact CSZ is a very good oxygen ion conductor; and one is one uses it extensively in for different purposes including sensor application, oxygen sensor application and also in high-temperature fuel cells those things will be discussed later.

So, CSZ is (( )) is good oxygen ion conductor. And, here what has been plotted is the diffusion coefficient major by 2 different techniques. One is the direct maybe diffusion coefficient measurement. So, where the conductivity is not coming into picture. When in another way from conductivity measurement also one can determine the diffusivity using the Nernst Einstein relationship. So, this solid line is has been plotted based on the conductivity data; whereas these experimental points has been measured by direct measurement of the diffusion coefficient; without application of electric field.

So, by concentration gradient one can measure the conductivity. So, it has been found this as you can see here that they are very good agreement with each other; both the conductivity data and direct diffusion measurement. Their good agreement also shows that the diffusion the validity of the Nernst Einstein relationship that means the conductivity and ionic and the diffusion coefficient, ionic conductivity at very very closely related.

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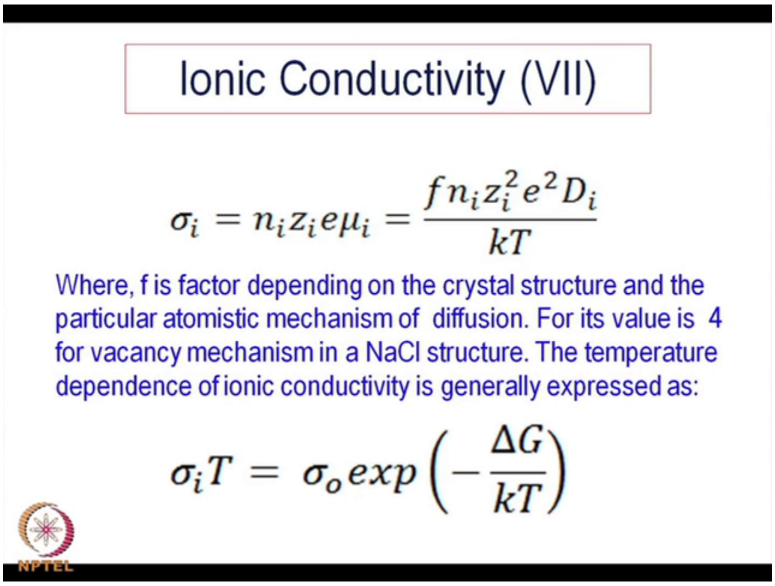

Ionic Conductivity (VII)

$$\sigma_i = n_i z_i e \mu_i = \frac{f n_i z_i^2 e^2 D_i}{kT}$$

Where, f is factor depending on the crystal structure and the particular atomistic mechanism of diffusion. For its value is 4 for vacancy mechanism in a NaCl structure. The temperature dependence of ionic conductivity is generally expressed as:

$$\sigma_i T = \sigma_o exp\left(-\frac{\Delta G}{kT}\right)$$

While, if you go little further in the same equations you will find that ultimately the sigma i is (( )) mu i; we have seen earlier the temperature dependence of mu i. Here the temperature dependence of overall sigma same thing is their mu is related to Di the division coefficient. And, factor f has been added here it is not 1 it is different.

So, sigma i is actually inversely proportional to temperature in addition to in addition to mu that means we have Di the diffusion coefficient is an exponential term of temperature or with an activation barrier. In addition sigma i is inverse; if this is taken as a constant although it is not a constant, but there is a in the denominator also the T term is there. So, that is an important consequence and important points to be noted. That the sigma i is also has in the denominator in addition to the exponential term is also as a theta. And, the factor f is dependent is depending on the crystal structure and the particular atomistic mechanism of diffusion. Well there are different mechanisms of diffusion in any system it may be vacancy diffusion, it may be a interstitial diffusion, it may be interstitial diffusion there are different mechanisms of diffusion. So, atomistic mechanism

So, atomistic mechanism so depending on that the factor will vary and also on the crystal structure. For example its value the f the value of f its value is 4 vacancy mechanism in a sodium chloride structure. If you have a rock salt structure or sodium chloride structure in which the diffusion is taking place by a vacancy mechanism. So, value is 4. The temperature dependence the temperature dependence of the ionic conductivity generally is expressed as from this it has been simplified like this. So, sigma i T sigma 0 exponential minus delta G by KT. Taking all the exponential terms together, but the most important thing is it is normally expressed as sigma IT it is multiplied by T. And, then only a log log plot log sigma T sigma iT sigma 0 and 1 by t not log log plot the Arrhenius plot.

