Fundamentals and Applications of Dielectric Ceramics
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Lecture No 25
Impedance Spectroscopy

So, welcome again to the new lecture of this course, Fundamentals and Applications of Dielectric Ceramics. So, let us just briefly recap what we did in the last lecture.

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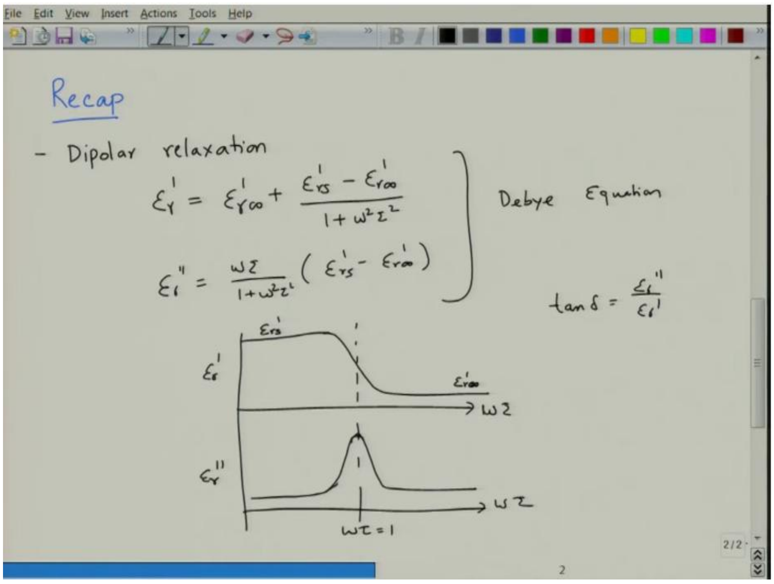

So, in the last lecture, we discussed the details of dipolar polarization. We looked at the whole analysis, which is called as dipolar relaxation. And what we saw was that, dielectric constant through the whole analysis worked out as:

$$\varepsilon_r' = \varepsilon_{r,\infty}' + \left(\frac{\varepsilon_{r,s} - \varepsilon_{r,\infty}}{1+\omega^2\tau^2} \right)$$

And,

$$\varepsilon_r'' = \left(\varepsilon_{r,s} - \varepsilon_{r,\infty}\right) \cdot \left(\frac{\omega\tau}{1+\omega^2\tau^2} \right)$$

So $\varepsilon_{r,s}'$ is called as basically the static dielectric constant and $\varepsilon_{r,\infty}'$ is called as high frequency dielectric constant. And you can see that there is dependence on frequency here. So, these are called as Debye equations as we saw. And when you plot them together, then ε_r', it goes from a value $\varepsilon_{r,s}'$, undergoes a relaxation before it converts, so this is $\varepsilon_{r,s}'$, this is

$\varepsilon'_{r,\infty}$. And this relaxation happens at a specific frequency for which we say.

So, it is better to plot ωτ because you can say that this happens at ωτ = 1. And the ε''_r undergoes maxima at this point. So, this is what the behavior is. So tan δ can be obtained from this as $\varepsilon''_r / \varepsilon'_r$. So when you plot, now this process is temperature dependent, because the relaxation time is a temperature dependent entity. So, when you make, for example when you look at variation of tan δ as a function of temperature.

