Electroceramics
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Lecture - 14

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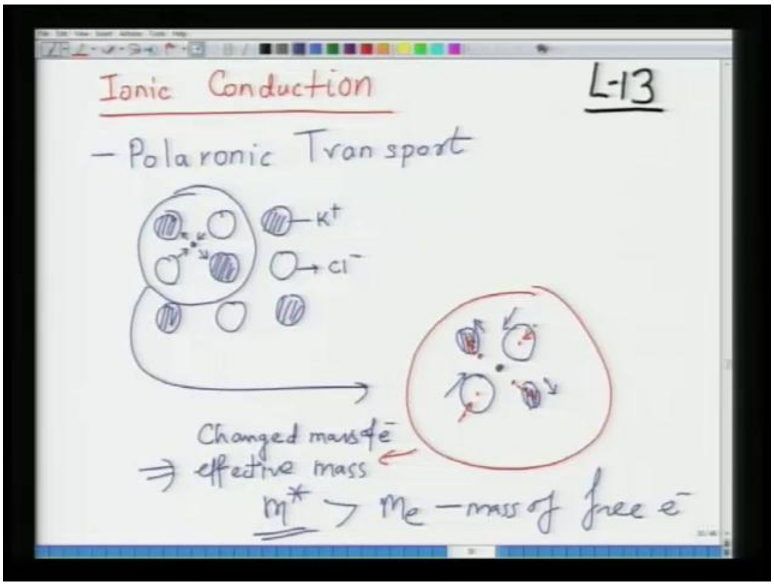

Ionic Conduction

L-13

- Polaronic Transport

Changed mass of e^-
$\Rightarrow$ effective mass
$m^* > m_e$ - mass of free e^-

Welcome to this new class. So, what we will do first is to review the last lecture, which is thirteenth lecture. So, in this lecture we discussed about the polaronic transport, which is nothing but related to mechanism of conduction in ionic solids. So, unlike metals and semiconductors where a transport happens in the bands, where electrons or holes move in the bands, here in in ionic solids it is the polaronic transport. Now, this polaron is nothing but it is a charge carrier which is in the proximity of lattice, and this proximity of the lattice leads to polarisation of lattice and this leads to a combined entities sought of lattice, and the lattice ions and the carrier and this is called as polaron. This proximity also changes the effective mass of in the electron, and it usually it is heavier than the mass of free electron. So, as and also since is it it is associated with the lattice it moves from one side to another.

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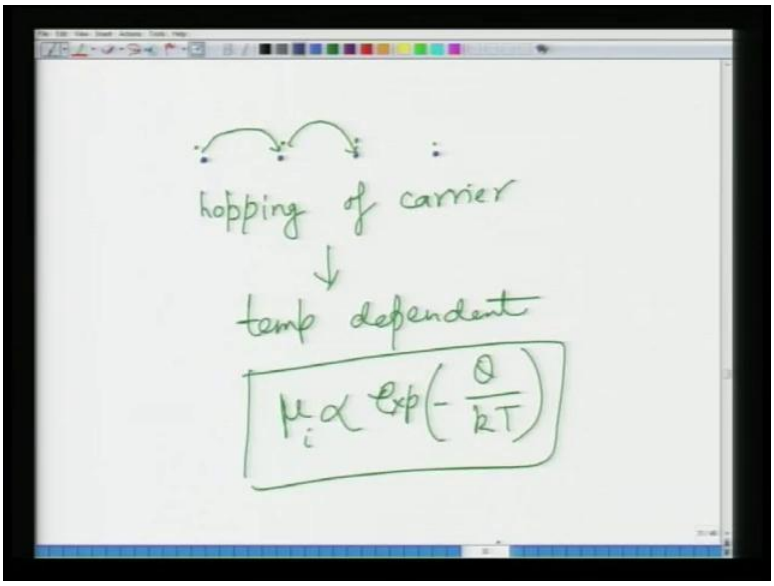

hopping of carrier

↓

temp dependent

$$\boxed{\mu_i \propto \exp\left(-\frac{Q}{kT}\right)}$$

So, it happens by hopping of carrier from one side to another, as a result it is temperature dependent. So, mobility in this case becomes temperature dependent in the form of exponential minus Q by k t, unlike in the case in metal semi conductors, where it is dependent t to power minus 3 by 2 form which is due to scattering. So, the dependence of temperature in say metals and dependence on temperature of mobility in metals semiconductor and in ionic solids is due to different reasons as a result you have different dependence.

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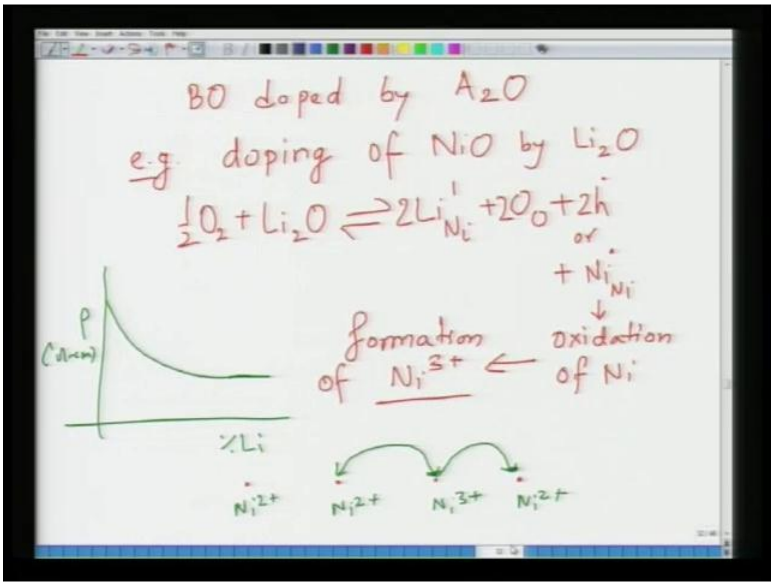

BO doped by A_2O

e.g. doping of NiO by Li_2O

$$\frac{1}{2}O_2 + Li_2O \rightleftharpoons 2Li'_{Ni} + 2O_O + 2h^{\cdot}$$

or $+ Ni^{\cdot}_{Ni}$

↓

oxidation of Ni → formation of $\underline{Ni^{3+}}$

Then we looked at the case case for example, how does the resistivity changes in ionic solid for example, in a doped oxide.

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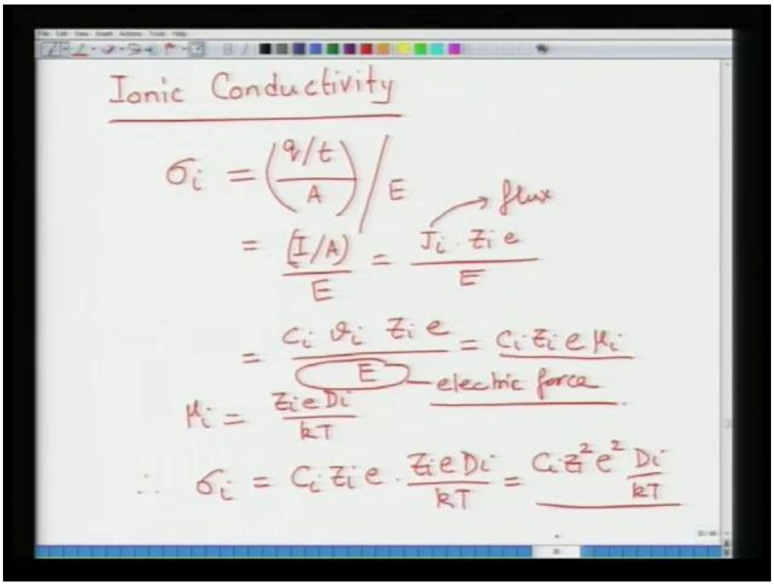

Ionic Conductivity

$$\sigma_i = \left(\frac{q/t}{A}\right)\Big/E$$

$$= \frac{(I/A)}{E} = \frac{\overset{\text{flux}}{J_i} \cdot Z_i e}{E}$$

$$= \frac{C_i \vartheta_i Z_i e}{\underset{\text{electric force}}{E}} = \underline{C_i Z_i e \mu_i}$$

$$\mu_i = \frac{Z_i e D_i}{kT}$$

$$\therefore \sigma_i = C_i Z_i e \cdot \frac{Z_i e D_i}{kT} = \underline{C_i Z_i^2 e^2 \frac{D_i}{kT}}$$

Then, we looked at what is ionic conductivity in these materials. Ionic conductivity is nothing but C i, Z i, e, mu i and you know what mu i is mu i is nothing but the ionic mobility.

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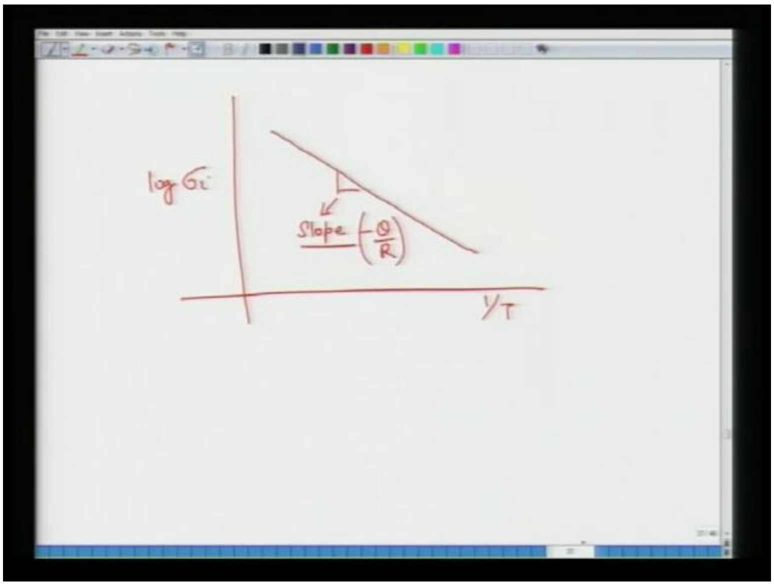

So, you can see that resistivity or conductivity has similar relation to temperature as diffusivity has. Simply because proportional to and again proportional to diffusivity and similarly, just like diffusivity it also has extrinsic intrinsic regions.

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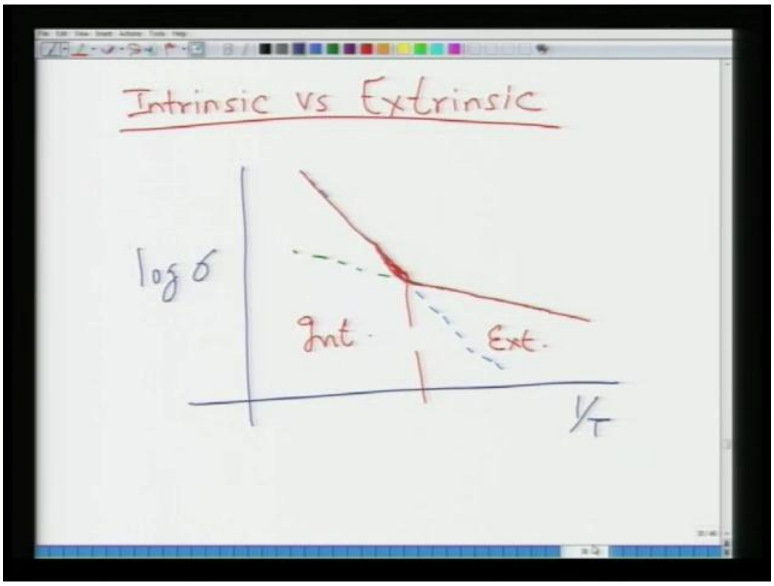

Intrinsic vs Extrinsic

In case of impure solids there will be extrinsic region, where conductivity will be will be governed by the concentration of impurities. There will be intrinsic region where conductivity is going to govern going to be governed by intrinsic defects.

