[SQUEAKING]

[RUSTLING]

[CLICKING]

JUEJUN HU: So in the last lecture, we already discussed about these four different loss mechanisms. One thing to again emphasize here is the language we use to describe these loss mechanisms. So we say loss and attenuation, which encompasses both absorption and scattering.

We want to make a distinction between the two, because the first two mechanisms, these are actually absorption. It means that you actually convert photons into, eventually, heat. But for the last two mechanisms, these are actually scattering. It means that the photons are still there. Their propagating direction is just diverted, which constitutes loss. But this is not absorption. Yes?

AUDIENCE: Wait, so loss and attenuation both mean?

JUEJUN HU: Loss and attenuation both cover absorption and scattering.

AUDIENCE: OK.

JUEJUN HU: But if you talk about absorption, it's only essentially energy conversion involved. So that's the one thing I just want to highlight here. So we have already mentioned that in amorphous materials, well-prepared amorphous materials, you should have electronic absorption, phonon absorption, and also Rayleigh scattering present. Defect scattering, this is non-existent if you have a defect-free material.

So now what I'm doing in this slide here is that I'm essentially listing all the possible contributing mechanisms in glass materials. I have categorized it into two categories, so extrinsic versus intrinsic attenuation. For extrinsic, I mean that this is something not relevant to the pure glass materials. It's due to some kind of impurities or due to some dopant you add into the glass. Whereas intrinsic attenuation is something directly associated with the glass network itself.

So for extrinsic absorption, as I said, this is due to impurities or dopants. This is usually caused by some impurities, for example, like transition metal or rare earth ions. And transition metals has unfilled 3D electron shells. Rare earth ions has unfilled 4f electron shells. We'll see a bit more details in the next few slides. But basically, these empty orbitals essentially means that there's a lot of possible transitions that can take place between the different electron energy levels.

And when the incident photon has energy that coincides with one of these transition energies, then you can actually promote electron to excited state and therefore essentially lead to a loss of photon. So that's basically electronic in nature. If you look at my color code here, I have my color coding here. I use three different colors that represent different kind of absorption mechanisms.

You can also have extrinsic absorption coming from vibrational or chemical bond phonon absorption. So one example for that would be oxygen impurities in chalcogenide glass. We mentioned that chalcogenide glasses, people like to use them for infrared transmission applications. This is what we showed in the demo in the last lecture.

So the reason they can actually transmit this infrared radiation is because they consist of heavy atoms, which give you weaker chemical bonds, lower phonon vibrational frequency, and therefore it pushes the transmission window to a much longer wavelength. However, if you get oxygen impurity getting into chalcogenides, they are much lighter. They also form much stronger chemical bonds compared to chalcogens.

So then that's going to essentially lead to impurity absorption bands due to this phonon vibration associated with oxide chemical bonds. So that's why for those manufacturers of infrared optics based on chalcogenide glasses, it is really important that every step of that process has to be done in a low oxygen environment. They actually process them, all the glass materials, if you look at it, how they do it, always in glove boxes, nothing in the atmosphere. So that's quite different from oxides.

Now for intrinsic attenuation, we are going to essentially go over the different electronic absorption mechanisms in the next few slides, phonon as well as also Rayleigh scattering. So we'll go through them basically one by one. So now let's start by taking a look at electronic absorption. So on this slide here, again I'm showing you the density of states plot that I quoted from the previous lectures.

The key features for the electronic band absorption in an amorphous material is that you don't have a well-defined bandgap. The density of states never really goes to 0. And you can have those localized states either located at Urbach bandtail, which is resulting from disorder of the entire lattice, or you can also have those localized states that's confined near the middle of bandgap. And these are the tightly bound states that usually are associated with single atoms or single chemical bonds, like dangling bonds.

So because of the presence of all these states, unlike crystalline materials, where essentially if you have energy, if it's defect free, if you have a photon energy below the bandgap, then you will not get absorbed. You just zip through. It's perfectly transparent. But for amorphous materials, you always get non-zero absorption regardless of photon energy, because you always have this continuous distribution of density of states.

So we'll be looking at a few mechanisms here. If your photon energy is sufficiently large, so that you can essentially promote one electron from the extended states in the valence band to the extended state in conduction band, and you still get band-to-band transition, you can also have a transition between the extended states to the localized states. These are what's responsible for so-called Urbach bandtail absorption.

You also have absorption related to essentially those mid-gap states. These are basically a defect state absorption there. And finally, if you have free electrons or free carriers in the conduction of the valence band, those can also move. And they can be driven to oscillate under the external electric field. And that can actually contribute to additional absorption there.

That's called a free carrier absorption, FCA. So these are the four mechanisms that's present in amorphous materials. In crystalline materials, you also get 1 and 4 and maybe defect state absorption, if it's a defective semiconductor, but much less contribution coming from the localized states.

So for the band-to-band transition, in the previous lecture, I have already mentioned about this quantity called Tauc gap. I mentioned that Tauc gap is really just a fitting parameter. It doesn't have a very concrete physical significance. It just roughly tells you where the density of states becomes small. And this is the fitting formula for the Tauc gap.

So what you will do, like in this plot here, is you are plotting essentially alpha h-bar omega square root, where alpha is the absorption coefficient, h-bar omega will basically be the photon energy. And you plot it against the photon energy. And what you will see on this kind of plot, like the example I'm showing here, is typically you will get a linear regime that allows you to fit the intercept with horizontal axis. That gives you the Tauc gap.

If it is an indirect bandgap semi-crystalline semiconductor, then the absorption will be pretty well described by just a simple straight line. But for amorphous materials, you also notice that the absorption doesn't go to 0, even if you go below this energy there. So this little tail here, this is the Urbach bandtail absorption.

I'm listing here the equation that people typically use to characterize the Urbach bandtail. You notice this exponential dependence, only photon energy here. That's because the density of states for Urbach tail tend to decay exponentially as you move into the bandgap. So to fit this kind of Urbach bandtail absorption, people actually use a different kind of plot here.

What you do is you basically plot alpha in logarithmic scale. So if you put a logarithm alpha, then what do you get? You essentially have a logarithm alpha u, and then the exponential just comes out. It becomes also plus h-bar omega minus E. I use Eg there, but you can use Tauc gap, ET, either way. So either Tauc gap or bandgap, either way, divided by Eu.