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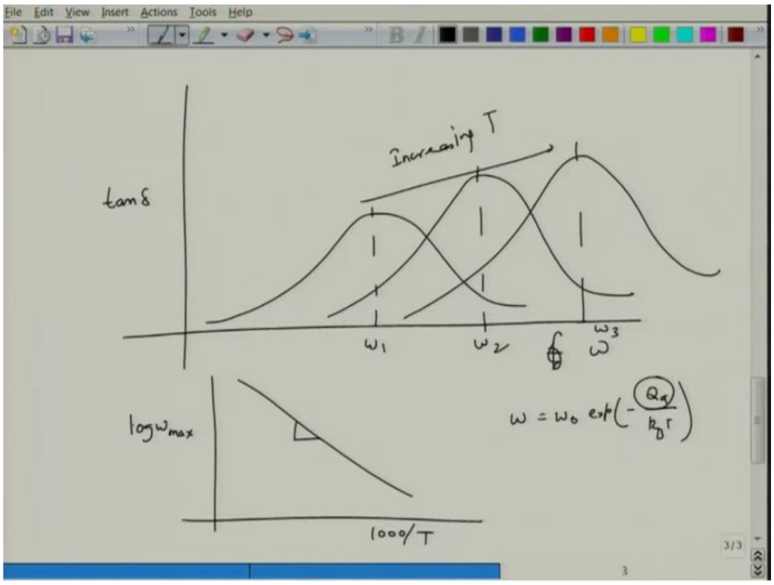

tan δ and you plot the frequency, let us say, at lower temperature, this is the frequency. At higher temperature it tends to show rightward shift. So, this is how it will vary. So, this will be basically increasing the temperature. So, the relaxation will occur at certain frequency, this is ω_1, so we can write it as ω_2, ω_3 and the frequency will shift to right, because the as you increase the temperature the diffusion becomes faster.

As a result, the relaxation times slows down, relaxation time decreases and the frequency you can do the relaxation at a faster frequency. So, this is generally the trend that you observe, that the tan δ peak shifts to higher frequency as you increase the temperature and as a result, there is a strong temperature dependence. So, when you plot, you can also plot the, for example, this maxima at which tan δ occurs. So, let us say, you plot log ω_{max} as a function of, so this has a Arrhenius kind of behavior.

One can determine the activation energy from these plots. The maxima of these plots as a function of temperature, will give you a behavior, which is basically:

$$\omega = \omega_0 e^{\left(-\frac{Q_a}{k_B T}\right)}$$

So essentially, one can determine what is the activation energy of migration or dipolar relaxation, when you do a temperature dependent measurement of dielectric properties. So, this is a very useful

So, when temperature dependent measurements of dielectric materials are very useful way to understand the intricacies of dielectric materials, the activation energy, what kind of defects you might have. Because activation energies are something which are, these activation energies are signature of what kind of our and processes are present in the materials. So, one can make very nice conclusions about what happens in various different kinds of materials.

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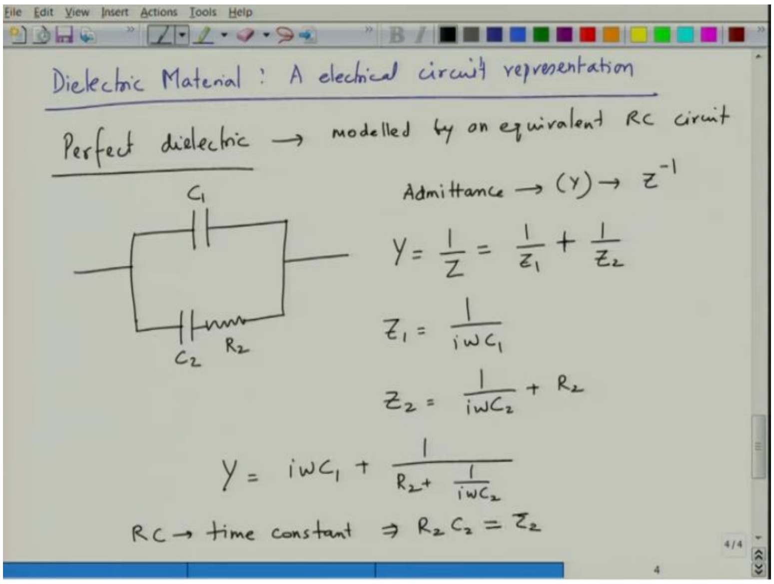

So now, what we look at is we look at little bit more details of how do you characterize dielectric materials. So, for characterization of electric materials, we need to define dielectric materials in a little bit electrical form. So, basically what we are going to look at from the characterization perspective now, how do you represent a dielectric material in a circuit form. So, dielectric material basically a electrical circuit representation.