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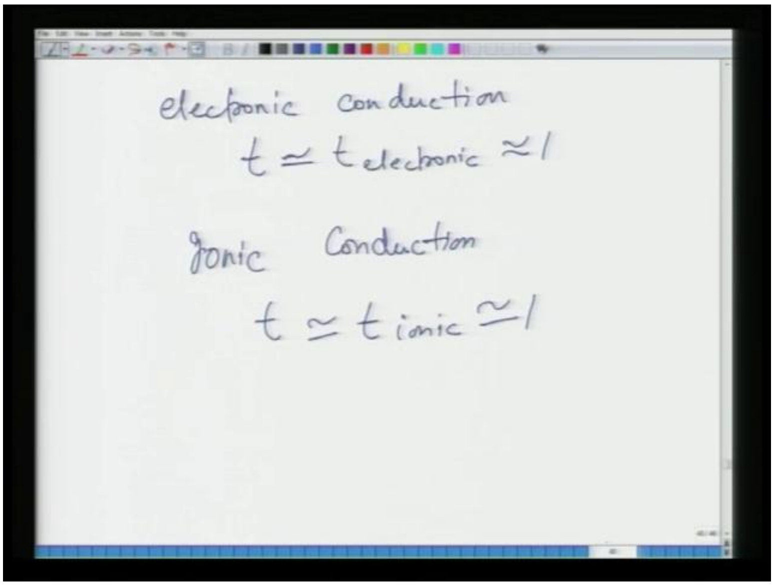

electronic conduction

$t \simeq t_{electronic} \simeq 1$

Ionic Conduction

$t \simeq t_{ionic} \simeq 1$

Then we have this ionic conduction.

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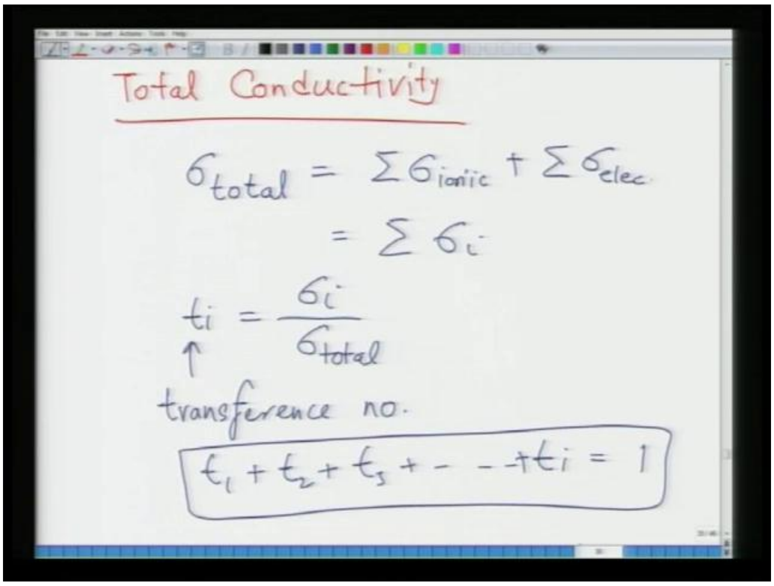

Total Conductivity

$$\sigma_{total} = \sum \sigma_{ionic} + \sum \sigma_{elec}$$
$$= \sum \sigma_i$$

$$t_i = \frac{\sigma_i}{\sigma_{total}}$$
$\uparrow$
transference no.

$$\boxed{t_1 + t_2 + t_3 + - - - + t_i = 1}$$

We looked at a transference number and this transference number is nothing but ratio of ionic or electronic conductivity to the total conductivity, so any type of conductivity divided by total conductivity because total conductivity is sum of all source of conductivities. So, for a perfect ionic conductor t will be equal to 1, t ionic will be equal to 1 and for perfect electronic conduction t electronic will be close to 1.

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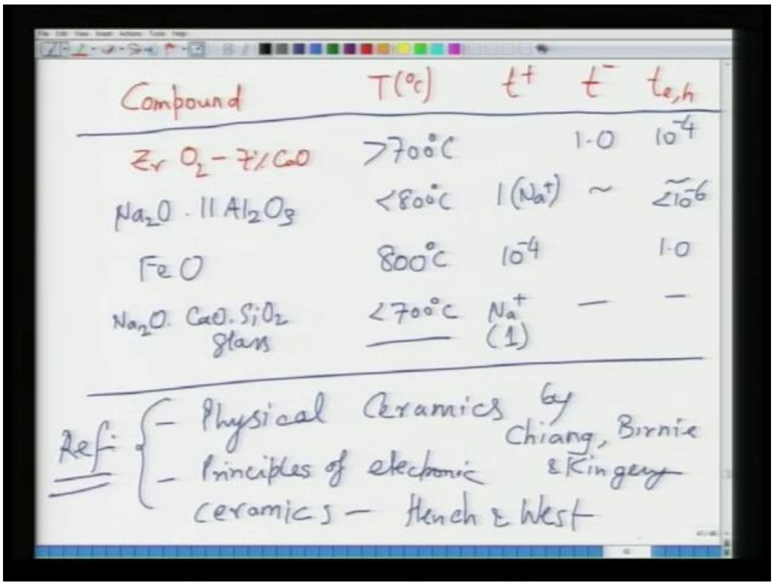

Compound	T(°C)	t^+	t^-	$t_{e,h}$
ZrO_2 - 7% CaO	>700°C		1.0	10^{-4}
$Na_2O \cdot 11Al_2O_3$	<800°C	1 (Na^+)	~	$\lesssim 10^{-6}$
FeO	800°C	10^{-4}		1.0
$Na_2O \cdot CaO \cdot SiO_2$ glass	<700°C	Na^+ (1)	—	—

Ref:
- Physical Ceramics by Chiang, Birnie & Kingery
- Principles of electronic ceramics – Hench & West

Then we had look at the certain material systems.

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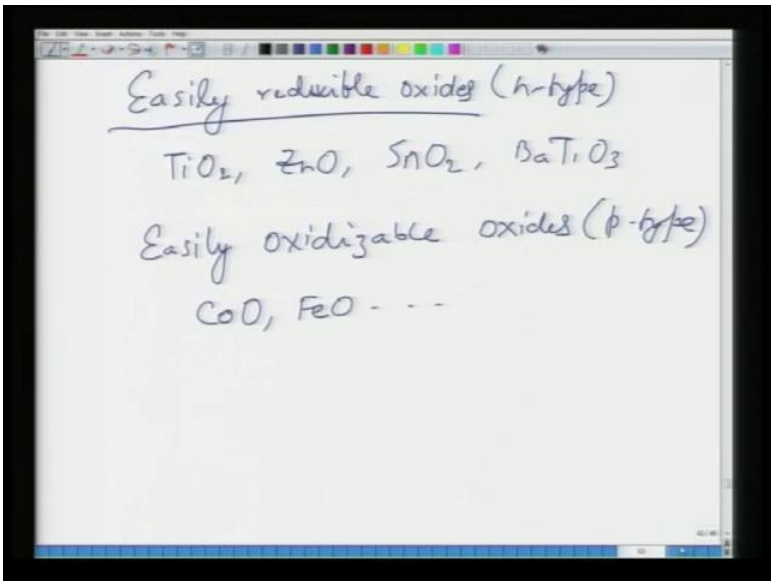

Easily reducible oxides (n-type)

TiO_2, ZnO, SnO_2, $BaTiO_3$

Easily oxidizable oxides (p-type)

CoO, FeO . . .

And then we show an example of magnesium oxide.

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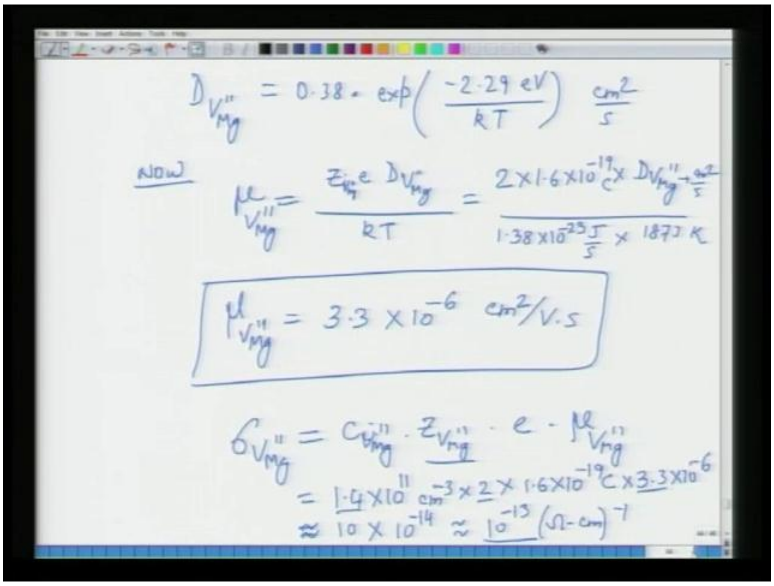

$$D_{V''_{Mg}} = 0.38 \cdot \exp\left(\frac{-2.29\ eV}{kT}\right) \frac{cm^2}{s}$$

Now

$$\mu_{V''_{Mg}} = \frac{Z_{V''_{Mg}} e\, D_{V''_{Mg}}}{kT} = \frac{2 \times 1.6 \times 10^{-19}\, C \times D_{V''_{Mg}} \rightarrow \frac{cm^2}{s}}{1.38 \times 10^{-23} \frac{J}{s} \times 1873\ K}$$

$$\boxed{\mu_{V''_{Mg}} = 3.3 \times 10^{-6}\ cm^2/V.s}$$

$$\sigma_{V''_{Mg}} = C_{V''_{Mg}} \cdot \underline{Z_{V''_{Mg}}} \cdot e \cdot \mu_{V''_{Mg}}$$

$$= \underline{1.4} \times 10^{11}\ cm^{-3} \times \underline{2} \times 1.6 \times 10^{-19}\, C \times \underline{3.3} \times 10^{-6}$$

$$\approx 10 \times 10^{-14} \approx \underline{10^{-13}}\ (\Omega\text{-}cm)^{-1}$$

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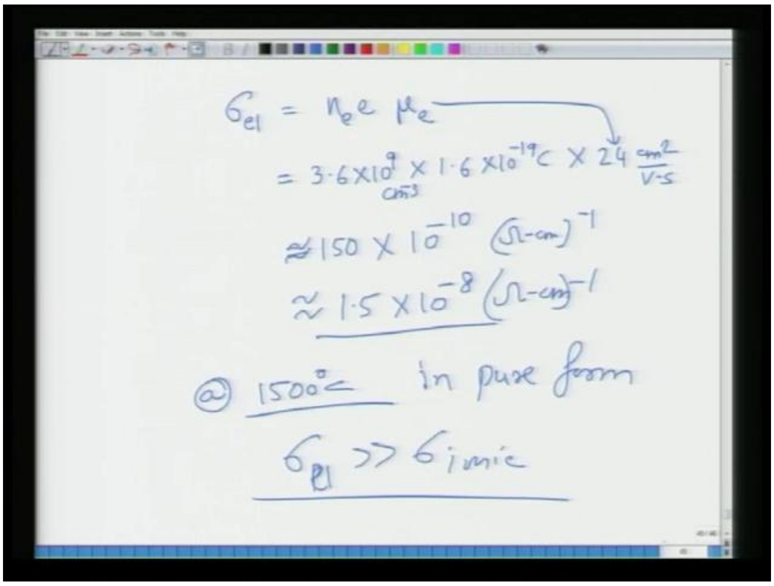

$$\sigma_{el} = n_e e \mu_e$$

$$= 3.6\times10^{9}\,\text{cm}^{-3} \times 1.6\times10^{-19}\,C \times 24\,\frac{\text{cm}^2}{V\cdot s}$$

$$\approx 150 \times 10^{-10}\,(\Omega\text{-cm})^{-1}$$

$$\approx 1.5 \times 10^{-8}\,(\Omega\text{-cm})^{-1}$$

@ 1500°C in pure form

$$\sigma_{el} >> \sigma_{ionic}$$

So, what we found in this example was that in the pure form at 1500 degree centigrade, sigma electronic is much larger than sigma ionic. So, what we will do in these classes is, we will look at what is the effect of doping on conductivity.

