Experimental Physics - III
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Lecture - 28
Topic - Measurement of Ionic Conductivity (Contd.)

I have discussed about the defect in last class because defect is the main origin of ionic conductivity. for the experiment what is the working formula we will use, so that we should understand this working formula.

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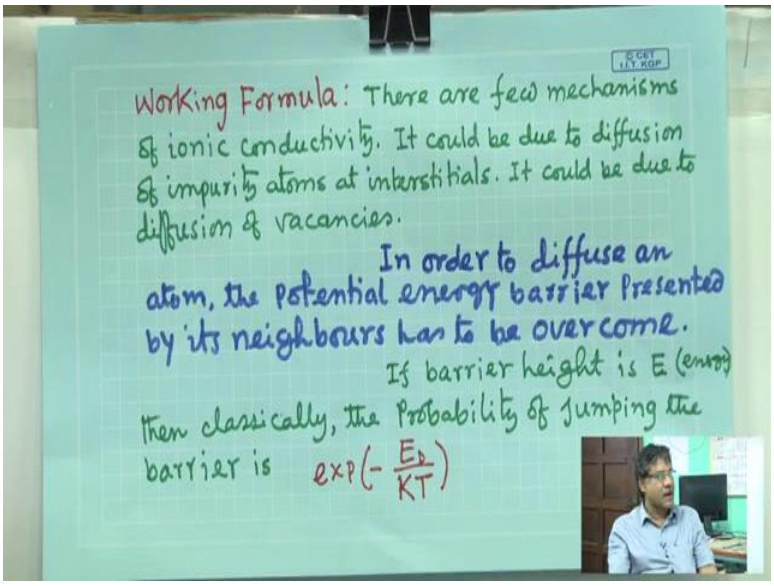

Working formula so there are few mechanism of ionic conductivity. Because ion has to move in an electric field then only we will see ionic conductivity

Therefore, there are few mechanisms for this ionic conductivity. One is diffusion; diffusion of impurity atoms or ions at interstitial positions. From the lattice point that ions or atoms can diffuse to the interstitial position, then it is creating a vacancy going to the interstitial position

In addition, as I told this it could be due to the diffusion of vacancy. to create to defuse the atoms inside the solids, so it needs energy basically. In order to defuse an atom the potential energy barrier from where it is coming presented by its neighbors, because neighbors these are also atoms. When original atom from a site lattice site when it will try to move there other atoms neighbor atoms will not prefer that one.

There will be electrostatic repulsion right. That is barrier it is the barrier always we express in terms of potential barrier it is a like height. To diffuse means to cause that height, to cause that barrier it needs energy. If this energy is this height is say E then the classically the probability of jumping the barrier is exponential minus E d by KT, E d d power diffusion ok.

To defuse that atom in a in a in a in a crystal. It has to cross the barrier if that barrier height is E d then probability to pause probability to diffuse is classically this, exponential minus E d by KT. from where it will get that energy it will get the energy from thermal energy. The energy will be supplied from the temperature increasing the temperature say energy will be KT. now, competition between KT and E d ok.

This is the classical probability. this is the probability of diffusion. Now, if there is a vacancy if there is a vacancy then this it will be easier to diffuse because already place is there to go. if there is a vacancy then the atoms will diffuse easily and it will go to the it will fill up that vacancy. Therefore, that means, what is happening ion or atom is moving forward filling up the vacancy; now the original position of the atoms or ions now that is vacant.

As if this ion is moving forward and vacancy is going backward. if vacancy is there so barrier height will be lower. To create vacancy it needs energy

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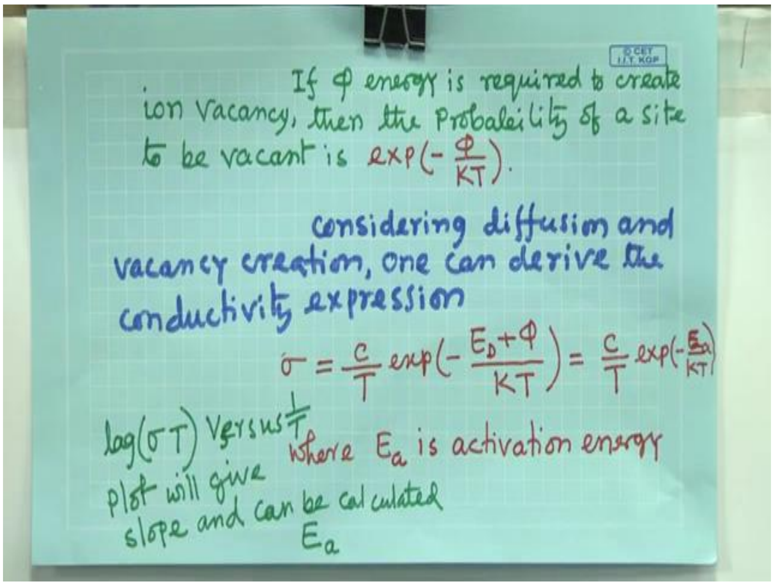

