[SQUEAKING]

[RUSTLING]

[CLICKING]

JUEJUN HU: All right, so let's pick up from where we left in the last lecture. So in the last lecture, I actually showed you this plot here. One key takeaway message I want to mention is that, for any amorphous material, its property critically depends on its history, processing history, in particular, thermal history. It's pretty clear, you can see from this diagram here, if you cool down glass from the same melt, even the same composition, if you cool down at different cooling rates, you get completely different properties.

So this is a quite universal trait for different kind of amorphous materials. So if you go to conferences, for example, you hear people reporting some great properties about amorphous material. You now only want to put down the composition. You also need to make sure to talk to the author, get all the details about how this material is getting processed if you want to really duplicate everything the author is getting. So that's one important message we want to keep in mind, history dependence of the properties of amorphous materials.

So now, in this slide here, I'm basically summarizing the different states of matter that we have talked about here. We obviously have liquids. And liquids, because all the atoms do not have a fixed geometric position, they can move around. There's no crystalline lattice whatsoever. So that's why they don't have a well-defined shape.

We also have crystals, where the atoms are arranged in a lattice. They exhibit both short-range order and long-range order. Finally, we have glass, which sits somewhere in between. You get short-range order, but you don't have the long-range order. The different lines here essentially connects these different state of matter together.

Between crystal and liquid, obviously, there's traditional melting and solidification. For glass, you can go from liquid to glass by the melt-quenching process. So the melt-quenching essentially describes this process we talk about. You start from a supercooled liquid. You quickly cool it down, suppress crystallization, and you get amorphous state. That's called the melt-quench process.

You can also start from glass. You heat it up, and then you go to liquid. So that process is often called softening. And the reason it's called softening is because glass is a rigid metal at room temperature, typically. But as you heat it up, it eventually transformed into this viscous fluid, supercooled liquid. So, radiologically, it shows itself, essentially, as the material is actually softening. That's why it's often called softening.

Now, between the glass and crystal, you can always go from glass crystal by essentially just heat it up. You heat up the material, you get more kinetic energy to the atoms. Eventually, they're going to find the thermodynamically stable state, which is a crystalline state. The temperature that we use to crystallize, this is usually called crystallization temperature. And it's customary in the glass community. People label it as Tx.

It gives you the temperature you need to crystallize the glass material for some fixed duration of time that you will need. I want to mention that this Tx, unlike Tf, this is very much an empirical parameter. It depends on lots of factors, how you process your glass thermal history. It depends on how long you actually anneal. It may also depend on a specific annealing technique as well.

So that's why, even for the same glass composition, you may see quite different Tx here, depending on who actually report it. So just keep in mind, this is just empirical parameter to gauge how stable the glass is against crystallization. Now, finally, you can also go from crystal back to glass directly. You can always amortize the material by essentially first melting it and then melt-quench it. So then you actually get glass.

What you can also do, you can directly go to an amorphization or so-called vitrification process. And what you will do there is you typically introduce some energetic process that distort the lattice structure. So, for example, you can bombard a crystal using ionizing radiation. And in this case, those ionizing radiation has enough energy, it's going to knock the atoms out of the original lattice position, which then create crystalline defects.

If you let that process go on and on, eventually, the defects pileup. You can actually transform a crystal into an amorphous structure. So that's, essentially, a radiation-induced amorphization. You can also do a mechanical amorphization. So you can induce plastic deformation in a material. And when you do that, based on what you have learned, if you do plastic deformation, you actually have dislocated motion. You generate defects, essentially.

So if you repeat that process-- it goes through very large deformation-- you can also transform from a crystalline state directly to amorphous state. And you can do that by, for example just doing more milling. You can do mechanical alloying. With large deformation, you can actually create directly amorphous materials that way without having to go through a melting state.

All right, so for this slide, there's one last thing I want to mention here. For liquid, I have listed here that the bonding constraint relaxes as temperature rises. So what does that mean? I need to first explain bonding constraints. So when we are talking about bonding constraints, there are two types of bonding constraints here.

If you think about chemical bond, it essentially defines a specific bond length that gives you the spacing between the two atoms that form a chemical bond. So from a topological perspective, this gives you, essentially, a geometric constraint. The atoms cannot randomly populate in space. They have to satisfy certain spacing between them. So this is called the bond length constraint, the bond length.