So, here because when you do characterization of dielectrics, often you need to model the dielectric properties. And when you do modeling of dielectrics, the modeling required some material to be represented in the form of electrical circuit. So, ideal dielectric material will have only capacitive contribution, but in a real life dielectric is hardly 100% capacitive, as a result it tends to have resistances in it. So, how do you model those capacitors and resistances for a dielectric.

So, let us say, a perfect dielectric. First take example of perfect dielectric, the perfect electric is basically modeled by an equivalent RC circuit. So, basically you have a capacitance C_1, which is in parallel to a capacitance C_2, so this is a capacitance C_1, this is C_2 and this is in series with the resistance, let us say, R_2. This is an equivalent RC parallel circuit, as it is called as. So let us consider our first admittance of this, admittance is represented by Y.

Admittance is basically:

$$Y = \frac{1}{Z} = \frac{1}{Z_1} + \frac{1}{Z_2}$$

And why this circuit has been chosen, it will also become a little clearer as we go on. So it is not all that coincidental. It is not all that, you know, fluke, there is a logic to it. So, we will see that in a little while.

So, this will become:

$$Z_1 = \frac{1}{i\omega C_!}$$

And,

$$Z_2 = \frac{1}{i\omega C_2} + R_2$$

So, admittance can be written as:

$$Y = i\omega C_1 + \frac{1}{R_2 + \frac{1}{i\omega C_2}}$$

Now, considering an electrical circuit, wherever you have resistances and capacitances, the product of RC is taken as time constant. So, in this case:

$$R_2 C_2 = \tau_2$$

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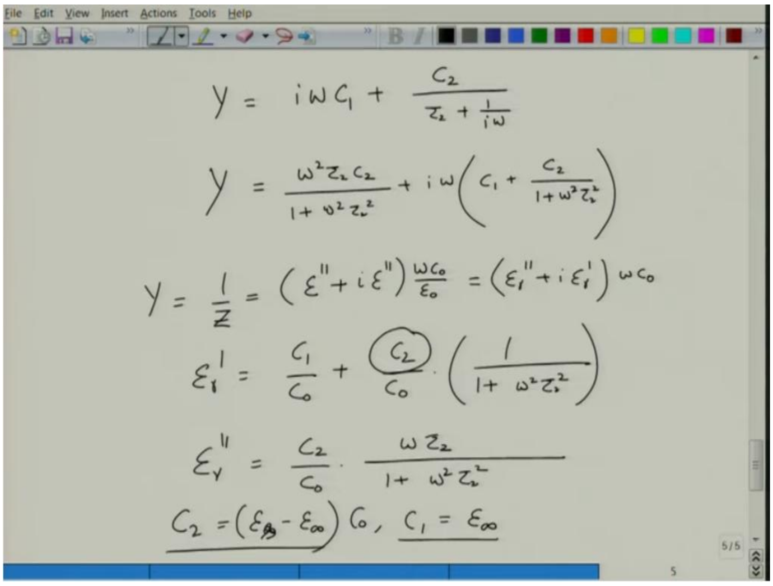

So, again we can express the admittance as:

$$Y = i\omega C_1 + \frac{C_2}{\tau_2 + \frac{1}{i\omega}}$$

Alternatively, we can write this as:

$$Y = \frac{\omega^2 \tau_2 C_2}{1+\omega^2\tau_2^2} + i\omega\left(C_1 + \frac{C_2}{1+\omega^2\tau_2^2}\right)$$

Now, you relate this to dielectric constant. So, what is this admittance is equal to:

$$Y = \frac{1}{Z} = \left(\varepsilon'' + i\varepsilon'\right)\frac{\omega C_0}{\varepsilon_0}$$