The probability of the probability of creating vacancy if phi energy is required to create ion vacancy. Then the probability of a site to be vacant is exponential minus phi by KT. this phi is the energy required to vacant a vacant a site of lattice. This so vacancy helps in conduction and also this ions has to move forward; ions has to move forward

When ions will move forward so it will it will it will it have to cause the cause the barrier. The 2 types of energy are involved to over to diffuse to move the ions; one is the one is the we are telling the diffusion energy required to diffuse that is the it's cycle to the potential barrier presented by the neighbors atoms. That is E d and another energy to create vacancy that is phi

Considering diffusion and vacancy creation one can derive the conductivity expression there some few steps; I i have not derived in details. One can write this conductivity expression; that sigma equal to some constant C by T exponential minus E d plus pi divided by KT

If you derive then you can find the form of C, but I do not need this form of C experimentally, I can because my aim is to calculate the activation energy. without knowing the C I can get that as well as this of course, conductivity experimentally we will measure; conductivity experimentally we will measure. I think this or C you may need C value I will get C value also I will get from the graph; C value also I will get from the graph. In addition, yes without knowing details about the C one can find out sigma as well as the activations.

Now, activation so C by T exponential minus E a by KT; E a is the activation energy whatever that we want to determine. The see in activation energy 2 types of energy are involved E d and phi. This E d is it is the is the for diffusion energy, energy required for diffusion and phi is to create the vacancy because both we need for conduction of the ions. Because if vacancy is not created ion will not be able to move forward. vacancy has to be created it is going to the interstitial position.

Now, next it has to get the vacancy then only it will go there and as if the vacancy is moving in opposite direction and of course, they are in opposite charge you know. that is why it is like hole and electron in semiconductor they are moving in opposite direction, but both are contributing the current. Similarly, here if ion is positive; so positive vacancy means positive ion is missing. It will be equivalent to a negative; negative charge negative charge as if moving backward and positive charge ions it is moving forward. Both will contribute in the in the conductivity ok.

Here you can see from this formula from this formula you can see so sigma T sigma T. If you take log sigma T log exponential this log sigma T equal to it will be minus E a by KT and some constant log C some constant will be there. log sigma T means if it is say y; then that will be equal to E a by KT plus minus something whatever Ea by KT, plus log C plus or minus log C whatever. y equal to mx plus C. this is a straight line and it will intersect the Y axis intersect the Y axis. from this intersection you can find out C and E by KT.

If you plot if you plot log sigma T versus one by T then you will get the straight line and from that straight line, you can find out the slope. In addition, from that slope that slope will be equal to E by E a by K, K value is known. A one can find out and this for from intersection you will find out this C value ok.

You can find out the conductivity you can find out the conductivity as a function of temperature as a function of temperature. One can plot this graph after taking data and from the data we can we will calculate the activation energy. The sample we will use you see this sodium point is the ionic it is a solid and ionic crystal, You may you may you may get the ionic conductivity. generally sodium chloride if you use in solution then it is the ionic conductivity in solution is not in solid; in solid condition also it will show ionic conductivity In that case which one will diffuse see depends on the, it depends on the mass of the atom. Lighter mass of the atom we will we will diffuse fast. in case of sodium chloride sodium will diffuse faster than chlorine. Actually so this ionic conductivity in sodium chloride will get because of the diffusion of the sodium ok.