But they are once you take not sigma i only but sigma only but sigma T that is that then only you can get a straight-line. So, this is not true or electronic conductivity or semiconductors. So, in semiconductors plot only sigma log sigma whereas, in a ionic conductors one need to plot; this sigma T to get a straight line or to get the value of delta G.

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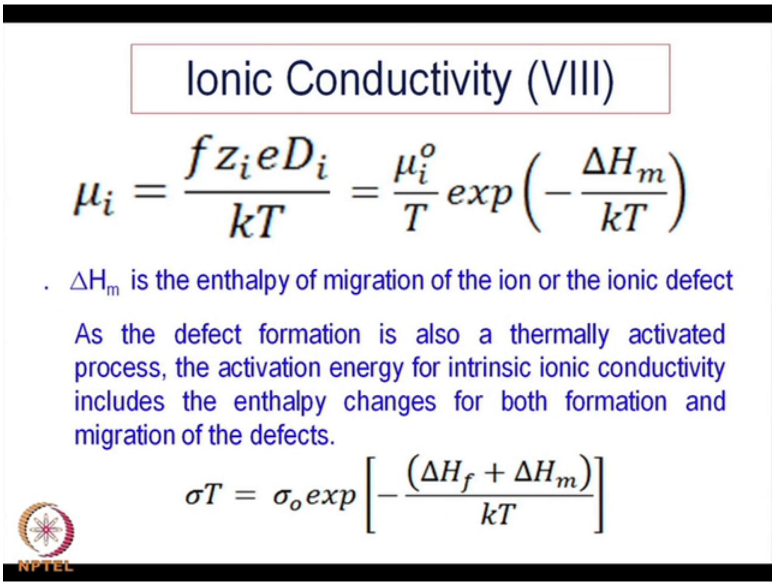

Ionic Conductivity (VIII)

$$\mu_i = \frac{f z_i e D_i}{kT} = \frac{\mu_i^o}{T} exp\left(-\frac{\Delta H_m}{kT}\right)$$

- ΔH_m is the enthalpy of migration of the ion or the ionic defect

As the defect formation is also a thermally activated process, the activation energy for intrinsic ionic conductivity includes the enthalpy changes for both formation and migration of the defects.

$$\sigma T = \sigma_o exp\left[-\frac{(\Delta H_f + \Delta H_m)}{kT}\right]$$

Now, there is something else also mu i the mobility we have already seen this; it can be again expressed as mu i 0 by T exponential KT. So, this is also mu i also as a in the dominator you have a T, but more important is here we are trying to concentrate on this term delta H m is the enthalpy of migration of the ion or the ionic defect. So, this delta G now may have 2 different components; one is called the migration that is actual mobility migration of the defect.

But as the defect formation is also a thermally activated process. The activation energy for intrinsic ionic conductivity includes the enthalpy changes for both formation and migration of the defects. So, when we are talking about sigma T; this is only for the migration the mobility term, but if you are talking about the concentration of the defects how many how many ions are actually taking part in the process that depends on the how many defects of there. Particularly we are talking about the defect; the vacancy mechanism of diffusion then we will find first of all the vacancy has to be created either thermally activated or by some extrinsic manner by adding some impurities and so on.

For example, in calicoes stabilizer zirconia by adding calcium oxide we are creating defects; we are creating oxygen vacancies. And, that oxygen vacancy concentration is proportional to the amount of calcium you are adding it is not dependent on temperature. However in some other cases when the impurity effect is not there the intrinsic defect are created by temperature temperature rise. And, therefore that defect concentration is proportional is dependent on the activation energy of that particular process which we have seen earlier in case of point defects. So, point defect creation need some activation energy its migration also needs activation energy. And, these are 2 terms which has been given here sigma t; so it is a formation defect of the activation energy for the formation of the defects, and the activation energy for the migration of defects. So, the overall activation energy consists of 2 different terms; one is the formation of the defects another is another is for the migration of the defect. It means if the formation is already there so the temperature will not be needed for the formation then only the migration will be effective.