So therefore, once you do this kind of plot, as I'm showing you on the slide here, you will also get a linear regime here. So region A, this is basically band-to-band absorption, characterized by a very strong absorption coefficient. Now here, this linear regime gives you essentially Urbach bandtail. According to the equation there, it should show up as a linear dependence if you plot the logarithm alpha as a function of h-bar omega.

And then from this slope of this line here, you can also essentially extrapolate Eu, or basically 1 over Eu. That gives you the slope. And then for the intercept, you can then determine what alpha u is. So that's how you actually fit this equation from experimental data here.

AUDIENCE: And Eu and alpha u are?

JUEJUN HU: Essentially, these are parameters used to characterize the Urbach bandtail. Eu gives you how fast the density of states decays into bandgap. The larger the Eu is, the faster it will decay. Essentially, you have a narrow Urbach bandtail, practically. And alpha u is just essentially a pre-exponential constant. The higher alpha u, the more states you get.

AUDIENCE: They're just state parameters.

JUEJUN HU: Yeah, these are basically parameters. But they do relate to structure disorder. So the larger the structure disorder, you expect that you actually have a larger alpha u, for example.

AUDIENCE: OK.

JUEJUN HU: Because you essentially get more states, more of those localized states. That's basically the idea. Yeah. Also, if you look at the plot here, we divide up the absorption into three regimes. We say that A is band to band, B is Urbach tail. You notice here that there's also this C here that does not conform to the Urbach bandtail model.

Essentially, you get additional excess absorption as you go deep into the bandgap for those small energy regimes. Those are typically associated with defect states like dangling bonds. And the strength of this kind of absorption will closely depend on how defective your material is.

We mentioned that this part of absorption, for example, if you think about amorphous silicon, you're going to get a lot of this kind of mid-gap state absorption if you deposit amorphous silicon by, say electron evaporation where there's no hydrogen. Whereas if you do PECVD, you expect this kind of tail absorption will decrease pretty drastically because most of the states are going to get passivated. So this is a very strong function of the processing condition and microstructure of the amorphous materials.

The other thing I also want to mention here is that the relative magnitude of this kind of absorption here. So for band-to-band absorption, because we are talking about essentially a large number of extended states, the absorption coefficients tend to be very high. They are typically above at least 1,000 inverse centimeters for band-to-band absorption. Similar to crystalline materials, very strong absorption.

Now for the Urbach bandtail, as you can see from this plot here, the typical absorption coefficient for Urbach bandtail is of the order of 10 to the maybe to the 1 or 10 to the 2 inverse centimeters. Whereas for the mid-gap state absorption, they really get pretty weak. It's of the order 1 inverse centimeter. So it's 3 to 4 orders of magnitude lower compared to band-to-band transmission.

And that's why despite the fact that you may get this kind of a defect state absorption here, because the absorption can be sufficiently weak, people can still make functional, transparent optical devices out of amorphous materials, even like amorphous semiconductors, like amorphous silicon, in this kind of a low absorption regime here, despite the presence of those defect states.

People actually make, for example, amorphous silicon waveguides with decent losses, provided that they can passivate these kind of defect states to a sufficiently low level. So it's still acceptable. It can still be used as a transparent material even in the presence of these defect states.

Now, last mechanism here, free carrier absorption. So the way to understand free carrier absorption is that anything that's electrically conductive is also optically absorptive. The reason something conducts electricity, most of the time, it's basically electronic carriers, you have electrons and holes that can freely move around. But when electrons and holes are moving around, you inevitably get some kind of dissipation mechanisms.

The electrons can essentially get scattered by the lattice. In the process, they essentially exchange energy with lattice, leading to energy dissipation from essentially the electronic domain into the basic heat. So you are basically heating up the material in that process due to this dissipation mechanism. And this can be characterized by the Drude model, which I suppose you have learned to model in 3033? OK, yeah.

So basically in Drude model, there's essentially this kind of damping term that characterizes any kind of friction, the effectivity the electron experiences as they move around in the lattice there. So the damping term is what accounts for the energy loss going from optical domain into basically phonons or thermal domain. So what I'm showing you here, this is basically the change of refractive index and absorption coefficient.

So this is real and imaginary power refractive index-- real power is n, imaginary power is k. The expression is coming from the classical Drude model. Now, what we see here is that Drude model not only predicts an absorption increase-- that's what we call free carrier absorption-- it also says that the refractive index of the material also changes if you have free carriers. That's called a free-carrier plasma dispersion.

You can understand it also from a KK relation perspective, Kramers-Kronig relation. When you change the absorption, inevitably you also change the refractive index because they're actually tied up together. So this is actually a way to modulate the refractive index of materials by essentially changing the free-carrier concentration.

This is actually something useful, like people in state-of-the-art optical communications, they can actually make optical switches out of this mechanism by essentially injecting carriers into semiconductors, change the refractive index, and therefore change the phase of the light propagating through them to create all kind of optical switches. With the caveat that any index change is accompanied with absorption change in this particular case here.

So since you already learned the Drude model, I'm not going to go into much details about this particular equation here. But one thing I do want to highlight is that if you go to some textbook, semiconductor physics textbook, they usually give you an expression that looks slightly different from what I'm showing here. I want to mention that those equations most often do not apply to amorphous materials.

The reason I'm saying that is because for most semiconductor physics textbooks, they are dealing with free electrons with very high mobility. We mentioned that the mobility typically is 1,000 or even higher volt-centimeters squared, whatever. So for those electrons with very high mobility, the larger the mobility, the smaller the damping term is and the less free-carrier absorption, which makes sense. If you have high mobility, it means that there's essentially less friction, less dissipation, so therefore there's less energy converted to heat.

However, that approximation actually fails when you go to amorphous materials because you get lots of lattice disorder. And as a result, you get very strong phonon scattering, very strong scattering of the electrons. And the mobility in amorphous materials tends to be much lower, as we have seen. And because of that, if you are plotting, for example, in this case, what I'm plotting here is actually imaginary part of the dielectric constant, which is related to absorption, as a function of mobility.

You see that the imaginary part actually peaks at some mobility here, which is about 100 centimeters squared per volt per second. Below that, for amorphous materials, we are typically talking about mobility in this region here. Within this side, the lower the mobility, the lower the free-carrier absorption, which is completely opposite from what you would predict based on those approximation equations in what you see in semiconductor physics textbook.