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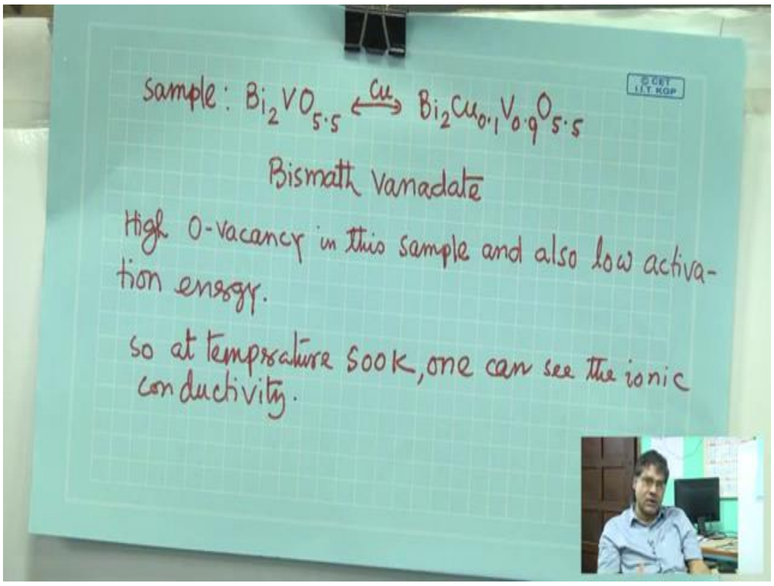

In our laboratory we will take we will take the sample this is Bismath Vanadate; Bismath Vanadate Bismath Vanadate. this is the formula actually this metal is derived from Bismath this B i 4 V 2 O 11 half of it this is also one this is also stable material Bismath Vanadate

Now, if you dope copper 10 percent copper if you doped replace it the vanadium. Our sample ultimately this is the sample B i 2 10 percent copper and 90 percent vanadium. Because copper replace the vanadium 10 percent copper is introduced in this in this in this parent material and then O 5.5.

these samples are prepared by our student using solid state reaction method after preparation they have characterize the sample structural characterization and they found that this oxygen here it is not 5.5, but it is oxygen O 5.35. Less oxygen's are there so;

that means, in this sample there is an oxygen vacancy. If oxygen vacancies there then this will show higher ionic conductivity at comparatively lower temperature

This will show easily this ionic conductivity even at the in the range of 500 Kelvin Above the room temperature around 2 2 300 centigrade, if you go up then easily you will see this nice conductivity of this of the sample. That is because of because of oxygen vacancy and because of oxygen diffusion. Because among this oxygen is the lighter atom so it will diffuse fast faster.

Both this oxygen vacancy as well as the presence of this lighter atom like oxygen. that is why this its activation energy will be lower. You need you do not need very high temperature to activate it that is why the sample is chosen in our laboratory. That within 2 3 400 degree centigrade we can see the quite reasonable change of the change of the conductivity, ionic conductivity of the sample ok.

This measurement is very simple you have to measure current and voltage; like we are going to measure the resistance resistivity as a function of temperature. the experimental setup so this is the manual is there experimental setup I will show you, but the circuit diagram is very simple. You have a furnace so sample is there you have a furnace and sample is there we will heat this sample using a temperature controller ok.

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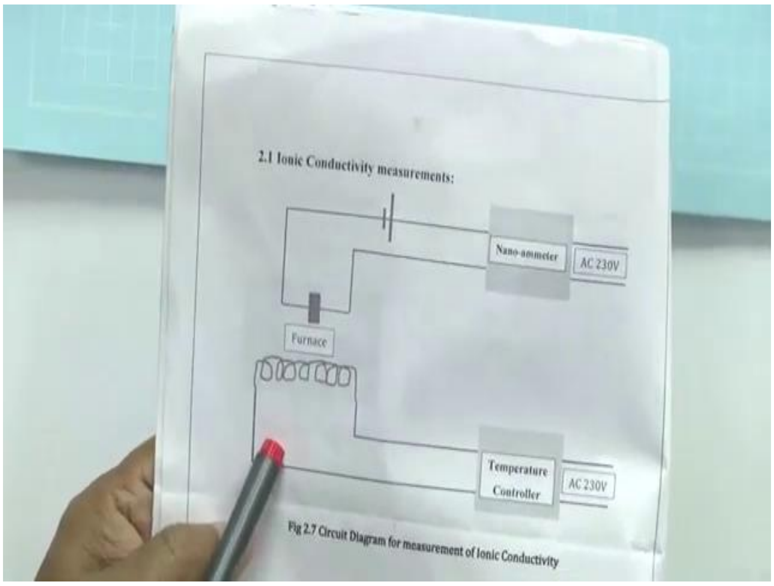

Now, across this sample this voltage will apply voltage will applied a for a constant voltage there will be Nano ammeter because current will be very small say it is it will be Nano ampere order. There will be Nano ampere ammeter in the in the circuit. with temperature only we have to note down the we have to note down the change of this current for a constant voltage. Circuit diagram is very easy I will show you the experiment. let us go to the experimental setup and see how one can perform the experiment.