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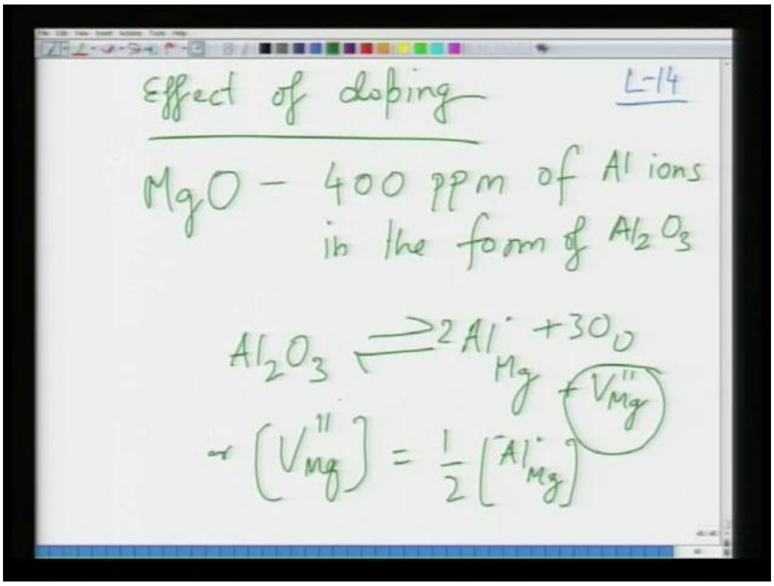

Effect of doping

L-14

MgO – 400 ppm of Al ions in the form of Al_2O_3

$$Al_2O_3 \rightleftharpoons 2Al_{Mg}^{\bullet} + 3O_O + V_{Mg}''$$

$$\rightarrow [V_{Mg}''] = \frac{1}{2}[Al_{Mg}^{\bullet}]$$

So, and effect of now this is because magnesium oxide is prone to having impurities so it contains about 400 PPM of roughly aluminium ions, in the form of A l 2 O 3. So, now you can write the defect reaction as you can. So, A l 2 O 3 going to so A l going to M g site and it is going to give rise to one positive charge. So, since both the aluminium's go to magnesium sites you have, you can have a various scenarios. One scenario could be all the three oxygen’s going to oxygen sites, creating one vacancy of magnesium or giving rise to all the excess oxygen goes out and giving rise to you know electrons. So, what happens in this case is vacancy concentration is dependent upon the concentration of aluminium oxide.

So, you can see V m g from this relation is equal to half of A l M g. So, if you know the concentration of A l 2 O 3 you can you can work out concentration of aluminium ions, from that you can work out what is the concentration of vacancies. So, using simple principles you can convert mol percent into per centimetre cube.

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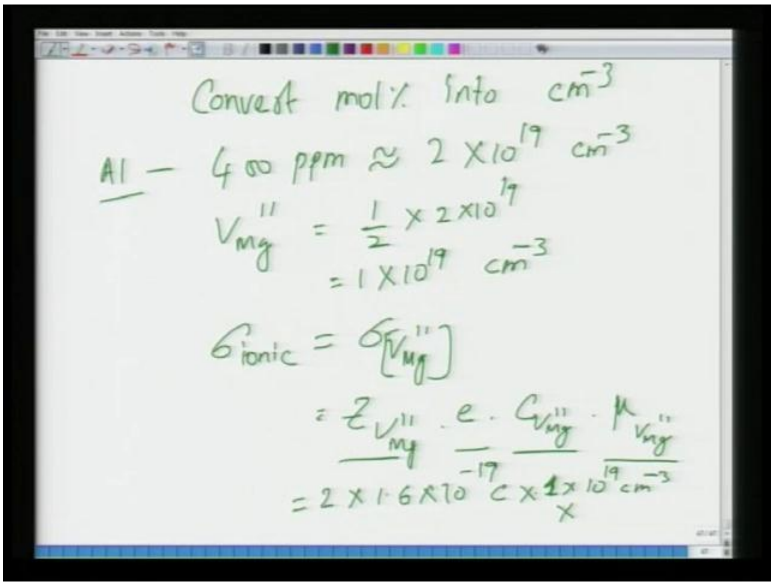

Convert mol% into cm^{-3}

$\underline{Al}$ — 400 ppm $\approx 2 \times 10^{19}\ cm^{-3}$

$V_{Mg}'' = \frac{1}{2} \times 2 \times 10^{19}$

$= 1 \times 10^{19}\ cm^{-3}$

$\sigma_{ionic} = \sigma_{[V_{Mg}'']}$

$= \underline{Z_{V_{Mg}''}} \cdot \underline{e} \cdot \underline{C_{V_{Mg}''}} \cdot \underline{\mu_{V_{Mg}''}}$

$= 2 \times 1.6 \times 10^{-19}\ C \times 1 \times 10^{19}\ cm^{-3} \times$

So, this 400 PPM works out to about 2 into 10 to power 19 per centimetre cube. Since, you know that so this is your aluminium concentration. So, your V M g is about half into 2 into 10 to power 19. So, this will be 1 into 10 to power 19 per centimetre cube. So, this will be your concentration of. So, here we have got, I am just trying to work out what is so V M g A l M g is equal to twice of V M g. So, V M g is half of a l M g. So, we are write there so 1 into 10 to power 19. So, now from this you can work out, what is sigma ionic? Sigma ionic is nothing but your basically sigma V M g which is nothing but Z V M g multiplied by e multiplied by C V M g multiplied by mu V M g.

Now, mu V M g we have already calculated C V M g we know what it is electron charge. We know and Z V M g is 2 so that this would be 2 into 1.6 into 10 to power minus 19 coulomb multiplied by 2 1 in sorry not 2 but 1. 1 into 2 10 to power 1 19 per centimetre cube multiplied by mu which is nothing but 7.6 into 10 to the power minus 6. If you go to previous slides, one of those we worked out mu as mu to be 3.3 into 10 to the power minus 6 centimetres square per volts second.

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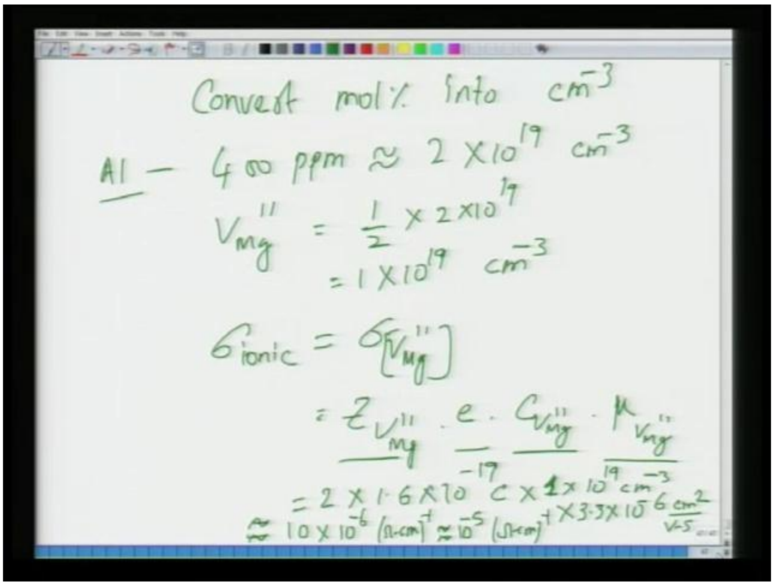

Convert mol% into cm^{-3}

$\underline{Al}$ — 400 ppm $\approx 2 \times 10^{19}$ cm^{-3}

$V_{Mg}'' = \frac{1}{2} \times 2 \times 10^{19}$

$= 1 \times 10^{19}$ cm^{-3}

$\sigma_{ionic} = \sigma_{[V_{Mg}'']}$

$= \underline{Z_{V_{Mg}''}} \cdot \underline{e} \cdot \underline{C_{V_{Mg}''}} \cdot \underline{\mu_{V_{Mg}''}}$

$= 2 \times 1.6 \times 10^{-19}\ C \times 1 \times 10^{19}\ cm^{-3} \times 3.3 \times 10^{-6}\ \frac{cm^2}{V\text{-}S}$

$\approx 10 \times 10^{-6}\ (\Omega\text{-}cm)^{-1} \approx 10^{-5}\ (\Omega\text{-}cm)^{-1}$

So, this will be your approximately 3.2 multiplied by 3.3 approximately 10. 10 multiplied by 10 to the power minus 19 minus 19 plus 19 will cancel each other, 10 to the power minus 6 so this will be in ohm's centimetre inverse and this will be 10 to power minus 5 approximately. I am saying approximately equal to 10 to the power minus 5 ohm centimetre inverse. So, now if you go to next slide, electron conductivity electronic conductivity has to be either due to electrons or holes. Now, we we have calculated what the intrinsic electron concentration is. We know that intrinsic electron concentration was 3.6 into 10 to power 9.

Now, let us see what is the electron concentration due to defect creation? So, under under in the normal atmosphere so let us say normal atmosphere case. Now, this means p O 2 will be equal to 0.21 of atmosphere.

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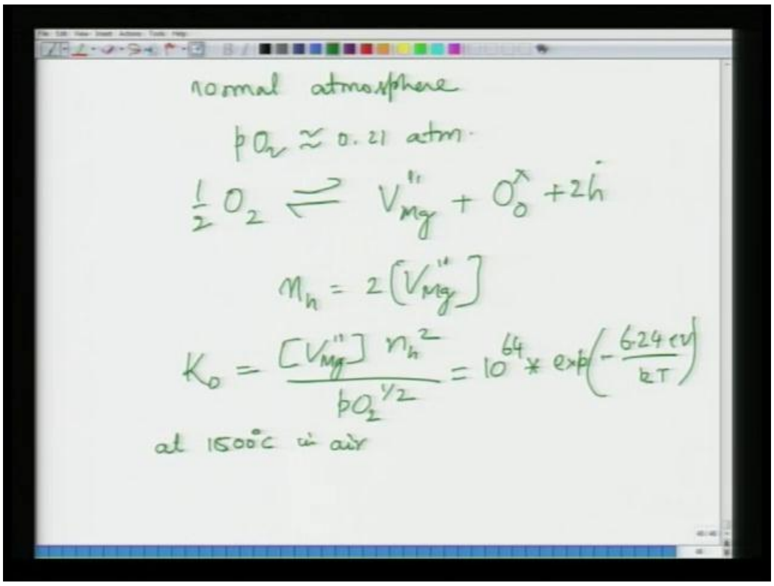

normal atmosphere

$pO_2 \simeq 0.21$ atm.

$$\frac{1}{2}O_2 \rightleftharpoons V_{Mg}'' + O_O^x + 2\dot{h}$$

$$n_h = 2[V_{Mg}'']$$

$$K_o = \frac{[V_{Mg}''] \, n_h^2}{pO_2^{1/2}} = 10^{64} * \exp\left(-\frac{6.24 \text{ eV}}{kT}\right)$$

at 1500°C in air

So, this we treat as a oxidizing condition. Under these conditions your half O 2 goes in gives rise to V M g plus O o x plus h dot, 2 h dot. So, n h is equal to 2 V M g. So, from this you can calculate what n h is? Now, you know that oxidation constant, you can calculate as V M g into n h square divided by p O 2 to the power half. From this reaction and this is given as 10 to power 64 multiplied by exponential minus of 6.24 e v by k T. So, from this at 1600 degree centigrade in air, is a correction to be made in the previous slides that is here it should be 1600 degree centigrade not 1500 that is the only change.