And this is basically nothing but:

$$Y = \left(\varepsilon_r'' + i\varepsilon_r'\right)\omega C_0$$

So, this Y. Just match the real and imaginary part and you will get the values of static and the real and imaginary dielectric constants. So, what we will get is:

$$\varepsilon_r' = \frac{C_1}{C_0} + \frac{C_2}{C_0}.\left(\frac{1}{1+\omega^2\tau_2^2}\right)$$

And,

$$\varepsilon''_r = \frac{C_2}{C_0} \cdot \left(\frac{\omega \ \tau_2}{1+\omega^2 \tau_2^2} \right)$$

Now, this is very similar to what we saw earlier. Earlier we said that $\boldsymbol{\omega}\, \varepsilon'_r = \varepsilon'_{r,\infty} + \boldsymbol{\Delta\varepsilon}$

So, if you imagine this equation if you remember this equation and compare this with, so basically C_1/C_0 is nothing but $\varepsilon'_{r,\infty}$. And C_2 is the difference between the two, **(** $\varepsilon'_{r,s}$ **-** $\varepsilon'_{r,\infty}$ **)**. So, that is what this equation is. So basically, your C_2 has turned out to be:

$$C_2 = (\varepsilon_s - \varepsilon_\infty) C_0$$

So, C_1 represents the high frequency dielectric constant and C_2 represents the difference between static and high frequency. And that is why this circuit is not a fluke, because this circuit gives rise to exactly the same equations that we derived using Debye equations. So, this is the equivalent RC circuit model for a perfect dielectric, which means which follows the Debye behavior. What happens when we do not follow the Debye behavior, then there is a deviation.

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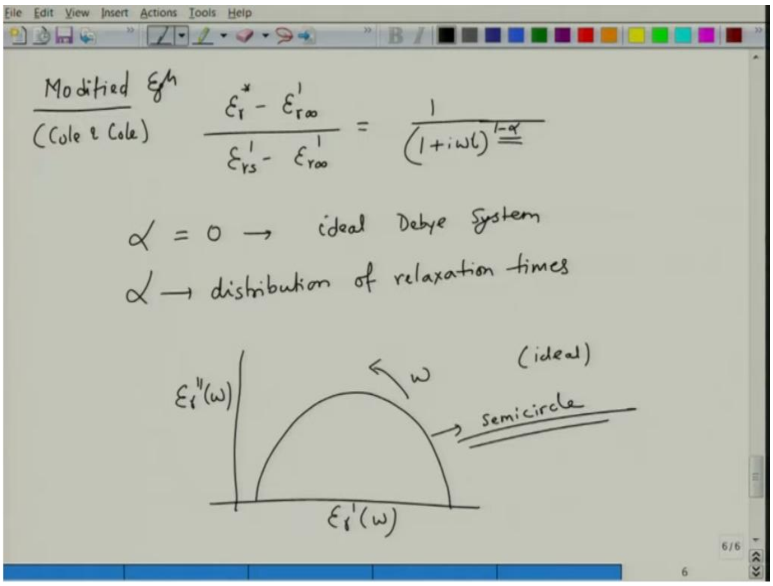

So, when you do not follow a Debye behavior, then what happens is that your relaxation time, you do not have a unique relaxation time you have multiple relaxation time. So, as a result, this equation gets modified as, the Debye equations get modified as:

$$\frac{\varepsilon_r^* - \varepsilon'_{r,\infty}}{\varepsilon^*_{r,s} - \varepsilon'_{r,\infty}} = \frac{1}{(1+i\omega t)^{1-\alpha}}$$

So this is modified equation and this was done by gentleman called as Cole Cole.