One way to intuitively understand it is think of the limiting case. If mobility is 0, you basically get insulator. If it's an insulator, obviously you get no free carrier loss. What happens here is as the mobility gets very low, these electrons are actually undergoing this oscillatory motion, the distance they move essentially becomes very, very small.

Well, that's the result. The dissipation effect essentially becomes less significant because of the very small distance they move. So that's the physics behind it. But the reason I want to highlight it is I want to mention that free-carrier absorption, number one, they tend to be insignificant in amorphous materials because of the very small mobility here.

OK, number two is that when you actually need to carry a free-carrier absorption amorphous materials, make sure to use the original formulation here without approximation. Don't quote the equations from typical semiconductor physics textbook. Most of the time, there's an implicit assumption that mobility is high when they give you those equations. So you have to use the original formulas in there. Is there a question? OK.

So just to summarize, this is something I have already mentioned. When you're looking at electronic absorption in amorphous materials, band-to-band, they tend to be very high, similar to in crystalline solids, above 1,000 inverse centimeter. Bandtail is typically like a few 100 inverse centimeters. Free-carrier absorption, they tend to be pretty low, generally negligible except in some exceptional cases in amorphous materials.

So that's electronic absorption. Now next we are going to look at here, this is essentially phonon absorption coming from lattice vibrations. As I mentioned in previous lectures, the way to model this kind of absorption is to think of chemical bonds, essentially approximating them as a masses attached to the end of the spring.

And then you can now characterize the characteristic resonant frequency of this kind of a simple harmonic oscillator with this equation here, where k in this case is the spring constant and m is the reduced mass of the spring. Sorry, I'm using a k in the previous slide. There k is emerging power refractive index. Here k is spring constant. It's a bit confusing here. I should really correct it.

Now, if you look at the table on the right-hand side here, what I'm listing, these are the typical sort of chemical bonds that's present in amorphous materials. And this is essentially the absorption band in microns, in terms of wavelength. Now, one thing we immediately notice here is that if you look at, for example, oxygen, O-H, versus S-H, this is basically isoelectronic substitution, oxygen and sulfur. They are basically isoelectronic.

You'll notice that as you increase the mass of the atoms, the absorption bands tend to red shift, go to longer wavelengths. Same thing applies if you look at, say silicon-oxygen, germanium-oxygen, again isoelectronic substitution, you see absorption band essentially pushes the long wavelength. So let's go back to what we have talked about. As you increase the atomic radius, you tend to have, of course, larger atomic mass, right?

And larger atomic radius also means that the interaction between the atomic nuclei and the outer shell electrons also gets weaker. So you also have weaker chemical bonds, and therefore a reduced spring constant. Both vectors will point to a lower phonon vibrational energy. So the phonon absorption band would then be pushed to longer wavelength.

If you go back to the absorption curve, for example, we are showing here, let's say, for silica glass, we mentioned that at the longer wavelength end, the absorption is basically dominated by phonon absorption. Now if you look at the table I show you in the next few slides, for Si-O, the phonon absorption actually centers at about 9 microns. That's the vibrational frequency. We are talking about 1-point-something microns here.

So we are looking at essentially a very long tail coming from the primary absorption band. It's exponentially the case. We are looking at a very small tail tale here. But if you want to extend this transparency window of glasses into longer wavelengths, what you will have to do is to essentially substitute oxygen or silicon with something that's heavier so that this curve can then move in this direction. And therefore you can actually extend this transparency window into longer wavelength range.

So that's actually what people do. For example, that's why chalcogenide glasses come into play. So what I'm showing you on this figure on the left-hand side here, basically this is the wavelength. And each of these colored bars essentially represent the optical transparency window for the different materials here. So you see clearly that silicon, they are transparent up to about 7 microns-ish.

Germanium, because it's actually heavier, it's actually transparent pretty much across the entire mid-infrared wavelength regime where people care about for thermal imaging. That's a demo I did in the last lecture for essentially thermal imaging or night vision. They are transparent up to about 16 microns, which is well adequate for most of thermal imaging applications.

Typical blackbody radiation wavelengths for human body is like 8 to 12 microns, like 10 microns-ish. As you go to higher and higher temperature, that emission band shifts to a shorter wavelength. So that's why the typical wavelength regime of interest for thermal imaging is somewhere between 3 to 12 microns is the typical band. So that's why for a long time, when people are trying to make those infrared cameras, they like to use a single crystal germanium to make it less.

The problem with single crystal germanium, a few issues here. One is that they're a single crystal. So in order to make lenses, you have to do a very careful grinding and polishing that gets quite expensive. Also, germanium is known to have a very high thermo-optic coefficient. As you raise in temperature, you generate lots of free carriers because germanium has a very small bandgap.

This not only causes free-carrier absorption, it also causes a refractive index change due to KK relation. So as a result, it means that your lens, the focal length actually changes with temperature. This leads to a big issue there. And finally, there's also supply chain issue recently because China turns out to be the largest supplier of germanium. So I'm going to stop there.

So that's why for quite some time, people have been trying to look for essentially alternative materials to germanium lenses. And one of the candidates they came up with, obviously, are these chalcogenide glasses. This is actually one example here. This one still contains germanium, not 100%, but still contains germanium. But there are alternative compositions where there is no germanium, if you want it.

This is a very common formalism called BlackDiamond that people use for infrared optics. Again, I don't know why they call it BlackDiamond. From every aspect, it's property seems to be opposite to diamond. Diamond is meant to be expensive. These glasses are essentially low-cost alternatives to germanium lenses. Diamond is known for very good mechanical properties, very hard material.

These glasses, if you ever do use the infrared optics, I would recommend that you be very, very careful. Because of the heavy atoms, they tend to have weaker chemical bonds, so they have a much poorer mechanical properties compared to the rest of glasses. You can very easily scratch them. So be very careful with those kind of materials. So anyway, I don't know why they got called BlackDiamond, but it is what it is.

The advantage of these materials is that, of course, you can see from this plot here, a lot of these chalcogenide glasses, they exhibit very wide transparency window in the infrared. And because they're amorphous, it's also very easy to actually process them into lens geometries by just simple compression molding techniques. So that's why they are really drawing a lot of interest in infrared optics there. The camera I showed you in the last lecture, as I said, the lens is actually made of one of those chalcogenide glasses.