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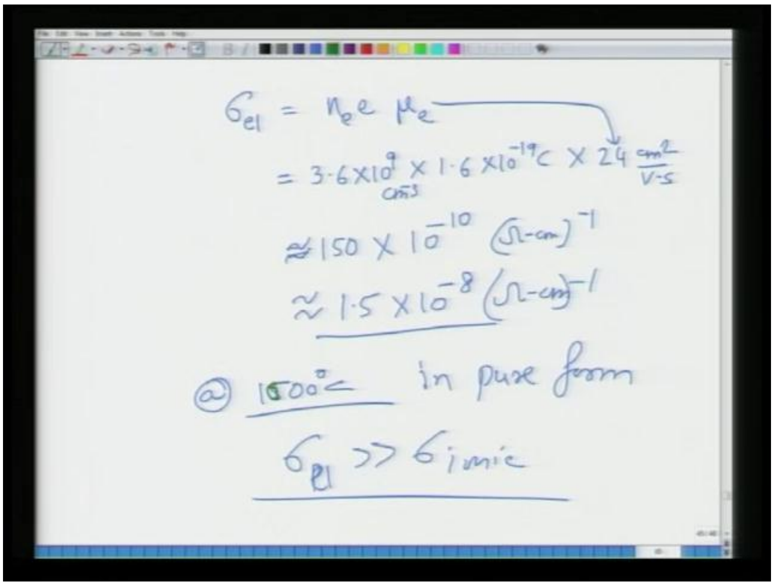

$$\sigma_{el} = n_e e \mu_e$$

$$= 3.6 \times 10^9 \, \text{cm}^{-3} \times 1.6 \times 10^{-19} \text{C} \times 24 \, \frac{\text{cm}^2}{\text{V-s}}$$

$$\approx 150 \times 10^{-10} \, (\Omega\text{-cm})^{-1}$$

$$\approx 1.5 \times 10^{-8} \, (\Omega\text{-cm})^{-1}$$

@ 1600°C in pure form

$$\sigma_{el} >> \sigma_{ionic}$$

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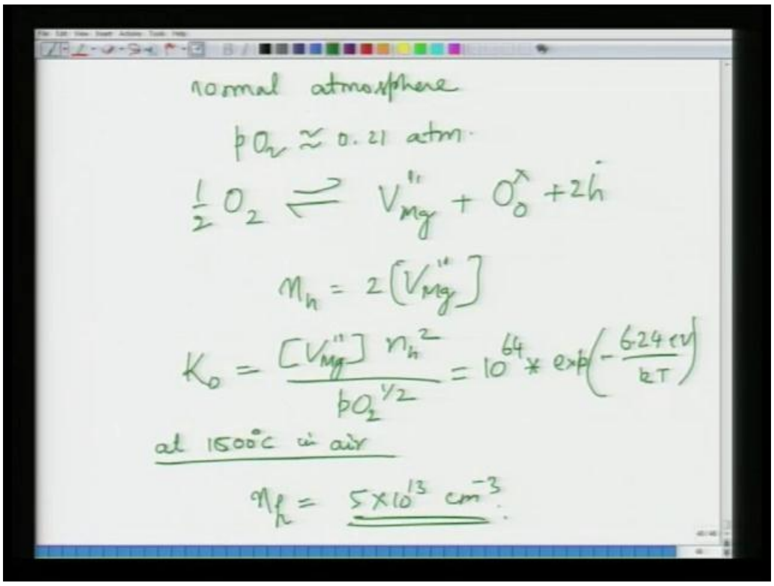

normal atmosphere

$$pO_2 \simeq 0.21 \text{ atm}.$$

$$\frac{1}{2}O_2 \rightleftharpoons V_{Mg}'' + O_O^{x} + 2\dot{h}$$

$$n_h = 2[V_{Mg}'']$$

$$K_o = \frac{[V_{Mg}'']\, n_h^2}{pO_2^{1/2}} = 10^{64} * \exp\left(-\frac{6.24\text{ eV}}{kT}\right)$$

at 1500°C in air

$$n_h = \underline{\underline{5\times10^{13}\text{ cm}^{-3}}}.$$

So, at 1600 degree degree centigrade in air, I can calculate using this expression. From this I I can calculate what n h would be and this n h works out to be 5 into 10 to power 13 per centimetre cube. This whole concentration works out to be much larger than the a electron or whole concentration, which are thermally generated, which are of the order of 10 to power 9. So, we will ignore those.

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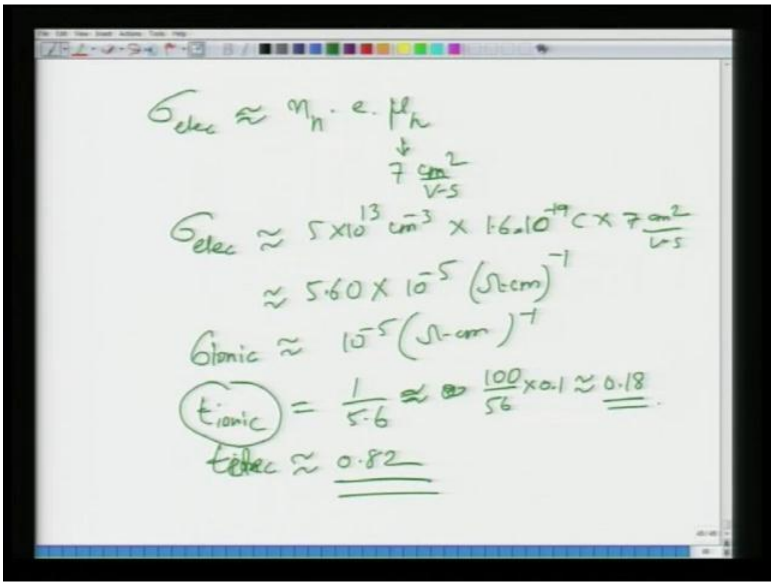

$$\sigma_{elec} \approx n_h \cdot e \cdot \underset{\substack{\downarrow \\ 7\ \frac{cm^2}{V\text{-}s}}}{\mu_h}$$

$$\sigma_{elec} \approx 5\times10^{13}\text{ cm}^{-3} \times 1.6\times10^{-19}\text{ C} \times 7\ \frac{cm^2}{V\text{-}s}$$

$$\approx 5.60 \times 10^{-5}\ (\Omega\text{-cm})^{-1}$$

$$\sigma_{ionic} \approx 10^{-5}\ (\Omega\text{-cm})^{-1}$$

$$\boxed{t_{ionic}} = \frac{1}{5.6} \approx \frac{100}{56}\times 0.1 \approx \underline{\underline{0.18}}.$$

$$t_{elec} \approx \underline{\underline{0.82}}$$

Now, if you calculate the electronic conductivity, sigma electronic this will because the electron concentration is very small as compare because thermally created electron hole concentration is very small. So, we can approximate this to n h e into mu h. So, this n h we can take as 7 centimetre square per volt second mu h and n h we know from that. So, sigma electronic is n h is 5 into 10 to power 13 per centimetre cube multiplied by 1.6 into 10 to power minus 19 coulomb multiplied by 7 centimetre square per volt second. This will come out to be 7 into 5, 35. So, this will work out to be 5.6 into 10 to the power minus 5 ohm centimetre inverse.

So, if you compare the two values. So, sigma ionic was 10 to the power minus 5 ohm centimetre inverse. Now, now if you compare these two values, they are not vastly different, I mean they they of course, the electronic conductivity is still higher, but if you calculate the t ionic, t ionic is merely 1 by 5.6. Now, this works out to roughly approximately so this is basically 10 by 56 or 100 by 56 into 0.1 approximately 0.1 and 44. Then approximately 0.18, which means t ionic is, t electronic is approximately 0.82. So, what it means is that it is a mixed ionic, mixed conduction because here 20 percent approximately, 20 percent of the conductivity is carried by ionic conductivity and remaining about 80 percent is carried by electronic conductivity.

So, this is a good case of mixed conduction. Now, if the ionic conductivity becomes much higher than electronic conductivity, then you of course, call it a ionic condition. So, this is one of the example where we saw that magnesium oxide in the pure form at 1600 degree centigrade is the perfect electronic conductor because electronic conductivity is much higher than the ionic conductivity. When it is in in the impure form, the ionic conductivity increases as a result of presence of impurities, which give rise to presence of extrinsic vacancies and this leads to significant increase in the ionic conductivity and it becomes a mix conductor.

So, you will have some more exercises of of the same kind. In the exercises same problems s, you can you can solve them and get a feel of what it is, basically about the ionic defects, effect of ionic defect ionic and electronic defect concentration on the conductivities and of course, the effect of diffusivity and mobility. So, this is sought of this I hope makes it clear the distinction between ionic and electronic conductivity. So, far we have discussed ionic conduction in a very qualitative manner. We have derived an expression from the Nernst Einstein relation, which relates ionic conductivity to the diffusivity.

Now, what we will do is that we will go back to fundamentals and derive the derive the equation for ionic conductivity right from the basics, which means starting from the hopping model. We will see whether what we did what we get here, is same as what we have derived from Nernst Einstein equation or not.

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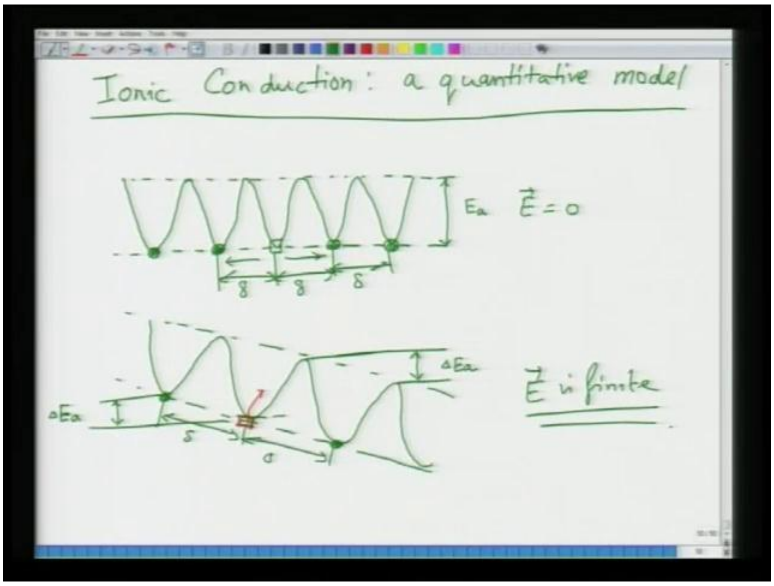

Ionic Conduction : a quantitative model

So, so basically the picture is something like this. So, we will develop a quantitative model for ionic conduction. Now, as you know that, as we have discussed that ionic conductivity is a hopping kind of model, where the carrier move from one side to another and it this could be movement of carrier from from one side of different charge to another site of another charge. It could be counter migration of defect and the occupied site. Now, usually it is defect you can consider it has a counter counter movement of defect and the field side. So, the basically the conduction will depend upon if some, if something if if an atom wants to move, it has to have a vacancy near it otherwise it cannot move.

So, its depends upon the presence of vacant sides in the vicinity of the mobile ions. Let us say so what happens so if if you want draw draw now a picture a potential energy picture for example, so let us say in a lattice you have various ions sitting. So, we will just make a one dimensional picture all these are spherical and not elliptical, suppose to be spherical. Let us say one of these side is empty, so I will make this site as empty site. Now, what will be the potential energy diagram for this? So, if I draw the potential energy diagram, potential energy diagram looks something like. So, this is a sort of potential energy diagram and this is the potential energy barrier delta E a ou can call it. So, this is also like activation energy.

So, now you have this various sites. So, this site can move to this side this. So basically this vacant side can move to right side, but it can also move to left side because in the absence of electric field now, this is the condition when E is equal to 0. So, in the absence of electric field this vacant side can has equal probability of moving whether to right or to left. Now, what happens when you apply electric field? When you apply electric field, then the same picture changes a little bit. So, what happens is depending upon the direction of electric field, let us say the direction is this.

So, here now what happens is, the now these are of course, not up to the scale. So, let us say this distance is delta, all of them are delta. So, delta is basically the spacing between two ion, two lattice sides. So, here again this is delta this is also delta. So, let us say this was your vacant site, these were your field site. Now, what has happened is, if you look at the energy barrier, the energy barrier on this side has decreased by this much amount because now the energy barrier is only this much and on this side, other side the energy barriers are increased by certain amount and what is this amount? This amount is nothing but so let us say this amount is delta E a this would be minus delta E a or let us say delta E a let us not I add confusion here. So, this would be again E a, delta E a.

So, because the potential energy well is symmetric so there is a symmetric displacement on both the sides, either on top or bottoms. So, here so if this vacancy which is let us say I make it red here so if this vacancy has to move to right the energy barrier which was delta which was E a earlier, sorry I I should make it E a which was E a earlier becomes E a minus delta E a. Here on the left hand side it increases by a factor delta E a. So, there is definitely the probability of moving to either side also changes. So, we will we will treat it mathematically a little later.

So, this is this is this happens when E is finite and we will see what delta E a is. So, so basically the presence of electric field provides reduced barrier or higher driving force to one particular side, then to then to other side and this of course, this ionic conductivity as we will see is also influence by other factors, but this is the basic model that we are looking at. So, first thing is in the absence of field. So in the absence of external field, what is the probability that the side can move to either side.