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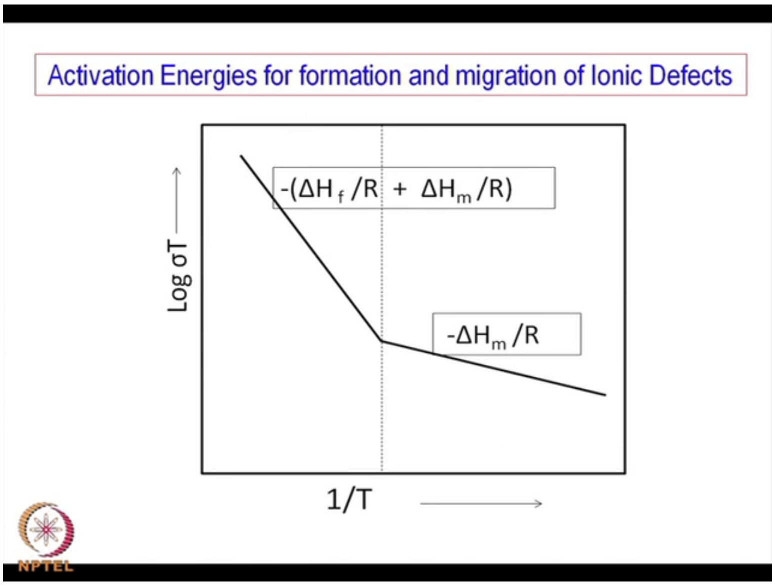

Activation Energies for formation and migration of Ionic Defects

So, formation energy is not required but generally it will have 2 different types. I think this I will discuss first and then go back. These are the activation energy for the formation and migration of ionic defects. So, if you plot log sigma T as a function of 1/T that is the normal Arrhenius plot kind of thing. Then, once again you have 2 different activation energies at the lower temperature it is only delta Hm; because you are not generating any defect here. The defects already been generated if that high-temperature and whatever migration because this energy is not sufficient for creation of the intrinsic defect. This at this temperature it may be impurity affect which becomes predominant; which we have seen earlier in impurity controlled semiconductor also same thing can happen.

So, if you have already introduced some defect by solving solution effect or impurity effect. Then, those defects or those active sites, active charged carriers will migrate at the low-temperature. And, the only energy to be supplied is delta Hm. However at higher temperature you need both the terms to be supplied both the terms here of course R as been written this is as per mole; you can also use K because if it is one number one number of charge carriers. So, delta H f is the additional energy you need to create the vacancy at high temperature.

So, you have a lower activation energy here and higher activation energy, there a steeper slope there and a lower slope here. So, from these 2 regions are also one can be identify this kind of extrinsic region these are an intrinsic region. So, just like as in semiconductors you can also have ionic conductivity 2 regions; one is the extrinsic region, another is the intrinsic region.

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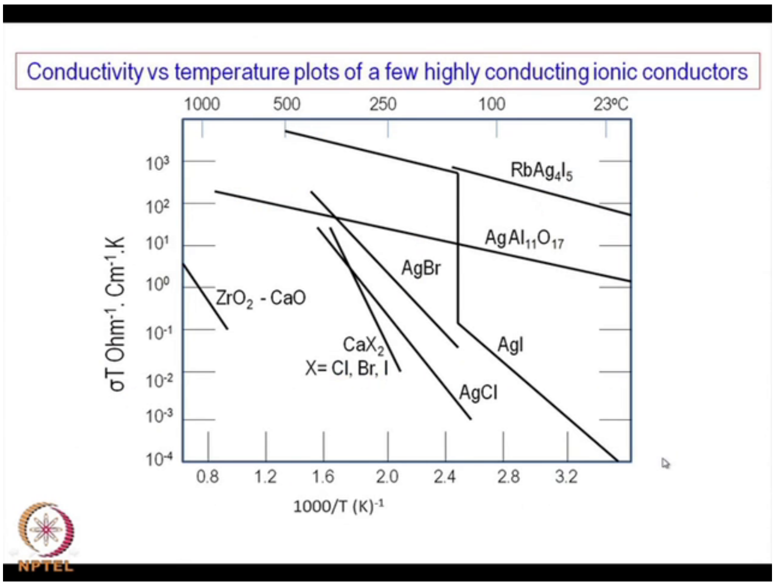