All right, next mechanism, we are talking about Rayleigh scattering. We have already mentioned that Rayleigh scattering comes from atomic scale inhomogeneity intrinsic to amorphous network. If you think about amorphous glass materials, you zoom in to look at every local geometries there, due to the statistical nature of amorphous structure, you are definitely going to get slight fluctuations of the atomic density at different locations.

As a result, different atomic density essentially also means that you get different polarizability. So different polarizability gives you different refractive index. So as light propagates through this amorphous material, you see this slight refractive index fluctuation that then leads to a scattering. This is what's called Rayleigh scattering.

I also want to mention again that this kind of Rayleigh scattering applies not only to amorphous glasses. Any kind of a structurally disordered material also has a Rayleigh scattering. The good example here would be air. Think of ideal gas. In ideal gas, all the molecules are not interacting with each other, and therefore the coordinate of the atoms are basically independent of each other, of all the molecules.

So what that also means is that there's always statistical fluctuations of density in air, just due to the random motion of air molecules. Now this is also going to lead to Rayleigh scattering. And that's why basically the sky is blue. Because if you look at the Rayleigh scattering formula here, the loss in this case-- this is not absorption, this is a loss coefficient, in this case-- it scales with wavelength to the negative 4th power.

So blue and purple light get scattered a lot stronger compared to red or orange part of the spectrum. And that's why the sky appears blue. It's not purple because human eye is not very sensitive to purple light. So that's why it's blue.

Now, one key thing to emphasize here is that Rayleigh scattering is only present if a material is inhomogeneous. If it's homogeneous, then there is no Rayleigh scattering. If it's a perfect, single crystalline material, no defects, then there's no Rayleigh scattering. It really only comes from this atomic-scale fluctuation of density.

For glass materials, more specifically, I'm showing you here, this is actually a quantitative model people have developed to characterize Rayleigh scattering. And the coefficient here, A1, it gets pretty complicated. You see lots of different numbers here. Again, you don't need to memorize it, obviously. But I just want to highlight a few terms here.

One is that it scales with refractive index to the eighth power. So the higher the refractive index, the stronger the Rayleigh scattering gets, which makes sense. If you have high refractive index, it essentially means that the polarizability fluctuation is also going to be a lot larger. So therefore light is going to see a lot larger inhomogeneity. And therefore you have a lot more scattering there.

Second thing is that you notice that you have a Tf coming in, also kB as well coming into the equation. Tf is fictive temperature. It's basically roughly the temperature where glass transition takes place. So why does Tf come into play? The way these density fluctuations are introduced, if you think about glass-forming process, you start from the melt.

In the melt, it's ergodic. You can essentially have all kinds of structural fluctuations. As you start to cool down through the glass transition regime, the glass structure essentially becomes non-ergodic. So at some point, you are going to freeze into one specific configuration, geometrical configuration. The density fluctuation associated with that particular structural configuration is actually dictated by the thermal fluctuation.

Any structural fluctuation relates to essentially thermal energy. That's why kB come into play. Now, more specifically, when you are gauging this kind of structural fluctuation there, you should be looking at the glass-forming temperature. Because that's when the structure is actually getting frozen there. So that's why when you are looking at the structural fluctuation, it scales with the kB Tf. This is the thermal energy before the structure essentially becomes frozen.

So the larger the Tf there, the more thermal energy you get, the higher the density fluctuation. That's why you have Tf here. It's related to glass forming. Last part, beta, this is the isothermal compressibility. Isothermal compressibility is essentially defined as how much volume change you can introduce per unit pressure you apply on the material

So a material with higher isothermal compressibility means that essentially it more easily deforms with the same amount of a given pressure. So of course, if a material can deform more easily with larger beta, you get more density fluctuation, and therefore you should have a higher Rayleigh scattering.

So that's why some of these terms, they actually come into play in this equation there. And photoelastic constant, this is basically just how much refractive index change you get per unit strain. So obviously again, higher refractive index difference, higher the scattering.

So this kind of local density fluctuation already scattering is universal to all amorphous materials. They are always present. They can be quite small because unlike defect scattering, the length scale we're talking about here, this is really atomic scale. Because Rayleigh scattering also decreases to the essentially to the negative 4th power with respect to a characteristic length scale of the scatterers.

So for small-scale fluctuations, the corresponding loss is a lot weaker. And that's why glass materials can still be extremely transparent, despite the presence of this kind of Rayleigh scattering. Unlike polystyrene ceramics, which have much larger grains, therefore induce much stronger scattering. That's why they tend to be opaque.

The second source that relates to Rayleigh scattering here is what's called concentration scattering. Concentration scattering has to do with multi-component glass materials. Let's just take a random example. Let's say you have instead of SiO_2, let's say you put some germanium in there. So this will be Si, this is a 1 minus x. This is x.

So if you throw in some germanium dopants into a SiO2 glass, then germanium can also occupy the site where silicon normally sits. They're still 4-4 coordinated, same as silicon. But what you imagine is that now if you only look at the sites that's supposedly occupied by silicon, you now have a random distribution of germanium and silicon.

And germanium has a higher polarizability compared to silicon because it's a heavy atom. So it means that this random distribution of these two kinds of atoms also leads to additional fluctuation of polarizability and hence refractive index. So this is going to lead to additional scattering loss here. This is what's called a concentration scattering.

It really only applies to this kind of multi-component glass. If it's SiO2, concentrated scattering is basically 0. But as soon as you start to add some kind of dopant, chemical modifiers, as long as you have random population of lattice sites due to two different kind of atoms, then you start to get concentration scattering. Yes?

AUDIENCE: So the concentration scattering, is that only for substitutional or would like an alkali glass that has also some other elements but not--

JUEJUN HU: Well, in fact, if you think about it, like for example, it applies even for interstitial as well. Even in crystalline material, think about crystalline material, you put in some kind of interstitial dopants. The distribution of dopants in the interstitial site is also random, statistically random. So it means that there are also little fluctuations of local polarizability and therefore also scattering.

It usually tends to be pretty weak. That's why people don't care about it, especially in crystalline materials. In crystalline materials, you don't have a media like fiber, which is kilometers long, that require that level of low loss. So that's why people typically don't even care about that kind of loss. But it is present. It's is definitely not 0.

AUDIENCE: OK.

JUEJUN HU: Yeah, as long as you get random spatial distribution of something, some kind of scatterers, you get scattering loss. Yeah. All right, so we have gone through essentially all these different kinds of mechanisms about losses in glass materials. if you put all of them together, you will get a plot like what I'm showing here.