So here, α is a parameter, whose value will determine whether it is ideal or not ideal parameter. So, α = 0 will mean your system is ideal Debye system and deviation from α would mean that your system is, so α > 0 would mean your systems is non-ideal in nature and what it means is that basically α represents the distribution of relaxation times in the material and what it means is that you have different defects responding to different frequencies.

As a result, you have multiple relaxation time. So, distribution of relaxation times. So, if you plot now, for example, ε_r'' versus ε_r', you should ideally get a semicircle like this and the frequency goes in this direction. So, this is for ideal dielectric. But in reality, you will see that your semicircles are hardly obtained, you obtain suppressed semicircles or raised semicircles, which means you have some values of α, which means material does not have a single relaxation time or single dipole

Rather it has multiple defects which respond differently to different frequencies as a result causing a variation in α. So now, let us look at, let us build upon the semicircle, what is the use of the semicircle? Well the use of the semicircle lies in what we call as, technique called as impedance spectroscopy.

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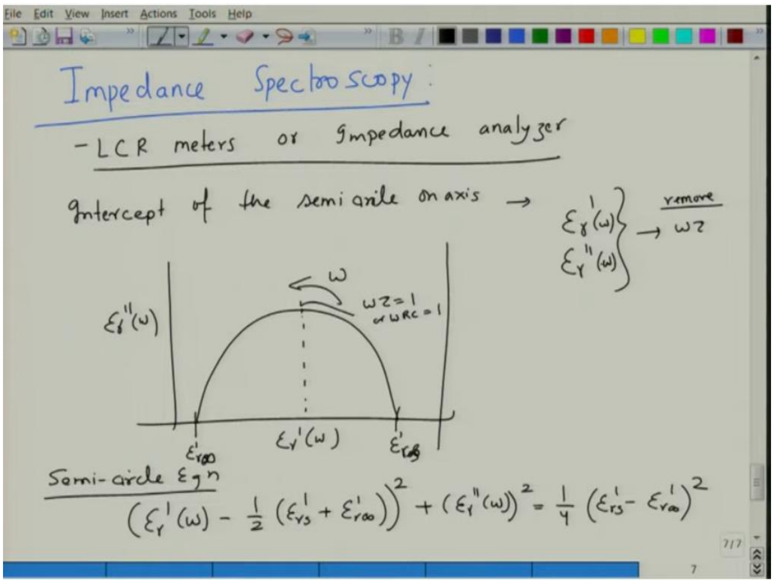

So, impedance spectroscopy is a technique, which is used to, impedance spectroscopy is a technique which is used to characterize dielectric materials. So, you saw that admittance is related to dielectric constant, as a result, the impedance is also related to dielectric constant, right. So impedances and admittances are related to dielectric constant. So, when you measure impedance, when the dielectric constants plot show the semicircles, you should also get the similar semicircle from the plot of impedances.

And impedances are measured on equipment called LCR meters or impedance analyzers. And there are various companies which make them. So, not going to advertise for any particular company, but. So, these are the equipment, which are used for varying, so essentially, you can say that intercepts of, if you take the intercept of semicircle, as we saw last on x axis, that would be basically. So, we saw that ε_r'' and ε_r' shows a semicircle, like this.

So, this is low frequency intercept. So, this is $\varepsilon_{r,\infty}'$ and this is $\varepsilon_{r,s}'$. So this is prime, let us, in this case, real part. So, the low frequency intercept is $\varepsilon_{r,\infty}'$. This is low frequency. So, the low frequency should be the static dielectric constant and the high frequency intercept of ideal semicircle should be the high frequency dielectric constant.