Conductivity vs temperature plots of a few highly conducting ionic conductors

Now, this is the conductivity versus temperature plots of highly conducting ionic conductors. There is loss plots of some compounds not all of them are oxides because oxides are not only the ionic conductors. There are many non-oxides; particularly the alkali halides alkali halides like this sodium silver iodide in fact silver iodide is one of the very important ionic conductors which all the conductivity is because of this silver ion and not the iodide ion. So, it is a ion; cationic conductor all these are basically cationic conductors. So, there is a phase transformation around 100 and 50 degree also.

So, it is a very some change of transformation the higher phase the higher polymorphic form as a much higher conductivity much higher conductivity than the lower polymorphic form lower temperature polymorphic form. And, either you can see the conductivity has been plotted here as a sigma T.

So, to get the straight line behavior you have to plot sigma T and just not only sigma (( )). So, silver iodide is one of the compounds having a very higher ionic conductivity. You have also silver rubidium iodide silver a part of this silver has been replaced by rubidium; and that increases the defect of concentration and even at the room temperature, even at the not only at room temperature, but also the lower temperature. So, this transformation has been avoided.

So, this transportation has been stabilized and even at room temperature. You can get a very high ionic conductivity which is very high compared to many other oxides. There is another compound silver aluminum oxide impact it is what we call silver beta alumina. Beta alumina is a compound which is a layered structure and in which one of the layer is a very disordered layer and this cations this cations are placed in this disordered layer. Either silver or sodium, lithium all these alkali metal ions can be placed or located in these disordered structure. So, at a very low temperature very close to room temperature within 100 and 50 degrees you have a very high conductivity of cations.

And, once again silver beta alumina or lithium sodium beta alumina and particular has a lot of industrial applications a once again as a one can generate power out of this one can make batteries. Sodium sulfur batteries making use of these compounds as their oxides again, but have been a very high conductivity comparable to these halides. And, at a very low temperature. Fairly low temperature 100 and 50 degrees they can be very highly conducting; and can be used effectively as electrolytes in some of the battery systems high-temperature battery systems.

You have silver bromide, silver chloride their conductivities are slightly low. And, then you have a host of calcium halides like calcium chloride, calcium bromide, calcium iodide all of them you have calcium conductivity calcium and conductivity. And, the only example in these figure of an ionic conductor is zirconium calcium which has been mentioning earlier calcium zirconium stabilized, but we will see later on that. Other stabilizers like yttrium oxides, scandium oxides etcetera also have a very good oxygen ion conductor. And, the conductivities or compared comparatively higher, compared to this calcium zirconium stabilize. And, in fact in sensors in sensor application and fuel cells we will see that it is the zirconium yttrium system more preferred than zirconium calcium. And, in some cases zirconium Skandia Se2O3 is also added and the conductivity is impact much higher although it is little costly.

So, for economic reasons it is not used that much but zirconium yttrium is one of the almost commercial material which is extensively used as a oxygen ion conductor in addition to other properties. Few more oxides also have a oxygen ion conductivity like cerium oxide, thorium oxide so all of them have a cubic fluoride structure; and you can have fairly good amount of oxygen ion conductivity. As you have seen from the concentration versus PO2 diagram of course in these not much of investigation has been made. So, for as the partial pressure dependence of either a silver or rubidium all that because these are mostly solid we do not get wafers out of that so easily. Whereas, when you talk about oxides; one of the consequence the oxygen is available in the form of the gaseous substance and it is available in atmosphere.