Now notice here, the vertical scale, horizontal scale, these are both in logarithmic scale. So this logarithmic absorption coefficient or logarithmic loss coefficient, I should say. And then the horizontal axis is logarithmic wavelength. So look at the terms here. The first one, A1 and A2 over lambda to negative 4th power, this is Rayleigh scattering. A1 corresponds to Rayleigh scattering universal to amorphous materials. A2 is an additional coefficient we introduce here to account for concentration scattering.

Second one, B, this term, this is coming from electronic absorption. If you look at the expression here, basically it says that absorption decays exponentially as you increase wavelength. This is really coming from those defect states.

And finally, last term here, this is coming from phonon absorption. Again, similar to electronic absorption, for phonon absorption, you basically have absorption peak that corresponds to the vibrational frequency of the lattice. But as you move away from that vibrational peak, the absorption decays exponentially.

Now if you put it on this plot here, you can see three different regimes here. At the very short wavelength, this is typically where you have high energy photons. You can excite these electronic transitions. Then you get electronic absorption here. This usually depends on the glass material. You can actually look at the glass material and tell where the electronic absorption comes in.

Essentially, if it's like silica, it's perfectly transparent. So you only get electronic absorption really in the UV range. If it's like chalcogenide, they're opaque in visible, so then you can actually absorb photons with energy like a couple of EVs. If you get to a longer wavelength here, lower energy, you get this linear regime here in the double logarithm plot with a slope that corresponds to basically 1 over 4.

This is Rayleigh scattering. So Rayleigh scattering tend to take over in the transparency regime of glass materials. And then the long wavelength absorption is really bound by phonon absorption. So in between Rayleigh scattering and phonon absorption, you can define the minimum loss window for glass materials. This is where the glass material gets most transparent, right in the middle here.

So now once you put it down, let's take a look at some actual real examples here. On the left-hand side, this is the absorption coefficient of silica glass, which I basically have shown in previous slides. There are a few different curves here. The thicker lines, these actually correspond to glasses with impurities. In silica glass, the most common impurity is basically hydrogen coming from water. If there's a water, they get incorporated into lattice, basically hydrogen.

O-H has a high-order absorption at about 1.4 microns. Let me see. If you come over here, the O-H functional group, the primary absorption band is about 2.9 microns. But you also get high-order harmonics. Essentially, if you look at phonon absorption, you can excite one phonon, which gives you h-bar omega. You can also excite two phonons, then you get 2 h-bar omega.

So it means that in addition to this primary absorption band, which has a high strength, you also get higher order, what they call overtones. Higher-order overtones. So these overtones are roughly integer multiples, in terms of the frequency, for the primary absorption band. So in wavelength, this then corresponds to about 1.4, 1.5 microns.

So that's why the high-order overtone is what's causing this little peak there. And that's why if you look back into Charles Kao, when he first developed these fibers, he has to spend lots of time looking into how to actually purify these glasses in order to get rid of all these impurities.

Now, in the bottom here, this gray line, this gives you the absorption coefficient of a high-purity silica glass. You see that, again, this end, short wavelength end, this is basically Rayleigh scattering. Long wavelength end, this is really phonon absorption coming from Si-O bond by vibration, out here at 9 microns, this is very tail. This defines the lowest loss window for silica glass at 1.55 microns, or 1,550 nanometers.

This is a very important wavelength. All the internet data in long-haul communications, that takes place all around this wavelength. They all take place right around this wavelength here because of the low-loss characteristics. If you have fiber to the home, this is how they actually send data. This is the wavelength they use to actually send data to your home or send the data across the Atlantic. This is what they use.

Now, this is already pretty impressive because as we mentioned, you can get to 0.2 db per kilometer, which is really good. But there has been lots of efforts, people are trying to push for even lower loss glass materials. So that you can have, for example, essentially fiber communication systems without having to amplify or regenerate the signal over longer distances.

So that's why especially like in the early 2000s during the telecom bubble time, there has been lots of interest looking into alternative glass materials outside silica to achieve even lower loss. The general strategy there is to look into material systems with lower phonon energy. Because what happens with low phonon energy materials is that it means that this photon absorption peak, this side, is going to get pushed to longer wavelengths.

There's not much you can do about Rayleigh scattering. But if you push the phonon absorption peak into the longer wavelength, you can extend this transmission window down to a much longer wavelength here, which also gives you a lower loss. So that's why I'm quoting you this paper here. This is actually from 1980s. This is theoretical prediction. This is not experimental data.

They predicted that for some of these fluoride glasses, also some chalcogenide glasses, you see that the transparency window is pushed to much longer wavelengths. You can get a much lower absorption in these glass materials compared to silica. Now obviously we know that nobody is really trying to make or replace silica glass fiber network using those kind of exotic glass materials.

There are a few reasons there. For practical reasons, these materials are a lot more difficult to process. They are not nearly as robust. They tend to be a lot more fragile both mechanically and also from the liquid fragility point. They tend to be a lot more fragile. It means that they are a lot more sensitive to temperature variations, if you think about it and draw a plot, any temperature fluctuation is going to lead to a very large change of viscosity, so they're a lot more difficult to process.

That's one reason. Second reason, if you look at this plot here, turns out that these loss numbers are actually unrealistic, even from a theoretical perspective, because in these early calculations, they completely forgot about concentration scattering. If you have these kind of multi-component glasses, obviously, you imagine that these different metal ions, they can occupy different lattice sites leading to rhythm fluctuation, it's going to completely overshadow these low-loss benefits.

Now you may argue germanium sulfide, it looks like a single-component glass. Maybe it can be a low-loss candidate. Turns out no, because chalcogenides is somewhat annoying in this regard, that they have different microstructure units. Take a very simple example. If you think about As2S3, this is archetypal, most commonly used chalcogenide glass. There are actually two kinds of structural units in As2S3 glass.

One is the regular As2S3, and then the other is As4S4 plus S. Because arsenic trisulfide actually has two polymorphs, if you look at the crystalline structures. And as a result, there are two corresponding structural units that are present in amorphous network. This is basically a orpiment. This is another one, realgar. And As4S4, they also, because they are excess sulfur, this sulfur actually forms in chains, linear chains or in rings around the lattice.