And the maximum of semicircle will occur at ωτ = 1 or you can say ωRC = 1. In this case, R_2C_2 and this should follow the semicircle equation. So, the semicircle equation would be, and these plots are also called as, they are called by different names, Cole Cole plots and so on and so forth. So, the equation of semicircle would be:

$$\left\{\varepsilon_r'(\omega)-\frac{1}{2}\left(\varepsilon_{r,s}'+\varepsilon_{r,\infty}'\right)\right\}^2+\left\{\varepsilon_r''(\omega)\right\}^2=\frac{1}{4}\left(\varepsilon_{r,s}'-\varepsilon_{r,\infty}'\right)^2$$

So, if you google, let us say, what is equation of semicircle, you will find similar form of equation of semicircle. So, this is the equation of semicircle, which is basically obtained by removing ωτ from the equations that we have derived earlier. So, we derived the equations for, let us see, which were these?

Yeah, so, we derived equations for dielectric constant. So, essentially we derived equations for ε_r' and ε_r''. If you remove ωτ from these equations, this is what you should get. The variation of dielectric constant, so this is as a function of frequency, we had the equation. So, if you remove ωτ, this is what you should get, which is the equation of a semicircle.

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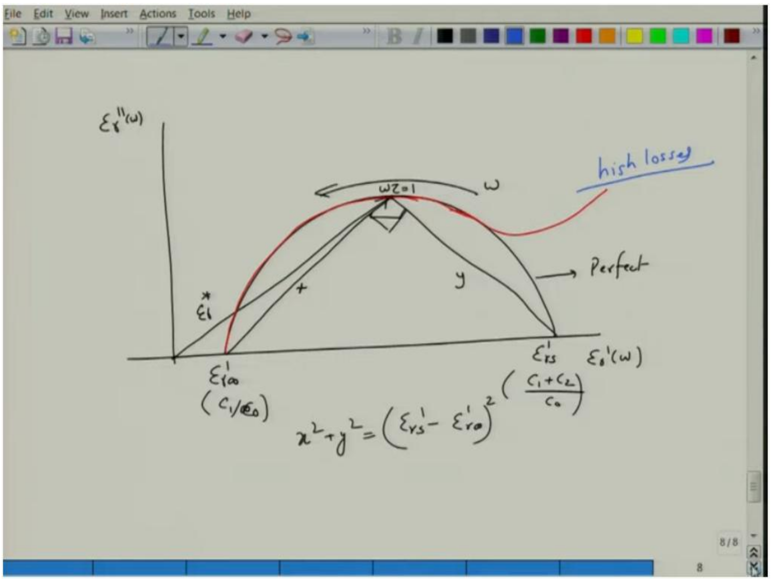

So, let us do a little bit more with this and before we, so when you plot ε_r' versus ε_r'', let us say we get this semicircle. So, the semicircle essentially the frequency increase is shown in the inverse direction, from right to left. And let us say, if you want to measure at this point, so the dielectric constant will be, so this would be ε_r^* and the dielectric constant. So, within this, you will have this as x and this as y. Now, using these x's and y's you can write the equation of semicircle.

And here, this would be $\varepsilon_{r,\infty}'$ and this would be $\varepsilon_{r,s}'$. And this is basically nothing but C_1/C_0 and this is nothing but $C_1 + C_2/C_0$. So, this would be the case for a perfect dielectric, where you can calculate x's and y's and you can find out at this point, this will be $\omega\tau = 1$. So, x's and y's and the difference between this. So essentially you will have:

$$x^2 + y^2 = \left(\varepsilon_{r,s}' - \varepsilon_{r,\infty}'\right)^2$$

For a perfect semicircle, this would be 90^0. And if you look at the previous equation, this is what you have. This is, you can say, some sort of x^2, this is y^2. The four will go of course on the other side, this is where it is.

So, what you should obtain for a perfect dielectric is like this, a semicircle. But for a real dielectric, often what you see is that you have these, sort of, upturns like these. And these are, when you see these upturns, basically you have high losses in the material. Material is loss, it has defects, it has other things which gives rise to these kind of losses and this is something that, there is a problem. And when you model this now, but in a real material, you hardly see one semicircle.