So, oxygen partial pressure dependence on these are quite important. And, it is not true that all oxygen partial pressures the oxygen ion conductivity available only in certain oxygen partial pressure range they so called intermediate oxygen partial pressure range; where the oxygen and conductivity will be predominant. But if the oxygen partial pressure is higher too high or too low the defects situation; the defect concentration compensation changes and one can get again the semi conductivity in those it tends to become a non-stoichiometric metric oxides and the semi conductivity keeps in that. When the semi conductivity comes in of course the material will not be useful as a solid electrolytes, but maybe it can be use for some other purposes. Well we are talking about only about the cations like alkali metals or the oxygen ion conductors.

But there are ionic compounds or ionic conductors in which even the proton, even the hydrogen ion not the proton the hydrogen ion can conduct there are oxide. We will see some of the example later on where even the hydrogen ions can the mobile species. So, of course the mechanism is slightly different there the originally hydrogen is little different, but it is possible to have hydrogen ion conductivity in some of the oxides.

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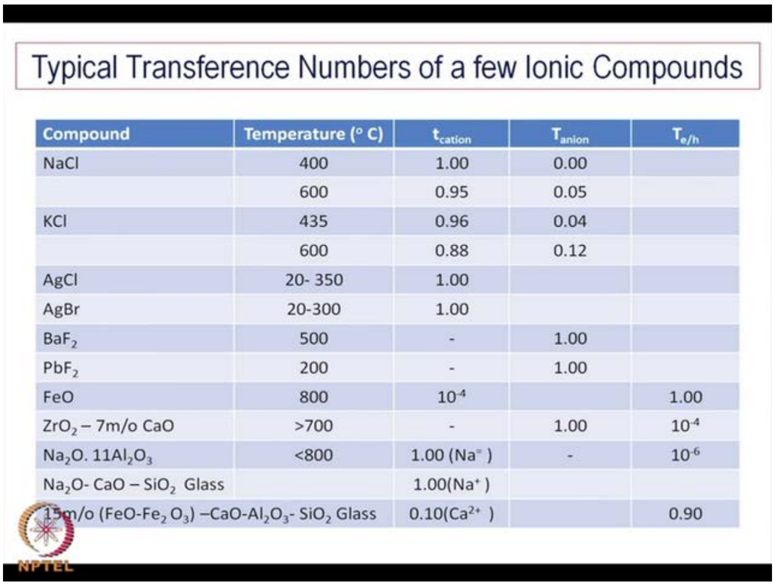

Typical Transference Numbers of a few Ionic Compounds

Compound	Temperature (° C)	t_{cation}	T_{anion}	$T_{e/h}$
NaCl	400	1.00	0.00	
	600	0.95	0.05	
KCl	435	0.96	0.04	
	600	0.88	0.12	
AgCl	20- 350	1.00		
AgBr	20-300	1.00		
BaF_2	500	-	1.00	
PbF_2	200	-	1.00	
FeO	800	10^{-4}		1.00
ZrO_2 – 7m/o CaO	>700	-	1.00	10^{-4}
Na_2O. $11Al_2O_3$	<800	1.00 ($Na^=$)	-	10^{-6}
Na_2O- CaO – SiO_2 Glass		1.00(Na^+)		
15m/o (FeO-Fe_2O_3) –CaO-Al_2O_3- SiO_2 Glass		0.10(Ca^{2+})		0.90

Now, when you are talking about the ionic conductivity one more important parameter we have to always consider. And, that we have been we have talked about earlier that is what is called the transference number. Transference number is a very important parameter in relation to the oxygen the ionic conductivity. And, here is a list of the transference number of some of the compounds have been mentioned which has been mentioned earlier. At different temperatures and the columns are cation conductivity, anion conductivity and the electron or hole conductivity these will be not capital T minute.

So, coming back to the table this are the typical transference numbers of a few ionic compounds to start with sodium chloride or structure you know. These there is a sodium ion diffusion sodium, and there is sodium ion diffusion considerable sodium ion diffusion and the cation diffusion is maximum and anion that is any except that is slightly high temperature. That means, some chlorine ion can be diffuse at higher temperature like 600 degrees close to its melting point. And, then there is of course no electronic diffusion, electronic conductivity or electron transport at all so it is purely ionic conductor.