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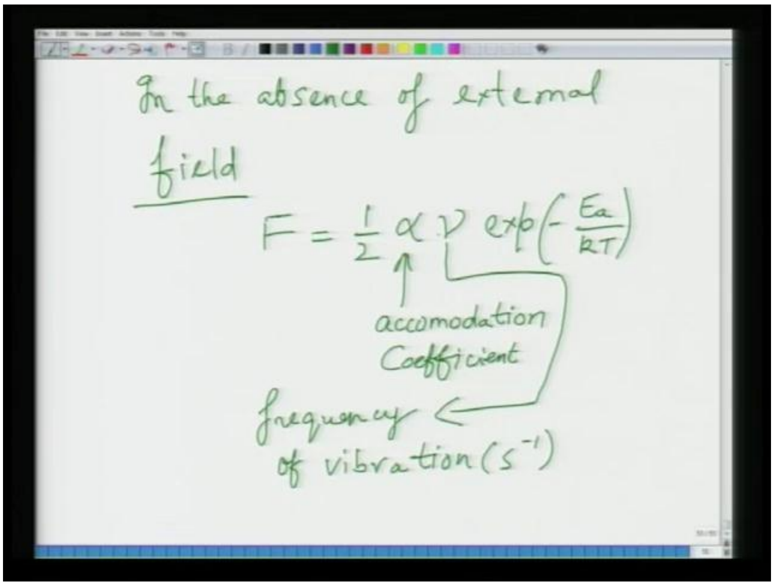

In the absence of external field

$$F = \frac{1}{2} \alpha \nu \exp\left(-\frac{E_a}{kT}\right)$$

accomodation Coefficient

frequency of vibration (s^{-1})

According to Boltzmann statistics, the probability is equal because the barrier is equal. So, let us say the probability is F. So, F can be given as half. Half is the factor because it can move to either side alpha. Alpha is let us say some some coefficient called accommodation coefficient multiplied by nu. Nu is the natural frequency of vibration or where vibrational frequency, multiplied by exponential minus of E a by k T. So, this is your typical Boltzmann equation.

So, this alpha is nothing but accommodation coefficient and this nu will be frequency of vibration, not vibrational vibration. This would of course, be in per second and this is unit less. So, this so this is the probability of moving to either side. So, what happens now when we apply the field? So, when you apply the new pay new new field then upon application of field E.

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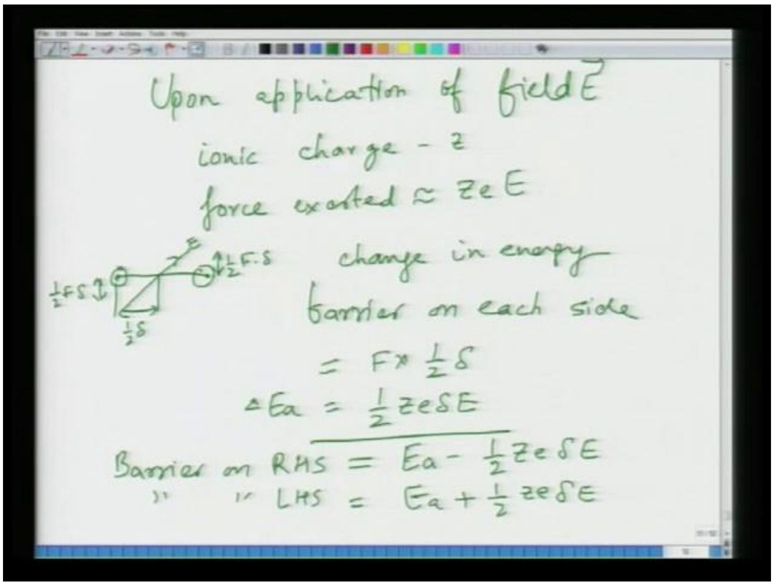

Upon application of field E

ionic charge - z

force exerted $\simeq zeE$

change in energy barrier on each side

$= F \times \frac{1}{2}\delta$

$\Delta E_a = \frac{1}{2} ze\delta E$

Barrier on RHS $= E_a - \frac{1}{2} ze\delta E$

" " LHS $= E_a + \frac{1}{2} ze\delta E$

What happens now, upon application of field E as you see that energy once I have tilted to one side, which means the barrier to one side has decreased another side it has increased. So, so let us say let us say the ionic charge was ionic charge was Z. Then what would be the force experienced? Force, let us say force given by the field. Force exerted would be Z e E and as a result of this force the the wells tilt on other side. So, the total change which occurs on either side. So, the picture would be like this so you apply the field. So, this is your half delta. So, it would increase it was it would change by half F into delta on one side and it would change by half F delta on others other side.

So, change in energy barrier on each side would be F into half delta which would be half Z e delta E. So, this is nothing but your delta E a. Now, whether delta E a would be positive or negative. It depends upon which side you are looking at. So, of course, on the right side it would be now, so barrier on right side. So, barrier on right hand side would be E a minus half of Z e delta E and on left hand side it would be E a plus half of Z e delta E. So, now we will look at what is the probability of movement on each side?

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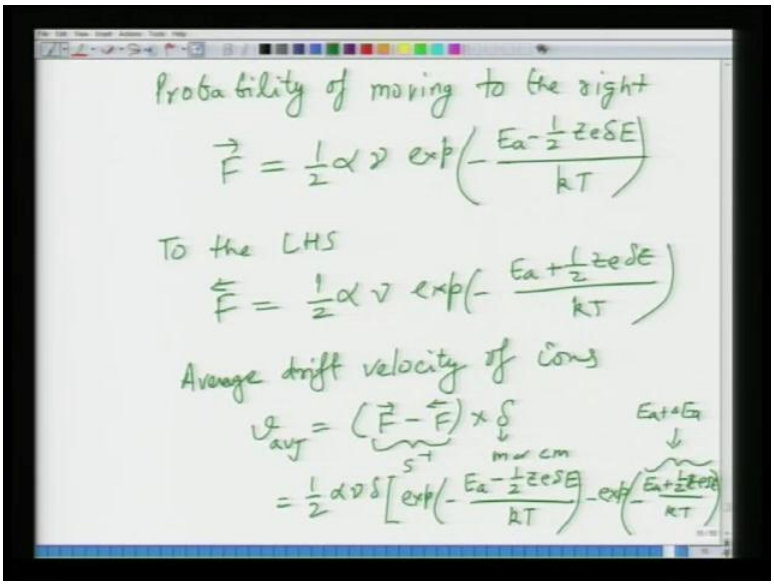

Probability of moving to the right

$$\vec{F} = \frac{1}{2}\alpha\nu \exp\left(-\frac{E_a - \frac{1}{2}ze\delta E}{kT}\right)$$

To the LHS

$$\overleftarrow{F} = \frac{1}{2}\alpha\nu \exp\left(-\frac{E_a + \frac{1}{2}ze\delta E}{kT}\right)$$

Average drift velocity of ions

$$v_{avg} = \underbrace{(\vec{F} - \overleftarrow{F})}_{s^{-1}} \times \underset{m\ or\ cm}{\underset{\downarrow}{\delta}}$$

$$= \frac{1}{2}\alpha\nu\delta\left[\exp\left(-\frac{E_a - \frac{1}{2}ze\delta E}{kT}\right) - \exp\left(-\overbrace{\frac{E_a + \frac{1}{2}ze\delta E}{kT}}^{\overset{E_a+\Delta E_a}{\downarrow}}\right)\right]$$

So, probability of moving to the right will now be. So, let us say I determined it as, I denote it as F right and this F right would be half of alpha nu exponential minus of now, the this energy would be E a minus half Z e delta E divided by k T that makes sense. So, what it basically means is that the probability also increase, on the right probability will also increase from moving movement towards right. Similarly, to the l h s left hand side this would be F again half alpha nu, exponential minus of it would be E a plus half Z e delta E divided by k T.

So, you have a net movement on one side simply because the probability of moving to one side is higher. So, as a result these ions which move there is of course, the movement of vacancy is nothing but movement of ions. So, which means that these ions acquire a net velocity and this net velocity is called as averaged drift velocity. So, I write it as average drift velocity of ions, simply because they drift on one side under the action of electric field simply and that is because of higher probability of movement. So, this is given as v average is given as. So, what would this be F right minus F left this is in per second, multiplied by the distance delta. Distance is the delta which they are covering which is in meter or centimetre depending upon.

So, this will be velocity unit metre per second and this would be nothing but your half of, if you if you do if you do the so this would be half alpha nu delta into exponential of minus of e a minus half z e delta E by k T minus exponential of minus E a plus half Z e delta E by k T. It has become a little smaller on the but so this would be basically E a plus delta E a and this is E a minus delta E a. So, when you open this up sorry now, the net so you can you can now write this as. So, this could be v will be equal to v average will be equal to, what we wrote was half half of delta.

You can write other expression as half of delta F into exponential of Z e delta E divided by 2 k T minus of exponential of minus Z e delta E divided by 2 k T. So, this is what it has reduced to the previous expression.

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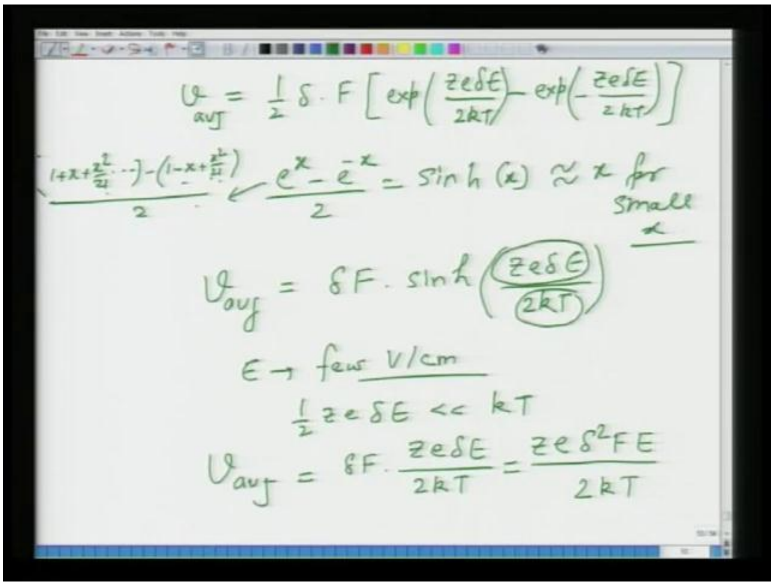

$$v_{avg} = \frac{1}{2}\delta \cdot F\left[\exp\left(\frac{ze\delta E}{2kT}\right) - \exp\left(-\frac{ze\delta E}{2kT}\right)\right]$$

$$\frac{\left(1+x+\frac{x^2}{2!}\cdots\right)-\left(1-x+\frac{x^2}{2!}\right)}{2} \leftarrow \frac{e^{x}-e^{-x}}{2} = \sinh(x) \approx x \text{ for } \underline{\text{small } x}$$

$$v_{avg} = \delta F \cdot \sinh\left(\frac{ze\delta E}{2kT}\right)$$

$$E \rightarrow \underline{\text{few V/cm}}$$

$$\frac{1}{2} ze\delta E << kT$$

$$v_{avg} = \delta F \cdot \frac{ze\delta E}{2kT} = \frac{ze\delta^2 F E}{2kT}$$

So, now we know that exponential of x minus exponential of minus x divided by 2 what it is called as this is called as sign of hyperbolic hyperbolic x. So, based on this principle we can reduce this v average to delta F into sign of hyperbolic Z e delta E divided by k T. So, this is what this drift drift velocity expression is reduced too. Now, under the normal circumstances when ceramics operate, this field is not too large it is very small. So, this field is typically let us say, few volt per centimetre or it is not very large field. So, what happens is that when this field is not very large, then this induced energy changes also very small as a in comparison thermal energy.

So, this if if so basically what what I am trying to say is, if this numerator is smaller than denominator which means the field has to be a smaller. So, basically this change in energy which is induced by application of field is smaller than thermal energy, then I can write. So, what I am saying is that half of Z e delta E is much smaller than k T. So, what it basically means is that we can modify this equation and we can write v average is equal to delta F multiplied by Z e delta E divided by sorry I have missed out 2 here so this would be 2 k T so this would be Z e delta E divided by 2 k T. This so you can what what basically I mean is that if if so sin hyperbolic is x is is equal to e to power x minus e to power minus x divided by 2 you can open up e to power x and e to power minus x.