This is one type of constraint coming from chemical bonds. You can also have bond angle constraint. And this happens, for example, if you think about silica. In silica, the basic structural unit is this Si tetrahedra. And we know that in this structure, we actually have two bond angles. You have this oxygen, silicon, oxygen bond angle, which is, of course, 109 degrees. This is [INAUDIBLE] tetrahedra.

You also have another bond angle. This is when one tetrahedra connect to the other. This bond angle, silicon, oxygen silicon, for crystalline, SiO_2, this bond goes 144 degrees. Now, this bond angle in a crystalline structure also specifies relative geometric position of the atoms. So there's also some topological constraints you place on the position of the atoms.

Now, what we are trying to argue here is that, if you go to high temperature, you go to liquid state, because all the atoms can now start to move around-- you have a lot more kinetic energy-- some of these constraints start to get relaxed. So bond length, you can have small variation of the bond length. But predominantly, the bond angle is getting compromised. You don't have to limit to these very specific bond angle values. There can be variations or dispersions of the bond angle in the liquid state.

So just to show you one example in the next slide, what I'm plotting here is actually the bond angle inside, essentially, a melt silica specifically for this silicon, oxygen, silicate molecule, so this one we're looking at here So this is measured by X-ray diffraction in, essentially, silica glass. But the idea here is that, in the liquid state, if you cool down sufficiently fast, you won't give enough time for the atoms to move around.

So the resulting amorphous structure captures a lot of structural features in the liquid state. And this kind of dispersion of bond angle is something that you actually inherit, the glass inherit, from the liquid state. So, clearly, you can see here that, for this bond angle, silicon, oxygen, silicon, you now have a pretty wide distribution here around the average value, which is 144 degrees.

Now, this applies only to this bond angle here, silicon, oxygen, silicon. The other one, you also have oxygen, silicon, oxygen. So for this one, this is the bond angle within the tetrahedra. The tetrahedra itself is actually pretty rigid. So even if you raise the temperature, this angle still pretty much stays constant, still about 109 degrees. What's changing is the essential interconnection between the different tetrahedras. So, essentially, you can imagine tetrahedras, they can actually sort of bend and distort with respect to each other.

Now, this is actually something that's quite important because it means that the topological structure of the network can be modified by temperature. Later on, we are going to see that this actually affects the stability of the glass, how stable this network is, because we're changing the network topology. So just keep that in mind for now. If you go to high temperature, some of the constraints can actually get relaxed.

All right, another point I also want to make here is that we have been talking about glass structure, essentially, in a very qualitative manner. We also want to introduce some parameters that allow us to quantitatively describe the glass structure. So we will be talking about, essentially, this pair distribution function here.

Before we go to that, I just want to make the statement that, any kind of structural description of amorphous solids or glasses, they are always statistical in nature. And that makes sense because, if you think about amorphous structure, if you zoom in to one location versus the other, there's always slight differences from one location to the other.

So when you're talking about any of these kind of macroscopic parameters to characterize glass structure, you are always doing ensemble average across the entire bulk material, across different locations. All right, so with that in mind, now let's look at, basically, this ensembled, averaged, parameter called pair distribution function.

So pair distribution function, g, to introduce that, let's first introduce this parameter here, rho, which basically is the average atomic density in amorphous solid. And g, we are essentially characterizing the number density of atoms. You first start out by defining an origin. You have one atom sitting at origin. And we now start to look at how the number density of atoms varies as you move away from that center atom.

g is defined, basically, as the number density normalized by the average density over the entire solid. So g will now be a function of r, where r gives you the spacing of the point where you're actually measuring density with respect to the origin atom. So we can start by taking a look at some general trends for this PDF here.

So if the r reaches 0, approaches 0, it means that you're looking at the point very, very close to your center atom. Now, because these atoms, you cannot place two atoms exactly at the same location, what that means is that, when r approach 0, the probability of finding another atom exactly sitting at the same location is basically 0. So that's why, when r approach 0, the g should also vanish.