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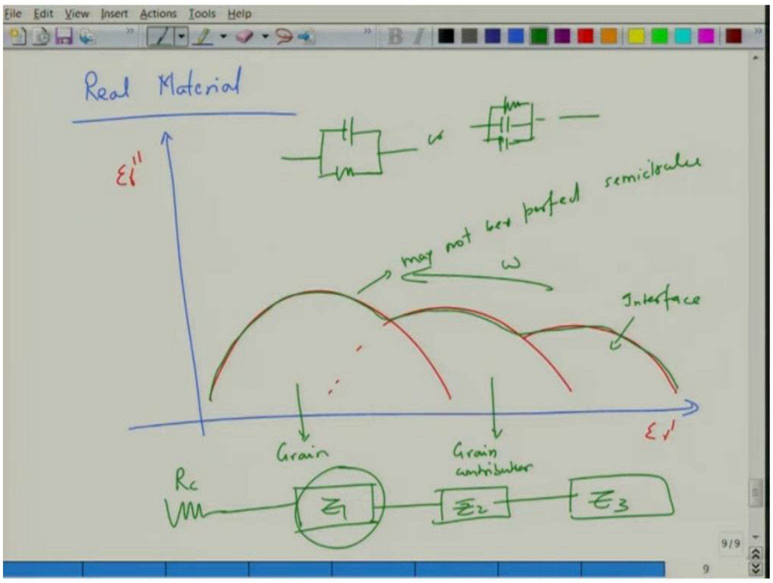

In a real material, the situation can be a little bit more complex. You might have a situation in which, so you plot ε_r'' to ε_r'. And you might have situation like in a one semicircle, you will have another semicircle, which is sort of overlapping this. You may have another, so that it could be something like that, then you may have another semicircle which is overlapping this. So, eventually you will obtain a plot which will look more like this, something like this.

And this is what you have to model, you have three semicircles here and these may not be perfect semicircles. So, may not be perfect semicircles. So, you need to make appropriate models for them. For example, let us say, if you have in a system, polycrystalline system, you have a grain contribution, you have grain boundary contribution and then you have some other interfaces, like electrode interfaces and things like that.

So, grains generally respond at higher frequencies, grain boundaries require at a little lower frequencies and this is increase in ω. And interfaces will respond at another frequency. So, it is possible that you have one impedance for this system, another impedance for this system, another impedance for this system and then you also have to take care of contact resistances in the system RC. And this Z maybe, it is like this. Or it could be series of, something like this.

There are various possible circuits which are possible depending upon the nature of defects.

So, as a result, this is far more complicated.

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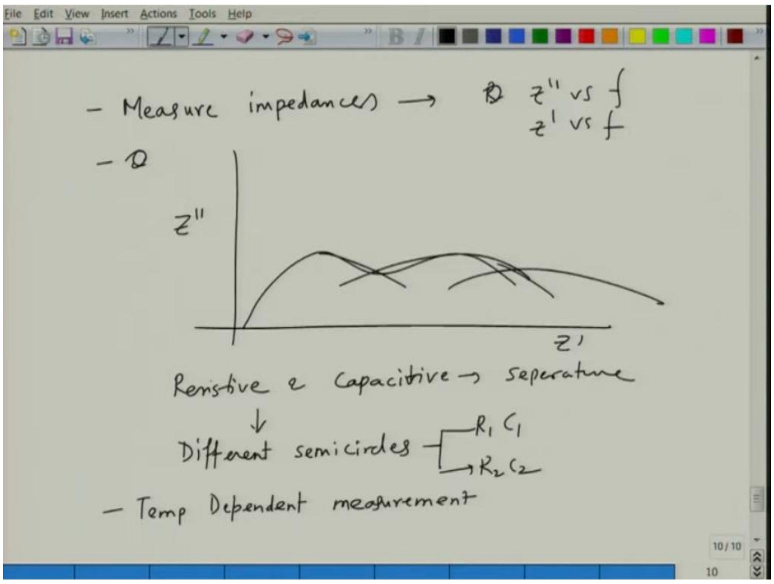

So, what generally we do as a scientist is that, we measure, in the impedance spectroscopy, we first measure imbalances. Convert these impedances, so from these impedances, we make plots of, you know, real, similarly, when you make a plot of Z'' to Z', we should also get these semicircle, like so, you should have these kind of semicircles as we saw earlier. And we make plots of Z'' versus frequencies, Z' versus frequency determine where the maxima is occurring, how they are behaving and things like that.