So, what basically it would mean is if x is very small so you can open this 1 plus x plus x square by factorial 2 and dot, dot, dot, dot, dot minus of 1 minus x plus x square by factorial 2 dot, dot, dot, dot divided by 2. If you ignore the higher powers what it would mean is basically x. So, sin hyperbolic would be equal to x for small x. So, v average has become delta f multiplied by Z e delta E divided by 2 k T and this would this is nothing but your Z e delta square F E divided by 2 k T. Now, we are very close to the expression of conductivity. So, now so what is the now so what is the expression for conductivity? Now, at low field strengths we can assume that ohm's law is perfectly valid and as a result, we can write this current density so at.

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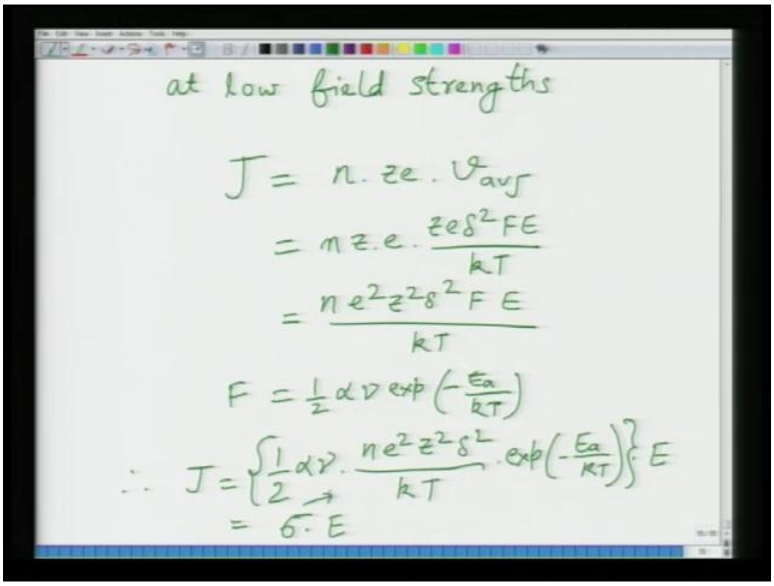

at low field strengths

$$J = n . ze . v_{avg}$$

$$= n z . e . \frac{ze\delta^2 FE}{kT}$$

$$= \frac{n e^2 z^2 \delta^2 F E}{kT}$$

$$F = \frac{1}{2} \alpha \nu \exp\left(-\frac{E_a}{kT}\right)$$

$$\therefore J = \left\{ \frac{1}{2} \underset{\rightarrow}{\alpha \nu} . \frac{n e^2 z^2 \delta^2}{kT} . \exp\left(-\frac{E_a}{kT}\right) \right\} . E$$

$$= \sigma . E$$

Low field strengths we can write current density as J is equal to n into Z e into v average which is nothing but drift velocity. So, now this would be n Z e multiplied by delta square what we wrote in the previous slide was Z e delta square F E divided by k T. So, this becomes equal to your n e square Z square delta square F E divided by k T. So, now we know what is F now. We know F is equal to half of alpha nu exponential minus of E a divided by k T. So, if you know F you just insert in there.

So, that is that means J is equal to half of alpha nu multiplied by n e square Z square delta square divided by k T into exponential minus E a by k T into E and from ohm's law we know that J is equal to sigma E, where sigma is nothing but conductivity. So, now you get the expression for conductivity and this expression for conductivity works out to be. So, this particular part will be your sigma.

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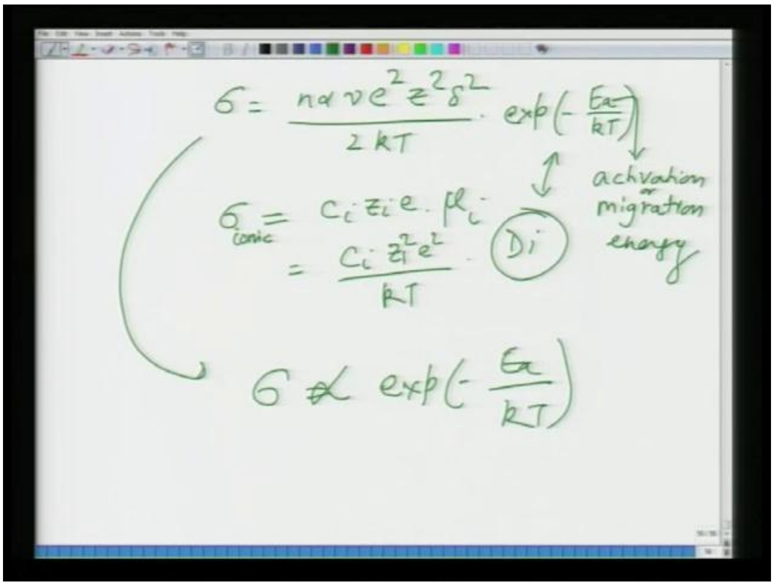

$$\sigma = \frac{n\alpha\nu e^2 z^2 \delta^2}{2kT} \cdot \exp\left(-\frac{E_a}{kT}\right)$$

activation or migration energy

$$\sigma_{ionic} = c_i z_i e \cdot \mu_i = \frac{c_i z_i^2 e^2}{kT} \cdot D_i$$

$$\sigma \propto \exp\left(-\frac{E_a}{kT}\right)$$

So, your sigma is n alpha nu e e sorry e square Z square delta square, e square Z square delta square divided by two k T into exponential of minus E a by k T. Now, you can see the relation with with the previous expression previous. In the previous expression we said that sigma was equal to sigma ionic was equal to C i Z i e into exponential of into sorry into mu I. This was made equal to C i Z i square e square divided by k T. So, basically this was the expression and this becomes your D i. Now, D i was D naught into exponential minus E a by k T because E a is nothing but your activation energy needed for migration.

Which is nothing but your migration or diffusion energy and this D i term includes the same. D i is nothing but if you remember what D was? D was D was the term which included your nu which is nothing but your vibrational frequency and some other constants multiplied by exponential minus E a by k T. Now, you see a correspondence between these two expression. So, basically this expression is also nothing but sigma is equivalent to sigma is proportional to exponential minus E a by k T. So, basically this analysis I explained that, no matter how you derive the ionic ionic conductivity, the conductivity is similar, the form is similar it is always proportional to exponential minus E a by k T or Q a by k T or h m by k T depending upon the convention and this energy is the migration energy. So, I will give you the sum of values now. So, so for example, some of the glasses and then activation energy and show you how these values match with each other.

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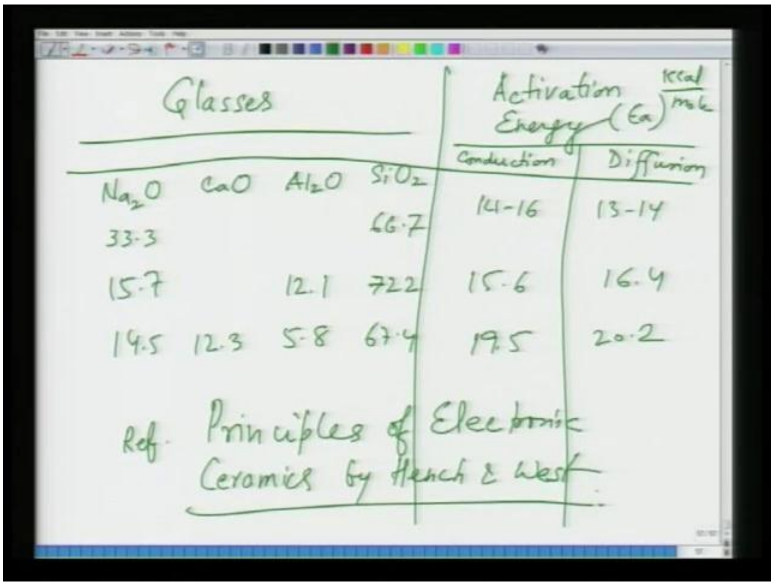

Glasses				Activation Energy (E_a) $\frac{\text{kcal}}{\text{mole}}$	
Na_2O	CaO	Al_2O	SiO_2	Conduction	Diffusion
33.3			66.7	14-16	13-14
15.7		12.1	722	15.6	16.4
14.5	12.3	5.8	67.4	19.5	20.2

Ref. Principles of Electronic Ceramics by Hench & West

So, for example, these glasses have composition of N a 2 O, C a O, A l 2 O, S i O 2. So, this is let us say 33.3 percent and 66.6 seven percent and this is and activation energy E a and one of these is from the conductivity data and another is from that diffusion data and both of these you will see match. So, this conduction values work work out to be 14 to 16 and these work out to be 13 to 14. So, this is in kilo calorie per mole, I can write the units. So, the there is fairly reasonable match between two values for some other glasses. If you take 15.7, 12.1 and 72.2 again the values are 15.6 and 16.4 not too far in these reasonable agreement. If you write one more for example, 14.5, 12.3, 5.8 and 67.4 four this gives you 19.5 and 20.2.

So, you can see that the values of activation energies, whether you measure from diffusion data or conduction data, they are similar, which means which actually validates the model. That models are correct and if you want to look at the data of many various materials, I would suggest you to go to principles of electronic ceramics by Hench and West. So, this now there are. So, you got the basic idea about how to work out the ionic conductivity in ionic solids. So, I will now give you some more data about these materials. So, for instance one of the very good conductors ionic conductors are good ionic conductors.

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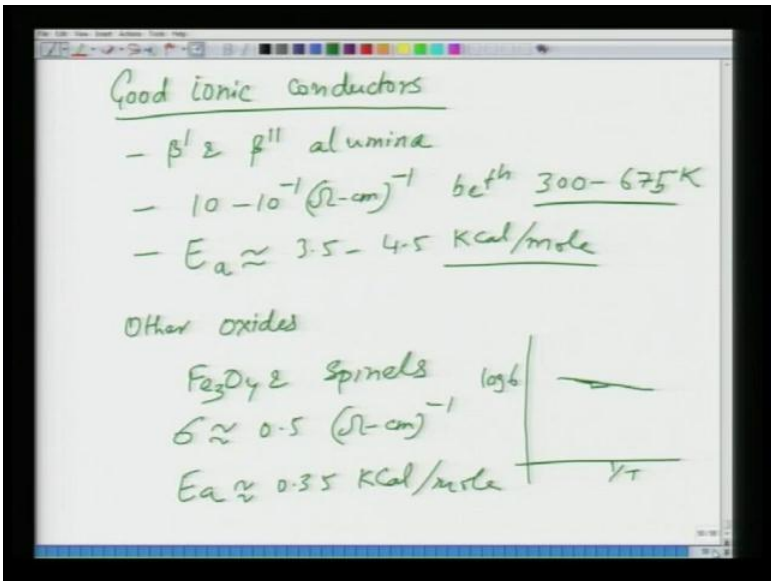

Good ionic conductors

- β' & β'' alumina
- $10 - 10^{-1} (\Omega\text{-cm})^{-1}$ bet^n^ 300 – 675 K
- $E_a \approx 3.5 - 4.5$ KCal/mole

Other oxides

Fe_3O_4 & Spinels

$\sigma \approx 0.5 \ (\Omega\text{-cm})^{-1}$

$E_a \approx 0.35$ KCal/mole

Let us say, your beta prime and beta double prime alumina’s and these have for example, your conductivities are of the order of 10 to 10 to power minus 1 ohm’s centimetre inverse. These are approximate values so of course, for each of these materials will be specific value. So, let us say between about 300 to 675 Kelvin. So, roughly in this range and that activation energy or Q. sorry Let me not change the convention here, it would be E a. E a is about 3.5 to 4.5 kilo calorie per mole, which is a very low energy. You can also convert it to kilo joule per mole and and so this is. So, these come in the category of good ionic conductors, there are some other oxides such as F e 3 O 4 and spinels which is nothing but a b 2 O 4 structured compounds.

So, sigma for these is about 0.5 ohm’s centimetre inverse and Q is very small or sorry E E a is very small. E a is of the order of 0.35 kilo calorie per mole very very small. So, what it basically means is that the temperature if you plot log sigma versus 1 by T the the plot will be almost flat.