On the other hand, if r approach infinity, you are looking at a point very, very far away from the center atom. Now, remember, we mentioned that in glass materials, you don't have this kind of long-range structure order. So if you move very far away from the center atom, essentially, what you're looking at is the average glass network structure. And you expect that now, in this case, the number density should approach the average number density of the entire glass network. And that's equivalent of saying that g should now approach unity.

So that's a general trend where this function has to follow here. Now, more specifically, I'll just give you one quick example, trying to compare this g in a crystalline solid versus in an amorphous solid. So in a crystalline solid, if you assume it's an ideal single crystal without any defects, and we approximate, essentially, all the atoms as a half sphere, so you can characterize that location using essentially one single coordinates, well-defined coordinate.

Then the g function should basically be a set of delta functions, where each peak correspond to, essentially, some neighbors, with respect to the center atom. So, for example, the first peak, this would represent that you actually find some atoms at this distance with respect to center atom. And this would be the atom that's closest to center atom. So this would be the nearest neighbors. This one would then correspond to the atoms. That would be the second nearest neighbor. This is the third nearest neighbor and so on and so forth.

So every time you have one shell atom coming up, you have, essentially, one delta function. For amorphous structure, the g carries similar characteristics as the crystalline counterpart. You also see peaks corresponding to each of the delta function there. But first thing is that you see the peak getting broadened a little bit. This is basically a slight change of bond length inside the material, especially for the first one. This first peak essentially indicates that the chemical bond length is varying slightly.

Now, as you move further and further, you see the peaks start to broaden even more. And that's because you are essentially losing this kind of a long-range order. As you move further and further away, the specific location of the atoms becomes less well-defined. So you expect to see the peak start to broaden.

And, eventually, this function is then going to approach unity, where all the peak gets smeared out. That's when you completely lose any kind of short-range order. And you essentially-- what you're seeing there is just an average structure of the network. Any questions? Does that make sense? So later on, we are going to also talk a little bit about, quantitatively, how you actually measure this kind of a PDF function and correlate it with diffraction data.

All right, this slide, you really don't need to put down any notes here. I'm just basically saying that, besides PDF, there are a bunch of other functions that are variants of PDF, that people also use in literature to characterize the glass structure. But they are all, more or less, trivially connected to a PDF. All right, so now let me just quickly summarize, essentially, this first chapter here about the general amorphous states. Some of the key points I want to mention is you need to understand the definition of amorphous solid versus glasses.

For amorphous solid, you need to have, essentially, a metastable structure. You need to have long-range structure order. For glasses, there's an additional definition there. You also need to exhibit this glass transition. Now, glass transition, we're referring to this smooth curve. When you cool down a supercooled liquid, it gradually transforms into this different structure here that we call glass. It's important to recognize that, glasses, they are not a collection of very small crystals. They are also structurally different fundamentally from the supercooled liquid.

So we will go into more details about the nature of glassy state and the nature of the glass transition later. We also just also want to mention here is that, unlike crystalline material, where everything is in equilibrium, if you do things slowly, you always have a reversible process. For glasses, cool down and reheating up, they usually do not retrace each other. You actually get two different curves. And they also depend on the specific processing condition. Different cooling rate, different heating rate give you, essentially, different process dependence.

All right, so now, before I move on to the next section about different glass families, I just want to show you that this concept of crystalline versus amorphous does not only exist in solid matter. It also exist in urban planning. So this is what I would call a crystalline city. In fact, if you look very closely, somewhere in the Grand Central Station, you actually see a little edge dislocation there. You can go and define the Burgers vector on the Google Map if you want. And then what about amorphous city?

AUDIENCE: [INAUDIBLE]

JUEJUN HU: Yes, as a driver, I can attest to the annoyance, actually driving in Boston streets. And this is amorphous. So we all live in amorphous city. All right, any more questions about the first part there? All good? So now, in this second part here, what I will do is I will give you a little bit overview about the different classes of amorphous materials we will be discussing throughout the semester.

I will start by introducing the concept here about network performance, modified intermediates. These are the concepts that relate to, essentially, inorganic network glasses. Again, metallic glasses, they are sort of a special family. They have different ways to actually characterize structures. We'll go through that later on in the semester.