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This is the experimental setup for ionic conductivity measurement and for determination of the activation energy. As I told that this measurement is, very simple it is an Ohms law experiment circuit diagram is just here you can see this is your sample ok.

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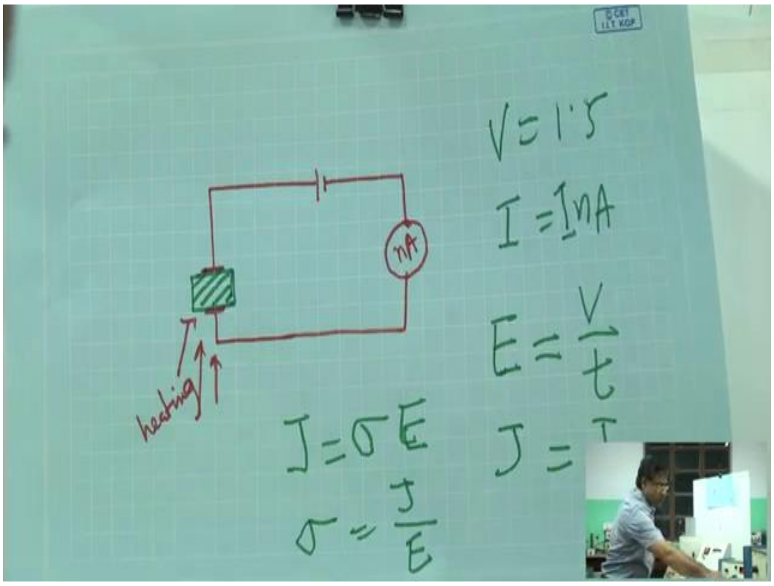

You should have provision to heat the sample and measure the temperature. for that you need arrangement as well as you just this is the simple circuit diagram. You have applied a constant voltage and what are the is the is the current flowing through this circuit. That we will known the from this nanoammeter or picoammeter in this case here we are using picoammeter. Naturally you can see this very small change of the very small change of the current we have to we have to determine.

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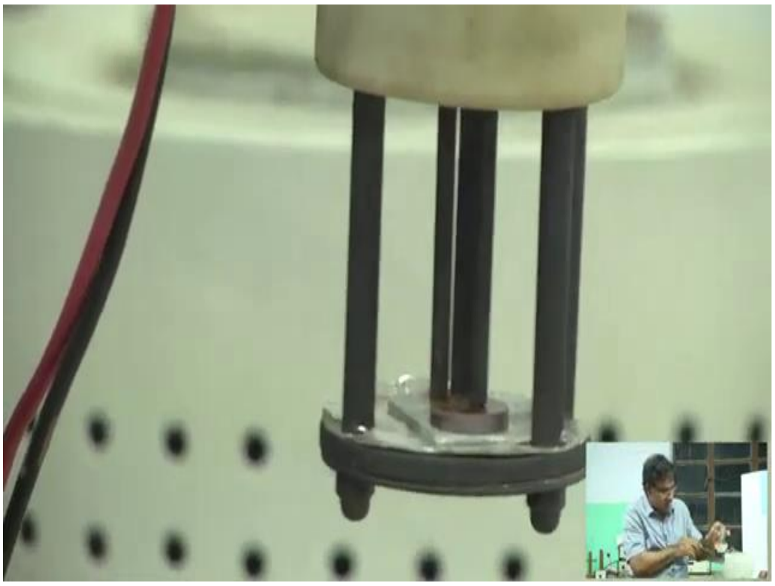

So let us see my sample here I can show you our sample. I think it is a slightly hot this you see this tablet rather sample here this a tablet kind of sample this is the sample. Thickness of this tablet it is the plate thickness of the plate and radius or diameter of the plate is known it is supplied or one can measure also.

Now you see on top of this on top of this tablet this one electrode one electrode and this bottom from bottom this connection is taken from this electrode from this electrode. one is on top and another is from bottom this connection from top and bottom these two electrode from these two electrode these are coming these are coming. These two are this and so this is connected there once one batteries connected; these batteries connected batteries connected is the 1.5 volt battery constant voltage it will give.