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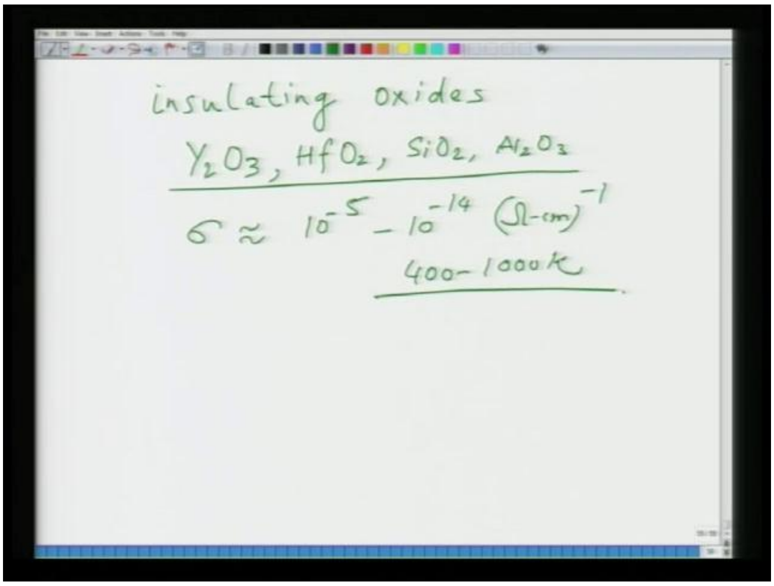

insulating oxides

Y_2O_3, HfO_2, SiO_2, Al_2O_3

$\sigma \approx 10^{-5} - 10^{-14}\ (\Omega\text{-cm})^{-1}$

400-1000 k

So, almost temperature independent behaviour, where as in case of other oxides like insulating oxides, insulating oxides like yttrium oxide, hafnium oxide, silicon oxide and aluminium oxide. In all of these cases the conductivities are in the range of 10 to power minus 5 to 10 to power minus 14 ohm centimetre inverse very, very low values and this is over about 400 to 1000 k and activation energies can be mixed. So, these are distinct materials which have distinct distinct values of conductivities. Now, in the in the case of conducting ceramics, you have two categories. One is called as glasses and second is called as in in the category of glasses, you have molten silicates as well and then second you have fast ion conductors. So, first we will look at the glasses.

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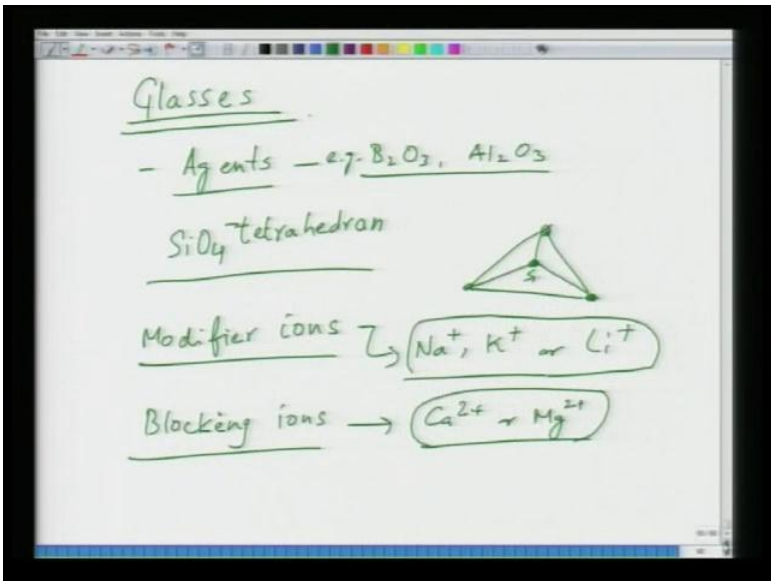

Glasses

- Agents — e.g. B_2O_3, Al_2O_3

SiO_4 tetrahedron

Modifier ions → (Na^+, K^+ or Li^+)

Blocking ions → (Ca^{2+} or Mg^{2+})

Now, we have not discussed the structure of glasses in detail in the structures, but the only difference with respect to crystalline materials is that that these are, these these materials do not have periodic arrangement of ions as a result they are they are amorphous. That is why they are called as glassy. They have a glassy behaviour which means when you melt them, they do not have a specific melting point rather they have a softening point and there viscosity tends to increase and then then they completely become fluid.

So, this low viscosity at reasonably low temperatures makes the glasses makes the glasses very useful in terms of fabrication because you can blow them and form them in different shapes. So, glasses basically have a random 3D network and they typically contain the glass forming agents. If you put because if you put all the basically they are all silicates, so there are various forms of silicates many crystalline form of sillicates as well. For example, quartz is a crystalline form of silicate. Now, in order to form the glasses typically you use the agents.

So, these agents are these agents are your impurities like boron oxide, you could have aluminium oxide, you can have many other impurities which are which are called as glass forming agents. Basically what happens here is when you put these agents so normally what would you have is a S i O 4 S i O 4 tetrahedra within these S i O 4 tetrahedra. So, in in between you have silicon ions and this is o o o o. So, what happens is that when you put these, when you put these ions notice that these ions do not have similar valence as of silicon. So, what happens is that they attach themselves to the ends of these tetrahedra’s reducing their corner connectivity.

So, lot of these tetrahedra’s has hang around in the in the in the net in the 3D space with the loose ends. So, as a result they do not have a inter connected structure and they tend to have lower melting point or softening point. So, these so these are so basically you have two types two types of ions. One is a modifier ion now, modifier ions are ions typically which which basically increase the conductivity and these are your smaller sized ions, sodium or potassium or lithium and then you can have blockers or blocking ions and these blockings ions tends to be bigger size cations, such as calcium or magnesium. The increase in the conductivity upon addition of these ions is much larger than upon the addition of these ions.

So, that is why there is a relative effect, these are called as modifier. These are called as blocker. Now, of course, as you increase the temperature, the conductivity increases because the barrier for migration of these ions increases and also as you can understand intuitively the the conductivity would depend upon ease of migration, which means smaller the ion is, smaller the mobile ion is larger the conductivity would be. In these cases now, the important thing is important thing about glasses is that they are commercially important. Commercially important means they have to be made by furnaces. Now, they have to melted by the furnaces and typically they are melted in electrical furnaces.

Now, when you will, when you when you melt them in electrical furnaces then resistive heating of of the glass is the is the mechanism which is used to melt them, which means the resistivity is an important factor. They cannot be too insulating, if they are too insulating you cannot use them for heating purposes, you cannot melt them in a furnace using resistive heating. So, how how do you tune this electric resistivity? The electric resistivity or electric connectivity of these glasses is tuned by adding various impurities, such as your alkali ions or alkali earth ions.

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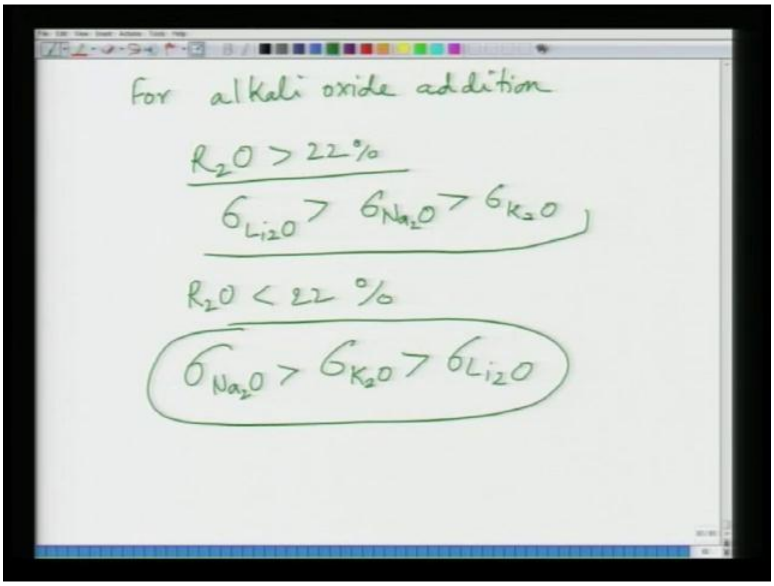

for alkali oxide addition

$R_2O > 22\%$

$\sigma_{Li_2O} > \sigma_{Na_2O} > \sigma_{K_2O}$

$R_2O < 22\%$

$\sigma_{Na_2O} > \sigma_{K_2O} > \sigma_{Li_2O}$

So for example, for alkali oxide addition. Let us say, it is R 2 O. So, R 2 O greater than 22 percent, the highest conductivity is sigma L i 2 O. Now, sigma L i 2 O means conductivity of glass upon addition of L i 2 O is larger than N a 2 O which is larger than k 2 O, but for R 2 O less than 22 percent, sigma of N a 2 O is the highest, followed by sigma of k 2 O, followed by sigma of L i 2 O. So, you can see that all though here you have a clear cut relationship with the size here you do not have really a clear cut relation with the size. So, intermediate ions such as sodium gives higher, highest conductivity. There is you can draw a plot as well. So, when you plot the resistivity of these glasses as a there is a relation with ionic size.

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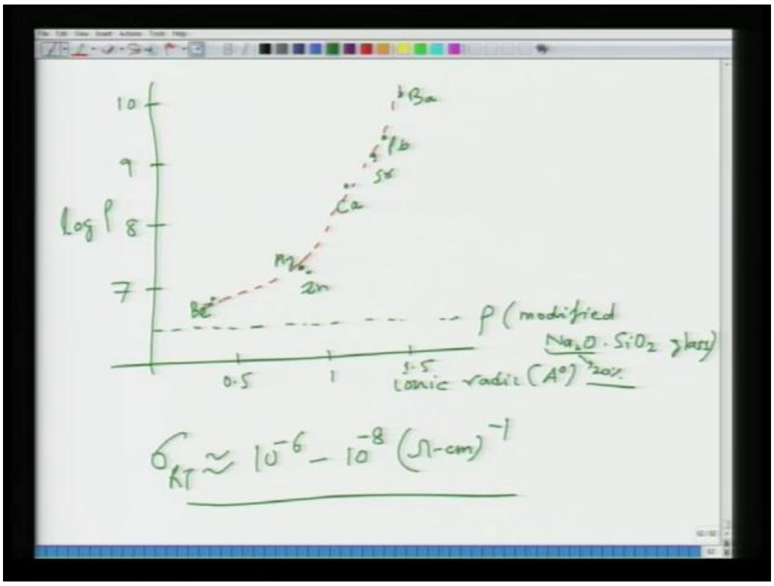

So, let us say log resistivity versus ionic radii. Let us say an Angstrom. So, let us say this is 0.5, this is one this is one 0.5 and this let us say, is about 7, 8, 9 and 10. So, the effect of beryllium would be somewhere this dashed line is the resistivity of of modified N a 2 O S i O 2 glass. So, this is so this N a 2 O is 20 percent and this so when you put beryllium into this the addition of beryllium increases. The beryllium is somewhere here, this could be beryllium magnesium zinc would come somewhere here. So, magnesium your zinc the increase of calcium goes somewhere calcium is between here and so the basically it goes something like this.

There are various ions which form at various places depending upon the size. So, you will have barium somewhere here, then somewhere here you will have lead then strontium so etc. etc So, the range of conductivity basically is from is is from 10 to power minus 6 to 10 to power minus 10, so resistivity 10 to power minus 7, 10 to power minus 6 to 10 to power minus 11 ohm’s centimetre. So, basically in in glasses thus the conductivity, sorry. So, sigma at room temperature varies from 10 to power minus 6 to 10 to power minus 8 ohm’s centimetre inverse. So, this is a typical conductivity of the silicate glasses at room temperature.