So even if it looks like a single component glass, if you cannot eliminate these two kind of local structure moieties, if you cannot eliminate this kind of structure inhomogeneity, you're also going to get lots of scattering loss, similar to concentration scattering. So that's why SiO2 still is the dominant glass material people use.

Now, in the homework assignment, in the P-set, I do give you a question asking you, can you still predict a glass or at least postulate a glass composition that will give you even lower loss compared to silica. OK, I'll let you think about it. I have already had all of those mechanisms here. Try to come up with one with reasonable assumptions there, accounting for all the loss mechanisms. Any more questions about loss before we move on to coloring in glasses? All good? Crystal clear? No scattering.

So now let's switch gears a little bit, talk about coloring of glass materials. This is actually a photo I took when I visited Rutgers University. They have a pretty comprehensive glass lab sponsored by Corning. And this is one of the displays they have. It shows different colored glasses and what's the chemistry actually behind them. So that's what we're going to talk about in the next section here.

So how do you generate color. Simply put, color, in order to get color, you need to introduce a wavelength-dependent loss. It can be wavelength-dependent absorption. It can be wavelength-dependent scattering. But you need some kind of wavelength-dependent loss mechanisms to get color. So you can do that either by absorption or do it by scattering. We're going to look at both.

Starting from absorption, the easiest way to generate wavelength-dependent absorption is to put in some kind of dopant ions, typically transition metal or rare earth metal. As I mentioned in the beginning of class, those ions have unfilled, either 3D or 4f shells. So this gives rise to a large number of possible electron transitions. And then these electron transitions, they lead to wavelength-selective absorption, essentially absorption peaks centering around the transition energy, which you can use to generate all different kinds of colors.

So one example here, this one, this is erbium, which is a rare earth ion. This is the energy level diagram I've quoted from this book here. There are a total of 41 energy levels in erbium 3-plus ion due to spin orbit split. So it's quite complex. Now, fortunately, you don't have to worry about most of them. Most of them are technologically irrelevant. People don't care about it.

The reason I want to cite erbium here is because it has one transition that corresponds to photon energy of 1.54 microns. Does that number ring a bell? It's very closely aligned with the low loss window of silica fibers. This is a very fortunate coincidence. That's why erbium actually becomes technologically very important for optical communications, because of that 1.54 transition there.

What I'm showing you here, you can see that it's 1.54. It centers at 1.54, but there's always some kind of broadening mechanism so that the transition actually covers, that's 1.54, but essentially covers a reasonable bandwidth. This covers essentially all the wavelengths that's needed for optical communication.

So that's why what people can do, they can make amplifiers out of this kind of erbium glass. So the type of amplifier people use is called erbium-doped fiber amplifier, or EDFA. But basically what they have here is you can simplify the energy band diagram into erbium, into a simple three-level system.

Essentially, you have a ground state. There are actually two relevant energy levels, really. Again, there are many variables. We'll only look at two of them. The transition energy for this one, this corresponds to wavelength of about 980 nanometers. This is our 1,540 nanometer transition.

Now, when you try to use this erbium ion as an amplifier media, what you will do is you start by essentially pumping, optically pump the system. You essentially promote lots of the electrons from ground state into this upper state right here. Now this upper state, turns out it's not very stable. It's short lived. It has a short lifetime. So a lot of these electrons then relax into this state.

So if you pump hard enough, then that means you can actually generate lots of carriers at this excited state here such that you actually get a population inversion. Once you have population inversion, if you send a photon with an energy that aligns with this wavelength here, then it's going to trigger essentially excitation or deexcitation of this energy level here.

And this, in the process, you essentially duplicate the photons, which then give you an amplification. So that's actually what people do in erbium-doped fiber amplifier. It's basically a section of fiber with high erbium doping concentration. And you can do that with changing the glass formula, for example, using phosphate glasses, which is what sometimes people use.

You put lots of erbium there. You then use a laser diode to essentially pump in this kind of for, example, 980 nanometer light. Then this 980 nanometer is going to lead to population inversion in that section of fiber. So then when your signal actually comes in to the same section of fiber, it's then going to get amplified. So that's how to actually transmit signal across very, very long distances. You need to essentially do this reamplification once in a while to boost the signal levels for optical communications.

Basically, this is one example to show you that you can introduce essentially light emission and similarly also absorption, because this is all reciprocal. So if you have photons with 1,540 nanometer comes in, if it's not population inverted, it's going to cause wavelength selective absorption. So what I'm showing you on this plot here, this is the absorption cross-section of erbium in these glasses. So it means that you can see that this absorption is quite wavelength selective. It peaks right at this 1,514 nanometers.

Now this is technologically important for communications. It does nothing to coloring because it's actually infrared wavelengths. You cannot see it. But the same mechanism, if you shift the absorption energy levels to the visible window, then you can actually get essentially the selective colors.

So in the table on the left-hand side here, I'm showing you the different kind of ions and their transition levels. Essentially, they give rise to different colors. For rare earth, most of the time the transition tends to be at longer wavelength, so there is only a handful of them that actually generate some colors there.

Most of the time, if you want to get more saturated, stronger color, people tend to use transition metal ions. Their transition energy usually lies in the visible region. You can see there are very diverse colors you can generate with these transition metal ions. One good example of transition metal ion that actually give you this color is just a iron, iron 2-plus.

Most of the windowpane glasses, they look transparent from surface normal direction, but if you look from the side, you see this green tint there. And that's because you always have a little bit of iron impurity. So if you're looking for colorless glasses without this green tint, two ways of doing it. If it's more high-end optical elements, in that case, essentially, you purify the glass, get rid of any of the iron impurities.

For other applications where you don't really care that much about this kind of absorption layer, what you could do, an easier way, is to leverage the fact that iron has two valence states, 2-plus and 3-plus. And they exhibit different colors here. 2-plus is green, 3-plus is yellow. And green and yellow, it turns out they are complementary colors. So what you can do is that you can actually oxidize, subject glass materials into oxidizing environment, and transform some of the Fe2-plus ions into Fe3-plus ions.

If you get the ratio correctly, then you can actually get seemingly colorless glass materials by essentially balancing the absorption at the two different wavelengths. Again, it doesn't work if you have high-end optical instruments. Because when you're doing that, you're actually introducing S-S absorption. You're not getting rid of absorption, but it works quite well if it's just for aesthetics, just to get it perfectly colorless. That's what you would do.