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In addition, this other circuit is completed through this whatever nanoammeter I have written, but it is the picoammeter

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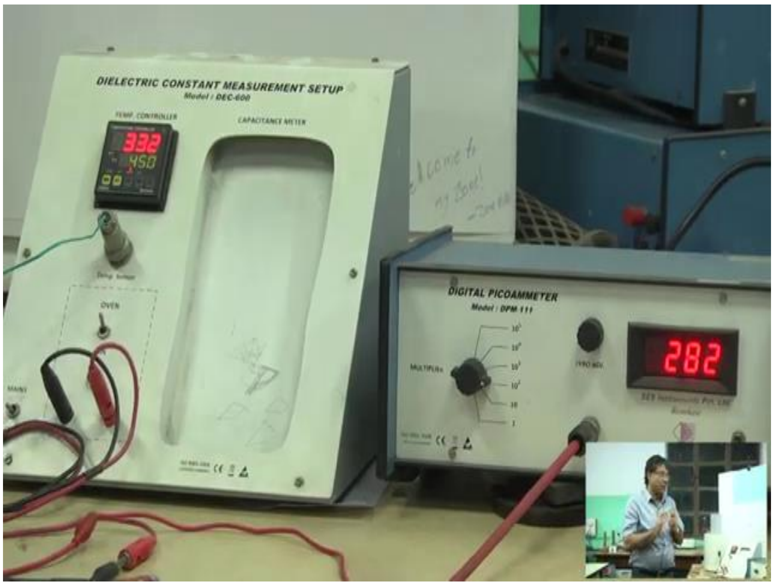

Here different scales are there whatever reading you will see we have to multiply with this one. this pico ampere into this reading. Different range one can choose. now so this is for as I showed you this circuit is made here, this circuit is made here it is a simple circuit. Now we need arrangement now we need arrangement heating arrangement this green wire whatever you are seeing that is thermocouple it is connected close to the sample.

It will give the temperature at the sample place so this is connected here. here temperature controller are there; so we will get the reading of the temperature from here. Whatever rate font you are seeing number you are seeing that is present temperature And 400 you can see they have 400 so that is the set temperature ok.

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Oven is off it is up its off when I will put down so this it will start heating. This is the oven so it is this is the power supply of the oven and temperature controller. Through this through this, it is the power to the heater is given so heater here inside heater is there. Power from here the is given to the heater.

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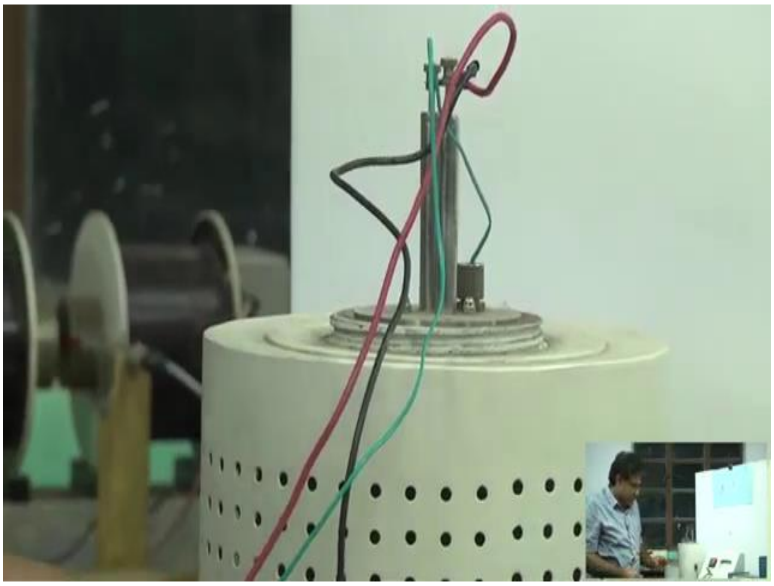

Now, this furnace kind of things hole is there. I will insert this one through this hole now; my sample is in oven; and for protection for less heat radiation to reduce the heat radiation.