So, is the case with potassium chloride as you can see it is the potassium ions which move cation conductors and that the higher temperatures some amount of anionic conductivity also comes in. Here still very little of anionic conductor is there; silver chloride there is a no ionic conductivity, fully cationic conductors from 20 to almost 350 degrees silver bromide same thing. Again cationic conductors 100 percent cationic conductors barium chloride, barium fluoride or lead fluoride these are the fluorides which have no cationic conductor conductivity. But fluorine ion conductivity; fluorine ion conductivity is there but, one thing you must know calcium fluoride CaF2 that is the fluoride structure from which the name fluoride structure as come they are that is also absolutely an insulating material.

But barium fluoride and lead fluoride has a good fluorine and conductivity. Iron oxide as we have discussed on several occasions that is its semiconducting oxide with cation vacancy and so there is hardly any cationic conductor 10 to the power of minus 4 is very very small. So, the transparent number of the cations, but, the electronic impact is the hole conductor. The whole conductivity is almost full in this sense purely hole conductor there is no cationic conductor. This we have discussed again calicoes stabilize zirconium above of course the conductivity is appreciable only above 600 centigrade.

So, at below 600 is purely a almost for all practices purposes it is a insulator the mobilities extremely low. So, only about 600 or 700 degrees you have appreciable amount of oxygen and conductivity. And, you can see there is hardly any electronic or hole conductivity whereas, its 100 percent t ion is 1 t ion is 1 that is means oxygen ion conductivity. We have mentioned about silver beta alumina; this is sodium beta alumina same thing silver has been replaced by sodium otherwise everything remains same structure and the formula is also is same; this is less than 800 degrees. In fact even at 150 degrees they have a very good conductivity and this is sodium ion once again there is some problem these is sodium ion.

And, once again we have very low electronic conductivity or whole conductivity ***a***lmost everything is because of this sodium ion conductivity is because sodium energy mentioned because there are 2 different cations; aluminum is not the conductor. If you talk about just a reference just a comparison to talk about glass, normal sodium silica glass there also you have 100 percent conductivity because of the sodium ion of course, it is actually used as a solid (( )) Ph meters.

So, that is the reason it has been listed here. And, finally you have a glass another glass composition just for comparison having some iron oxide FeO-Fe2O3 that is kind of a system. And, these is a purely electronic conductor almost like pure electronic conductor except there is a very little of calcium oxide conductivity. So, what we can why these two glasses have been mentioned here? That by just changing the composition the glass basic glass can be changed from a ionic conductor to an electronic conductor. And, the conductors conductivity is primarily because of the presence of the semiconducting oxides.

So, that more or less completes our description on ionic conductivity and also the electrical conduction in oxides, ceramic materials to just summarize we have discussed various concepts of conduction mechanisms. And. the basic parameters, basic theories to explain the conductivity of different solids whether it is metals, whether it is elemental semiconductors or some of the insulators. And, when you are talking about oxides we have all possibilities, we have insulators, we have semiconductors and we have even conductors in some of the oxides which we have not discussed that much in details. But it very much there is some metal transitions.

And, in addition particularly in ceramics we have a range of solid electrolyte or ionic conductors; which are also of very much technological importance and their mechanisms which have discussed their temperature dependence we have discussed. But one important thing for oxides is the partial pressure dependence the atmosphere has a very very important role to play.

So, for as the charge carrier concentration is concerned and of course the temperature has a very important effect in most cases it is exponential dependent. And, in case of ionic conductivity we have a temperature term also in the denominator and that makes the situation slightly different. But in general it is exponential dependent on temperature. So, that completes our discussion on the electrical conduction in ceramics materials. Later on we will see how the insulators because many of the oxide or many of the ceramic materials are actually insulators. So, how they respond to the electric field whether it is the dielectric material, piezoelectric material or the pi electric material. With this we come to the end of this particular module.

Thank you. Thank you for your (( )).