This is one case you may not want the color. When you actually want the color, these are some examples where you can get all kinds of colorings there. Cobalt blue, this is a very well-known glass formulation to get blue colors. Chromium, again gives you this very highly saturated green color. Manganese, it's called amethyst, manganese amethyst, basically a purple color.

Now this last example here, uranium. Uranium doping gives you this kind of a light yellowish color that looks similar to Vaseline. That's why they also call it Vaseline glass. They are also unique in that if you expose them to sunlight for some time and then you move them and actually illuminate them with UV, you just directly illuminate with UV, in a dark room, they're going to glow.

You get this very nice green fluorescence. Now, these uranium glasses, they're actually pretty popular starting from 19th century for quite a while, for several decades. And then starting in late 1930s, they basically disappeared from commercial markets. You want to guess why?

AUDIENCE: Radiation.

AUDIENCE: Because they're made of uranium.

JUEJUN HU: Sorry, what was that again?

AUDIENCE: Radiation.

JUEJUN HU: Radiation, OK. Sort of. Turns out the uranium contained in these glasses is pretty low. It's at most, a couple percent. So it's not really that much of a health hazard. The radiation is actually pretty low. You can detect the radiation if you have a high-sensitivity Geiger counter, but it doesn't really cause a lot of harm unless you sleep with it and stay with it all the time.

So they are, in general, considered safe. The reason they disappear from commercial market is because towards the end of 1930s, you have what? Manhattan Project. So the government essentially confiscated. They essentially have a monopoly on all uranium supplies because they want to make atomic bombs. So in fact, that's why.

AUDIENCE: For the bombs!

JUEJUN HU: We want these glasses, not bombs. In the 1950s after the Second World War, there was actually a short period where they actually restored the supply of uranium glasses. But it quickly, again disappears because the Cold War begins. And then again, they want to make more bombs. So if you ever get a chance to get your hands on one of these Vaseline glass, keep it. They tend to be quite pricey because there is no stable supply nowadays.

AUDIENCE: What if we contact course 22?

JUEJUN HU: Ask them for uranium? Good idea.

AUDIENCE: Course 22 in glass lab to make and sell.

JUEJUN HU: You need to convince MIT EHS that you are playing around with the uranium in the glass lab. You're not doing something that's more dangerous than that.

AUDIENCE: So once the uranium's in the glass, it's stable in there?

JUEJUN HU: 23, obviously. This is going to be like, yeah. It contains a little isotope of 354, obviously. You don't need a lot of uranium. Just a little bit uranium, like 1%, a couple percent will bring you this very nice. That's all you need. That's all you need. Not a lot. You don't want a lot anyway.

AUDIENCE: The cup.

JUEJUN HU: Oh, right, the cup. You've seen that before. Well, scattering. This is the second mechanism to introduce color. There, we are looking into essentially wavelength-dependent scattering. There are two kinds of scattering mechanisms. You can just introduce a scattering simply by putting in some nanocrystals.

And that kind of scattering basically is Rayleigh scattering. Rayleigh scattering tends to be pretty featureless. We said that scattering intensity scales with wavelength to the negative 4th power. So it monotonically decreases as you go to longer wavelength. So for those glass materials that contains just a simple dielectric scattering centers like nanocrystals, they tend to be so-called opalescent.

An opalescent glass has this kind of unique behavior here. This is what's shown here. Basically, what it's doing here, you have a piece of opalescent glass. You put it on the edge of this white paper. You notice the different colors on two sides. On this side where there's essentially nothing at the bottom, it's just a dark background, the color you're seeing here kind of scatters light.

Those are the essentially backscattered light due to the nanocrystals. And for those backscattered light, you get more stronger scattering at shorter wavelength. And that's why it appears blue. Same mechanism as why the sky is blue. On the other hand, if you look at the transmitted color, you can see the transmitted light spot here. It has this very intense amber.

It has this amber color because all the short wavelength component preferentially gets scattered. So what's left behind is this long wavelength component. That's why it appears orange or amber. Now if you look at it against the background here, it looks yellowish because this white background reflects most of the transmitted orange light. There's also a little bit of a blue scatter light, but not completely because the blue scatter light essentially gets scattered in all directions.

So only some of that essentially comes back. So you get a much stronger component of amber with a minor component of blue, which is what gives you a yellow here. So this is also quite a common characteristic for color formation through scattering. If you look at it through different kinds of illumination modes at different angles, you tend to get different color, basically, because of this kind of a unique attribute of scattering there.

Now, that's for opalescent glass. Downside about opalescent glass is that because again, Rayleigh scattering is just depend on lambda to negative 4th power. There's not much you can do about it. So you really cannot very actively try to change it to generate different colors. If you want to generate different colors, you want to introduce scattering mechanisms, they are a lot more sensitive to wavelength.

So that's why people are using metal nanoparticles, because they support so-called a plasmon resonance. I assume you have learned a little bit of that in 3033. You probably did the experiment trying to measure metal nanoparticle solutions. Is that the experiment still there? No? It used to be there. You have to measure essentially like colloidal solutions of metallic nanoparticles. They do have this kind of very intense color. Yes?

AUDIENCE: Maybe, but it hasn't been since.

JUEJUN HU: Whatever.

AUDIENCE: We talked about it.

JUEJUN HU: Bottom line, if you have little metallic nanoparticles, you have lots of free electrons, radiation comes in, electromagnetic field is going to drive the electron oscillation in the metallic nanoparticles. So as a result, you separate the center of mass between the positive and negative charges. And this kind of oscillation can actually be amplified if the size of the nanoparticle and the wavelength of the incident radiation has some specific values.

That's called a local surface plasmonic resonance, LSPR. LSPR. Bottom line, because it's a resonance, it means that this kind of scattering is enhanced at one particular wavelength. And you can tune that resonance wavelength by changing the composition of metal nanoparticle, change the size, change the shape. So there are lots of knobs you can use to essentially tune the wavelength-dependent scattering behavior.

And this is a lot more useful for coloring of glass materials, because now, as I said, you have many, many additional knobs that you can use to engineer color. This is also something that people have known for thousands of years. As I said, you probably have seen this picture many, many times. This is one example, people like to cite to prove that people are already using nanotechnology, despite that they have no idea what nanotechnology is.