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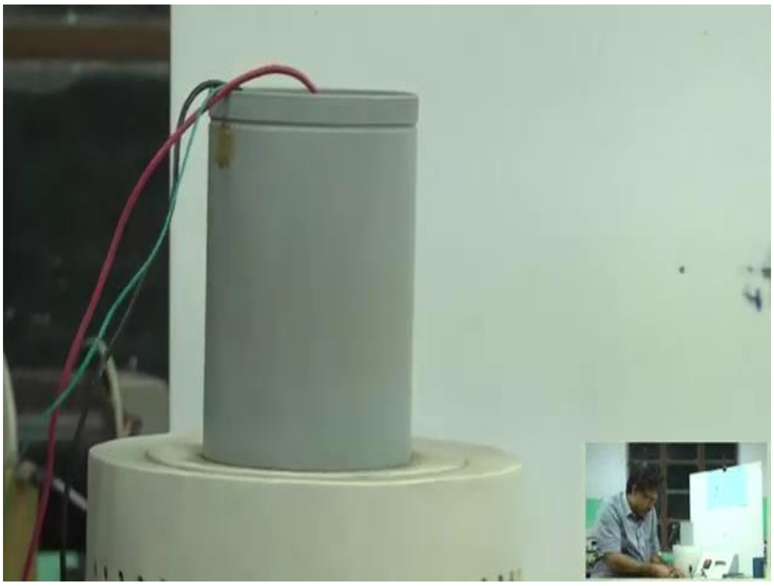

This coppers we are using this coppers. I will put this copper. Now it is ready-made setup. inside things are there I showed you. Now, this from this oven present temperature it is 78, but I have set here these options are there 400 I can change these temperature. say if I wish to change this temperature say 450. I can make it 450 here or 10 20 30 40

50 ok; so 450 then I set it. now, it is set at 450. In addition, this temperature is coming from the sensor temperature sensor and we are getting reading here. This part is for oven and this battery constant voltage 1.5 volt.

Now, we will change the temperature we will put on the oven and change the temperature at different temperature we will note down this reading. In addition, you should note down this whatever you have chosen here 10 to the power 10 square 100. whatever reading that is into 100 picoampere at present it is then it is 60.5 nanoampere ok.

We have to note down at this temperature this is the current. Now I will switch on the oven; now oven is switched on switched on now you can see the temperature will increase and it will go up to 450 and we should take reading say I think every 10 degree centigrade step we can note down the reading. It is a now eighty three and that is the same value it is the conductivity is not changing with temperature at initial temperature.

Now 85 yes 86 87; so it will change fast because I have said it is at very high temperature 450 degree centigrade it is not Kelvin it is a centigrade 91 90 so at 90 one should take readings. it is now started to increase, but not increasing much it is going towards 7 nanoamperes; 7 nanoampere. Now it is a 100 degree centigrade so this is 7 nanoampere. We will note down a reading we will note down this reading.

it is the so when temperature will be around 200 so that reading will be I think the change will be very high. now, 110 you should take them 120 whatever the reading say 7.5 nanoampere at 120 7.8. Now it is going towards 8 nanoampere say it is the 130 8 nanoampere ok.

This way so let us see how fast it is changing. Actually what we have to do just we have to increase the temperature; we have to set 100 degree first then go there Then you change set to the 200 degree. Then slowly it will increase the temperature and you will be able to take data smoothly ok.

However, since here just within short time I want to just demonstrate show the reading. that is why I have put at highest value. you can see clearly that it the change is very fast now; now it is 12 nanoampere it is a. from 6.5, now it is 12.5 ok; it is the almost 200 degree centigrade it is 14 nanoampere. Since temperature change is quite fast, that is why this reading change also fast but we should not collect data hurriedly.

Systematically we should set the temperature 100 200 300 then 400; then this will temperature will change slowly and you can record the data peacefully I think so this way you take up to 450. I think I will stop oven still it will it may increase some temperature. this is a very simple experiment; experiment setup and measurement everything is very simple, but from this experiment we can learn about the crystal defects. As I that is why elaborately; I discuss about the crystal defects.

What we learn from this what physics we learn from this experiment that is about the crystal defect and without crystal defect, it is not possible to; it is not possible to get ionic conductivity. In ideal crystal it is impossible almost slight conductivity you can get, but you have to you have to increase temperature to maybe 2000 degree centigrade but that is not the realistic case so here the data we have to take right.

Now from this data what you are getting you have volt V equal to 1.5 volt and then current I you have in nano ampere ok; some nanoampere. V we have to find out E electric field. That is V by t, what is the t; t is the thickness of the sample that value is given it is the around 1 millimeter. V 1.5 so you know E electric field.

Electric field is constant, but current is varying with temperature. you can find out the current form current density J; you can find out the J, J equal to I what is the relation I by a, a is tablet diameter if it diameter is d then t by 2 are the radius. Pi r square so that is the area. you are noting down current I; current I nanoampere you convert to the current density.