When you make these plots, from these plots, you determine what is the resistive contribution. So, you separate out the resistive and capacitive contributions. From these different semicircles, you find out for different components, so if you have, let us say, two semicircles, you will have for one R_1C_1 and for another one, you will have R_2C_2 and so on and so forth. So, you differentiate between different relaxation times, different resistances and that you also make temperature dependent measurements.

To distinguish clearly between the grain and grain boundary contributions. For example, the activation energy for grain will be different, the activation energy for the grain boundaries will be different.

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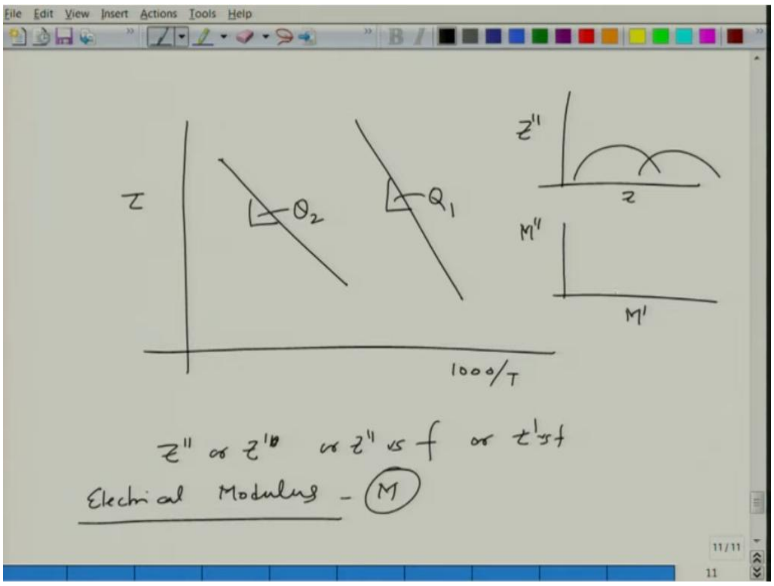

So, as a result, when you plot the relaxation times as a function of frequency or temperature, there is a possibility in some cases you will have distinct behaviors. So, at high temperature, you may have this activation energy, at low temperature you may have this activation energy.

And these will correspond to different entities, one may correspond to grain, another may correspond to grain boundaries and so on and so forth. So, doing temperature dependent, and then, of course, not only you can make Z' versus Z'', Z'' versus Z' or Z'' versus frequency or Z' versus frequency plots, you can also calculate a quantity called as electrical modulus. Electrical modulus is called as M, which is related to Z.

And then using electrical, so the problem with Z'' is that high frequency contribution in the impedance, in the impedance spectra, when you plot Z'' versus Z, often you will see that high frequency contributions are little subdued, but when you make measurements of M'' versus M', high frequency contributions are more explicit than the low frequency contribution and this is because of the correlation between the two properties.

So you measure impedance, you analyze electrical modulus from impedance, do a temperature dependent analysis and find out the contribution from entities such as grains, grain boundaries and find out differences between the two. So impedance spectroscopy is a very powerful technique to analyze materials. Unfortunately, it is not the focus of the course, but there are several papers. For example, there is a book on impedance spectroscopy by Ross MacDonald.

And there are very good review papers written on impedance spectroscopy of dielectric materials. So, go through them and read about the details of impedance spectroscopy, how it could be used for in characterizing dielectric materials.