But for now this applies to things like oxide glasses, chalcogenide glasses, halide glasses, essentially, inorganic glasses bound together through covalent bonds. Now, these network formers and modifiers essentially refers to the constituent atoms inside the glass. The network formers are the ones that actually form the backbone of the glass network. This would be ones like, for example, silicon. If you think about silica glass, SiO_2, silicon would then link with, essentially, oxygen atoms. And, eventually, they will interlink together-- this tetrahedral interlink together-- to form a three-dimensional network.

So in this case, silicon is basically a network former for this silica glass. Now, what about network modifiers? Network modifiers are the ones that essentially enter the glass network and actually disrupt the glass network. So they typically are some of these metal ions. So one example here, let's think about, for example, sodium. What happens if you're adding sodium oxide into a silica glass?

So significantly, what I'm plotting here, this is a flattened version of a two SiO_2 tetrahedra interlinked with each other through this oxygen atom. So in this case here, these two oxygen tetrahedra, they basically share one corner. So this is called corner-sharing tetrahedra, in this case. If you add the sodium in there, now the sodium is going to actually break up this silicon oxygen chemical bond. Instead, you essentially break this connection between these two tetrahedra there. And you form, essentially, an oxygen ion that's electrostatically attracted to the sodium ion. Yes?

AUDIENCE: What would you consider the oxygen as, a former, modifier, or intermediate?

JUEJUN HU: Ah, great question. So the question is about, how do you classify oxygen? This theory is really the only classification people derive from oxide glasses. So they essentially treat oxygen as just one ingredient in the oxide glasses. It's not classified as network former or modifiers. It's just part of the network.

AUDIENCE: So if you were to do metallic glass, then since it would be oxygen, then--

JUEJUN HU: The whole thing breaks down.

AUDIENCE: [LAUGHS]

JUEJUN HU: As I said, this really only applies for oxide glasses, maybe chalcogenide, which would replace oxygen with sulfur and selenium. For metallic glasses, the concept is different. They are talking about clusters, actually. It's like how you actually pack the meta atom together tightly into different kinds of clusters. And then we are going to talk about, that you essentially have center atoms and then the surrounding atoms, and how they fulfill different topological roles, so you can actually get tight-packing structures. So completely different theory, basically. So this part here is only for inorganic network glasses. I just want to emphasize that. Does that answer your question?

AUDIENCE: Yes.

JUEJUN HU: All right, so now, talking about oxygen, I'm going to talk a bit more about oxygen. So this kind of oxygen, when oxygen link together two tetrahedra-- or more generally, two polyhedra-- this is called bridging oxygen because it's like a bridge that connects two network formers. If you have oxygen, like what you have here, it only links to one of the network formers. And the other end is actually, essentially, hanging. This is called non-bridging oxygen, NBO.

So, basically, if you put in things like sodium, each sodium ion creates one non-bridging oxygen. The net effect is, initially, you have a very tightly connected three-dimensional network in silica. But now, once you put sodium in there, you start to break up these connections. So you decrease the connectivity of the network. This is a very important terminology I'm going to refer to many, many times in the lecture, connectivity, is how tightly these different tetrahedra or polyhedra are linked together with each other.

If you have a lot of these kind of broken connections, then we say that this is not very well-connected network. It has a poor connectivity. And as you'll see, they have very significant impact on the properties of the glass. So simply put, network formers, these are the atoms that make good friends with other atoms. They can essentially form the backbone network. Network modifiers, they are loners. They get in there, break the connections, essentially create a much less connected network.

You can also have what's in between. These are called intermediates. And intermediates, they can sometimes become network former, sometimes become a network modifier, depending on specific chemistry. All right, now, if you look at the periodic table, let's take a look at where this different network formers and modifiers sits in the periodic table.

You immediately notice here, I use different color code to actually code different kind of atoms here. So you notice that these different kind of modifier and formers, they all cluster in specific regions in the periodic table. The network formers, they tend to be these non-metallic atoms that has a relatively high-valence state. Typically, they have a lot of outer shell electrons. Whereas, the network modifiers, these tend to have a low-valence state and they tend to be metals.

Now, this actually makes a lot of sense. If you think about what network formers does, you need to essentially form a polyhedra of oxygen around these network formers. And then they have to be able to link with each other to form 3D network. So in order to form a 3D network, the valence state of these network formers should be at least two.