Now, you know J equal to sigma E J equal to sigma E from your data you can calculate sigma equal to J by E now, we calculate sigma and you noted down temperature. Sigma at different temperature now plot graph. here our student plotted they took data and plotted. I will show you they plotted this you see this current versus temperature. Here you can see these initially the change is very slow, with temperature then it become fast ok.

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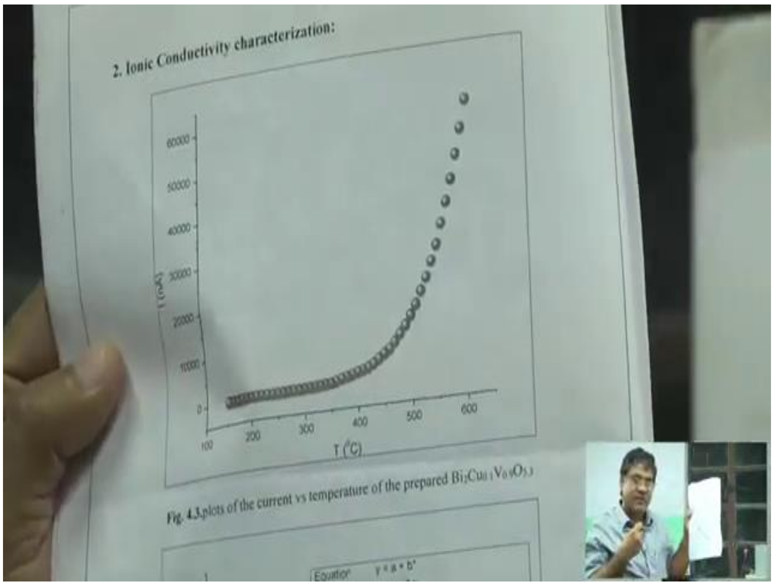

This type of change one can see when activation energy is required. Initially the temperature is not sufficient to activate the diffusion or creating vacancy it needs minimum energy to activate it that is a when temperature is just crossing the threshold; activation energy is the above activation energy. Then it is an it is increasing very sharply

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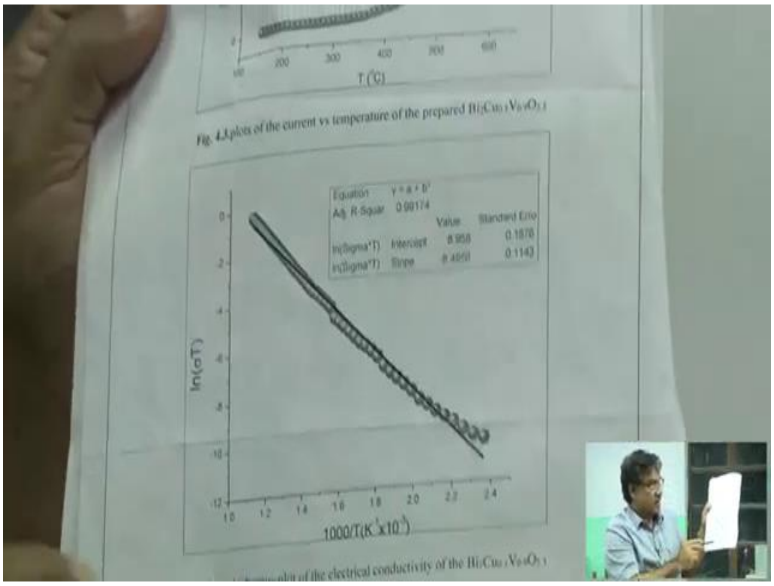

Now as I told that you have to plot log sigma T as a function of 1 by T sub factor 1000 factor, but that does not matter. It is a so 1 by T if you plot then you will get straight line.

it is the more or less straight line; very high yes it is a very low temperature. Low temperature is a there will be some inner because value is very small close to the 0 value. that is why so now, feed these data feed these data. If you feed this data from this slope you will get and from the slope; slope is E by k E a by K as I told E a by K ok.

Negative slope it was minus there; so negative slope. K is known you can find out E that is why the determination of the determination of the activation energy from ionic conductivity Yes I think this is a very simple, but nice experiment it is a reach of physics in this experiment at least this defect what is defect that student can learn and I also tried to explain details. I will stop here.

Thank you.