This is from ancient Roman times, Lycurgus cup. They have this kind of unique color because of metallic nanoparticles. And you also see that the color actually depends on illumination. So if you look at it from the outside, you're looking at essentially scattered light. That's why it appears green.

But if you have essentially a light source put it inside, you look at the transmitted color, it becomes pink and red. Because again you see the complementary color. The scattered color mostly gets diverted. You're looking at only the light that's less scattered. That's why you have different colors there.

But even until today, addition of metallic nanoparticles is still a very prevalent technique for people to generate color in glass materials. In fact, the process they tend to use is called the striking color or color striking. It's just a terminology that you use to describe a group of glasses where you have to heat them up, go through some kind of heat treatment to generate, to reveal the real color.

So the specific chemistry and the recipe that people use for color striking usually is proprietary. You can buy different kind of striking colors from online catalogs like glass vendors, but they will not tell you how they actually make it. And of course, you don't know what the underlying mechanism is. A few ones that people know very well, for example, this one, gold-ruby striking. This is a standard one that people want to use to essentially generate this kind of very intense, highly saturated red color.

The mechanism behind it is in the untreated glass. So in unannealed glass, gold exists in the form of ion. If it exists in the form of gold ion, then it's perfectly transparent, so it's colorless. But if you heat it up, you anneal it, then you actually reduce this gold ion into gold nanoparticles. They start to essentially precipitate out from the glass matrix. And then it goes through this process of nucleation and growth.

So by controlling the annealing temperature and duration, you can basically control the size of these metallic nanoparticles. It's classical kinetics, nucleation growth, Ostwald ripening. That's what all takes place during this firing process. But then gold nanoparticles, they can generate this kind of very intense red color after firing. So that's how you actually get a striking color in this case.

Again, as I said, there are many other kind of striking color examples. You can actually buy them from online catalog. If you burn it with a butane torch, which I have done at home, you can actually generate different kinds of colors. Interesting exercise.

So up to this point, we have been talking about static color. If you generate one color, it's basically fixed for the lifetime of the glass material. You can also control dynamic color generation through so-called photochromic or electrochromic glasses. So essentially, photochromic, it means that if you illuminate the glass material with light, typically UV, they can actually change the color.

Same thing, electrochromic, it means that you actually apply electric voltage across the glass material. You can actually change the color appearance. For photochromic, the chemistry can be pretty simple. Usually, most commonly, what people do is they add a silver chloride into glass materials during the batching process. Now, silver chloride, normally is basically silver ion.

But under UV illumination, they can transform into silver nanoparticles, which then generates color. There are commercial products you can buy, those kind of sunglasses, they're sensitive to sunlight. Essentially, when you generate silver nanoparticles, they start to absorb sunlight and reduce the transparency of the material. So that's one way of doing it.

If you are not using it in organic glass as a matrix, a lot of those kind of color-changing sunglasses, they are now made of polycarbonate, which is basically a polymer. In that case, they use actually photosensitive organic molecule to introduce similar transitions. So it's not silver anymore, but mechanism is similar. So both are still being used depending on which vendor you go to. But that's a photochromic color generation mechanism.

For electrochromic, you probably have seen those kind of windows if you sit in a Boeing 787 Dreamliner, instead of having the window shades, you have a little button underneath it where you can press and change the transparency. That's basically electrochromic glasses. Again, there are multiple mechanisms of electrochromic glasses.

What they are using specifically for the Dreamliner, they actually use an organic molecule. By essentially oxidizing it and reducing it, essentially pumping ions into it, you can actually change the transparency of the material and therefore change the color basically. So that's one example how you can actually introduce color change in glass materials.

I will show you another example here. For this example, it's entirely inorganic components. And what they have demonstrated in this study is that they were able to generate not just two states, like opaque transmissive states, they were able to actually generate three different states to give more functionalities. So in the component, the glass consists of basically two transparent electrodes, sandwiched in between them, there's electrolytes with an ion reservoir that contains a lot of lithium ion.

And the glass also contains niobium oxide as one of the matrix materials. So when you start to apply a bias across these two electrolytes, initially, you generate lots of free electrons. You inject lots of free electrons into the nanocrystals. So once you put a lot of free electrons into the crystals, you then start introducing free carrier absorption.

And for free carrier absorption, its absorption coefficient increases as you go to a longer wavelength. So it means that in this particular state, initially, when there is no voltage, it's basically a transparent glass. It allows all the radiation to get through. But then when you go to this electron-injected state, because of the presence of free carrier absorption, the longer wavelength components get preferentially absorbed.

So it means that the infrared radiation tends to get absorbed versus the visible part of the spectrum. So in this mode here, this is what they call cool mode. This is what you may want to use, for example, during daytime in the summer day. You still want the visible light to transmit through for illumination.

But for the infrared radiation, you want to reject it to keep the room cool. So this is what you use here. This is still a visibly transparent state, but free carrier absorption selectively absorb infrared radiation. Finally, if you continue to increase the voltage, then you lead to the motion of the lithium ions here. And then this actually changes the structure of the glass network.

So through this kind of redox reaction, you form this kind of lithium niobium oxide crystals, which has a brown-gray color. So this then turns the color into essentially something opaque. So then this will allow you to block both infrared radiation and also the invisible radiation. So this is what they call the dark mode here.

So this slide, this is actually a little photo showing the actual operation of glass. You can see that right-hand side here, this is actually where it's perfectly transparent. In the middle here, this is where you have this kind of a cool mode. You see a little bit of tint but not too much. Most of the visible light still gets through. And then right here, this is the cool mode where essentially it becomes a lot darker.

So there are lots of interesting things you can do. This has been an area of research that people have been doing for a few decades, essentially looking at all kinds of different chemistries where you can modulate the optical properties of these glass materials. So I'm looking forward to hearing more from your course project about that.

So now just to summarize what we've talked about here, bottom line, there are three important optical attributes we have discussed about-- refraction, loss or attenuation, and coloring. For refraction, you need to know what's the microscopic mechanism, electronic and atomic polarization.

You need to understand the wavelength dependence of the refractive index due to the KK relation. And then for loss, we talk about four different loss mechanisms. And coloring essentially is just how you actually engineer the wavelength dependence of optical loss in glass materials in order to generate different colors.

All right? Any more questions about this before we conclude this lecture here? In the next lecture, we're going to talk about the application side. We are going to discuss about how you can use glass materials as the optical fibers and waveguides to transmit light. All right. Thank you.