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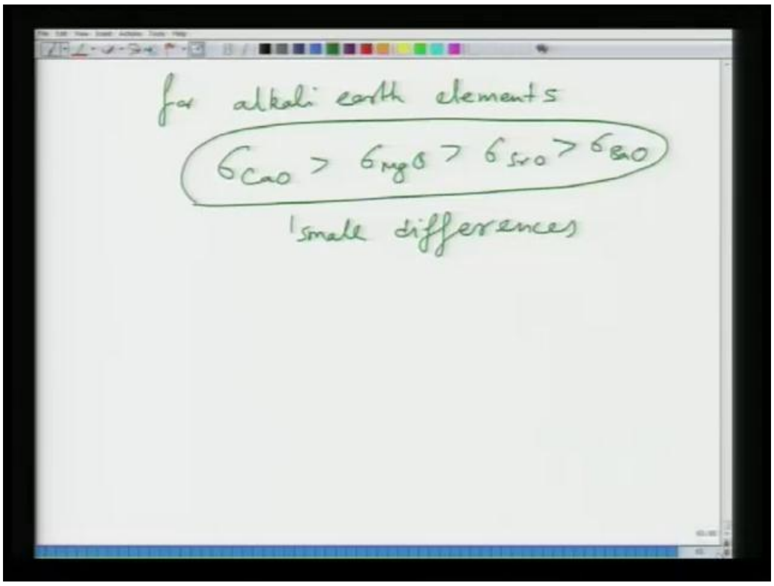

for alkali earth elements

$\sigma_{CaO} > \sigma_{MgO} > \sigma_{SrO} > \sigma_{BaO}$

small differences

Whereas for for alkali earth elements sigma C a O is larger than sigma M g O which is larger than sigma S r O, which is larger than sigma B a O this is a typical trend. But the difference in this is case r is smaller, a smaller difference is, as compared to alkali ions. So, the effect on the increase of conductivity of silicate glasses is very large in case of alkali ions than in case of alkali earth ions, because alkali ions ions are much more smaller and and alkali earth ions are bigger and once the ion becomes bit too bigger the the the the effect on the conductivity is insignificant. Another category of conducting materials is conducting ionic solids is fast ion conductors.

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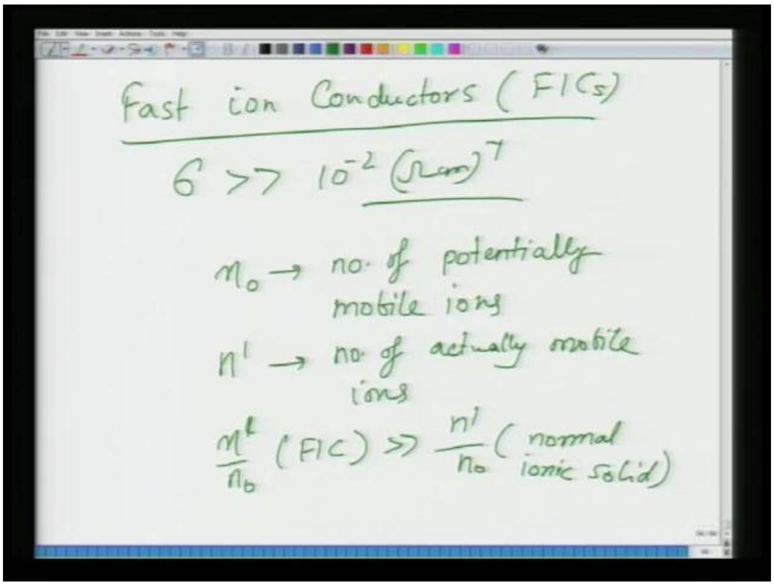

Fast ion Conductors (FICs)

$\sigma >> 10^{-2} (\Omega cm)^{-1}$

$n_0 \rightarrow$ no. of potentially mobile ions

$n' \rightarrow$ no. of actually mobile ions

$\frac{n'}{n_0}$ (FIC) $>> \frac{n'}{n_0}$ (normal ionic solid)

These are also called as FIC’s. Now, fast ion conductors are the materials which show very large ionic conductivity, much larger than a typical ionic solid as we saw just a few slides ago in case of beta alumina. So, these conductivities sigma’s are typically greater than 10 to power minus 2 ohm’s centimetre inverse. So, these are typical values and and and at temperatures much lower than the melting point. Typically in a ceramic what you would expect is, as the temperature increases very and when it reaches very close to melting point or at least half of melting point, then the conductivity starts increasing. Here the conductivities are much larger even at very low temperatures.

This is because of first of all the number of mobile charged carriers, number of charged carries which depends upon the number of mobile ions. So, the fraction of ions which are present at mobiles ions which can actually move is much larger, so then in normal ionic compound. So, what happens let us say is n naught is the number of potentially mobile ions. Let us say, n prime is the number of actually mobile ions. So, this ration n prime by n naught in fast ion conductor is much larger than in a normal ionic solid. So, that is why one that is one reason. Second reason is second reason is that that the diffusion energies are very small and in in many of these compounds the structure tends to be a very open. So, the migration energy requirement in order for the, in order for these ions to move is also very small. So, what we will now do is we will categorize them into two categories.

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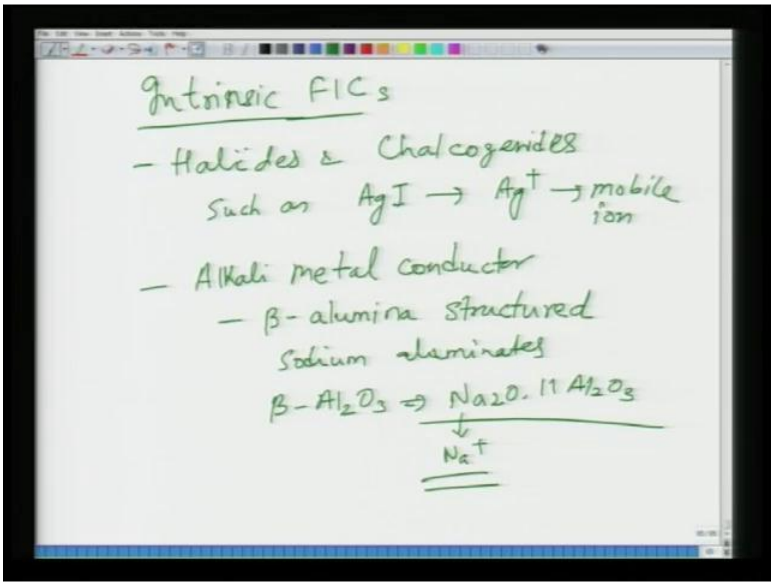

Intrinsic FICs

- Halides & Chalcogenides
  Such as AgI → Ag^+ → mobile ion
- Alkali metal conductor
  - β-alumina structured
    Sodium aluminates
    $\beta\text{-}Al_2O_3 \Rightarrow \underset{\underset{Na^+}{\downarrow}}{Na_2O} \cdot 11\, Al_2O_3$

So, one is Intrinsic FIC’s. So, in the intrinsic FIC’s we have materials like Halides and Chalcogenides. So, Halides and Chalcogenides of typically silver and copper such as A g I so here mobile ion is A g plus and many of these A g ions are mobile. You can have alkali metal conductors such as beta alumina, structured beta alumina, structured sodium aluminates. So, these are for example, beta A l 2 O 3 this is nothing but your N a 2 O dot 11 A l 2 O 3. So, here the mobile ion is N a plus ion and many of these sodium ions can move. So, monovalent sodium ions are highly mobile ions, because of their smaller size and also the open structure and then you have extrinsic.

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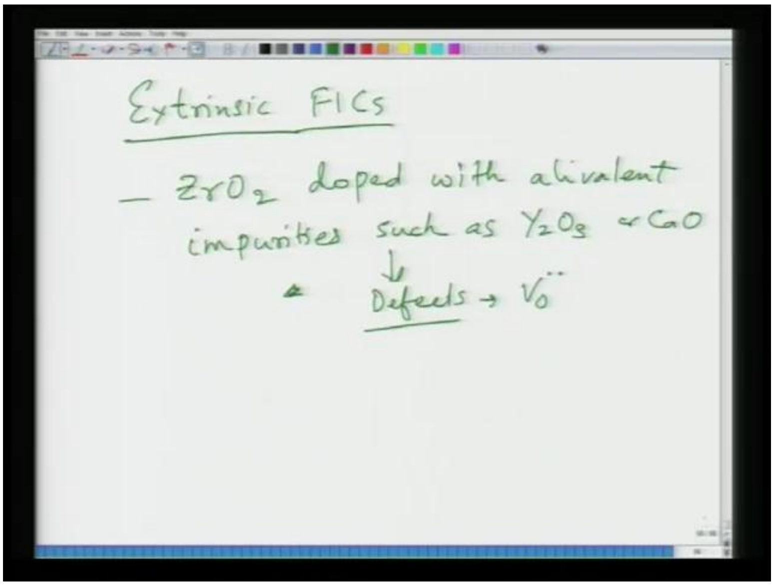

Extrinsic FICs

— ZrO_2 doped with alivalent impurities such as Y_2O_3 or CaO

↓

Δ Defects → $V_O^{\cdot\cdot}$

The previous compounds are intrinsically mobile so they do not you are not doping them with anything. They are they are the structure is based on parent iona and these parent ions in the lattice are the mobile ions in the extrinsic FIC's you have to intentionally dope them. So, for example, zirconium oxide doped with aliovalent. Aliovalent means ions having different valence impurities such as yttrium oxide or calcium oxide and here the delta, here. This basically what it does is it creates defects, which could be in the form of oxygen vacancies. More over these zirconium oxide structure is based on fluid structure, which is a open structure.

If you have to call the structures, go back to structure module and you will recall the structure of zirconium oxide is a open structure. So, when you create oxygen vacancies by these means, these oxygen by vacancies tends to be very mobile and the enthalpy of migration in these materials can be extremely low, which gives rise to which give rise to large conductivity in these materials. So, these are so extrinsic fast ion conductors are those which are intentional, intentionally doped with some impurity in order to increase the defect concentration and they have open structure which gives rise to larger conductivity . So, I will I will basically give you some examples of these materials and then I will finish of this lecture.

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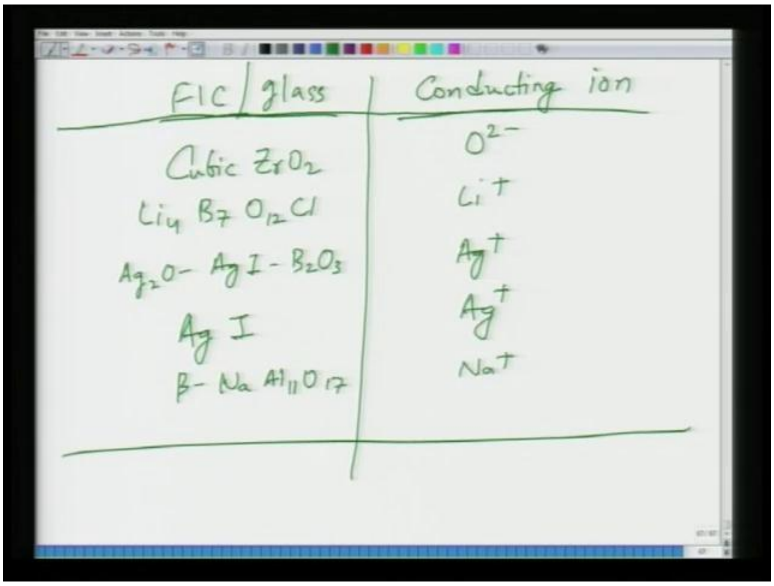

FIC / glass	Conducting ion
Cubic ZrO_2	O^{2-}
$Li_4B_7O_{12}Cl$	Li^+
$Ag_2O-AgI-B_2O_3$	Ag^+
AgI	Ag^+
$\beta-NaAl_{11}O_{17}$	Na^+

So, so FIC’s and conducting ions, so if you take cubic zirconia oxygen ion is the conducting ion. Naturally if you create oxygen vacancies which means oxygen ions would be the conducting ion. Similarly, if you have boracite for example, L i 4 B 7 O 12 C l this as lithium ion as mobile ion, if you take A g 2 O, A g I B 2 O 3. So, you can say FIC slash glass. Here you are A g plus is the mobile ion. So, in silver iodide A g plus is the mobile ion and beta N a A l 11 O 17 your sodium plus. So, these are the some of the examples. So, basically what we have done in this lecture is, we have developed the quantitative model for conductivity and ionic solid using Maxwell Boltzmann statistics, upon the under the application of electric field and we found that the expression which we get from here, is similar to what we got from Nernst Einstein relation.

Basically this conductivity is related to exponential of minus of migration energy divided by k T. So, these two expressions are similar which validates that what we have done is right and then we compare the experimental, and theoretical values and the values obtained from diffusivity data values obtained from conductivity data and both of them match reasonably well. So, that gives us confidence that our model was right. Then we looked at some of the examples of conduction in various glasses and fast ion conductors and found that, these glasses and fast ion conductors can be significantly conducting as compared to normal ionic solid which are typically insulators.

So, what we will do here is, we will finish this lecture here. In the next lecture we will take up the topic of electrochemical potential, and we look at certain examples of these ionic solids conducting ionic solids, in practical applications.

Thank you.