If you have a two-fold-coordinated atom, you start to try to train them together. The best you can do is typically a long 2D train. If you own the 3D network, you also want to do some kind of interconnection between them. So, usually, you will essentially want something with a valence state greater than 2, so you can form a 3D network. And that's what these non-metal atoms does.

Now, the other thing is that this these non-metal atoms, they tend to form covalent bonds with oxygen. So for inorganic network glasses, it's really important to have covalent bonds because, unlike ionic bonds or metallic bonds, covalent bonds are? Directional. They have fixed orientation. Being directional means that there's actually a lot of space between the different atoms. Typically, covalent solids, they're never close packed. From simple crystallography, you know that.

So if they're not close packed, there's lots of space in between atoms. It means that you can easily accommodate geometric distortion. All the atoms and chemical bonds, they have a lot of wiggle room. They can distort. They can change the bond angle without causing a lot of energy penalty. And that's really important for amorphous network because we want to introduce a structure disorder. If you can do that without raising the overall Gibbs-free energy of the system too much, then you get a stable glass. So that's why you want to have these kind of non-metal atoms, essentially, as network formers.

Now, network modifiers, obviously, these are the ones that actually form metallic bonds. So they will be attracted to the oxygen atoms, just via electrostatic force, which is, of course, a lot weaker compared to covalent bonds. And that's why you also decrease the network connectivity. Also, because they're a low-valence state, that essentially decreases topological connection between different clusters. So that's what they do.

All right, so now, let's essentially take a look at a few examples of the glass systems that we'll be dealing with later on in the semester, starting with, I will call almost a model of glass silica, SiO_2. It's the basis for any kind of silicate glasses. So for SiO_2, if you look at the crystalline structure, what I'm showing you here is just a pancake 2D version of the crystalline structure of cristobalite, which is one of, essentially, the structural variants of crystalline SiO_2.

If you look at it, same thing. Basic structural unit is you have, essentially, one silicon for oxygen around it to form this tetrahedra that interlink together to form 3D network. One thing I want to highlight here is that you look at what's called the ring structure. You look at, essentially, these rings here, closed loop atomic structures. These are called rings.

In a crystalline silica, all the rings are so-called six-membered rings. It means, if you start to count the number of silicon atoms on the ring, it's always six in each of the ring structures. If you go to amorphous silica, on the other hand, you start to find out that you can get other kind of ring sizes. You may get seven-membered rings. You can get five-membered rings, even three-membered rings.

These ring statistics is quite important structure aspect of amorphous materials. People can actually use it as a way to probe the structure of this network there. You can accommodate this different kind of a local structure variance here by varying the bond angle of, essentially, this SiO Si bond. This is the bond angle that changes to accommodate structural variations there.

Despite this kind of structure distortion, in a silica glass, you still have a fairly tightly connected 3D network. All of the oxygen in a silica glass is bridging oxygen. All oxygen atoms always connect to two silica, so they are always bridging oxygen. There's no non-bridging oxygens in silica glass. So this very high-network connectivity means that you have a very rigid and very strong network that does not easily default.

So this dictates many important properties of silica glass. They have a very high-softening point. Atoms doesn't really move until very high temperature. They have low-diffusion coefficient because it's quite tightly packed. You don't have lots of room for small atoms to come squeeze through. You have small coefficient of thermal expansion. Let me talk about that a little bit.

So for coefficient of thermal expansion, in your solid state physics class, you probably talk about, discuss-- well, did you know about origin of thermal expansion? You talk about it in solid state physics class? I can quickly cover it. No worries. So if you think about interatomic interaction potential, so this would be-- for example, this is energy, u. And then this is basically the spacing between atoms, this-- what letter do you like?

AUDIENCE: y.

JUEJUN HU: Ah, OK good. Great.

[CHUCKLING]

So then you would, essentially, have this kind of function there, for example, where the minimum indicates this is the optimum spacing between the two atoms. Or this will give you equilibrium position. You will have a-- if you are at, say, 0 Kelvin, then the atom will sit right at the bottom of the potential well there. You have a well-defined structure there.

As you start rising temperature, essentially, your network starts to get more energy. It means that you actually can now access higher energy levels in this potential well. So if you have an-- in an idealized scenario, this potential well, you can approximate it as like a parabola. So it's symmetric. If it's symmetric, even if you access these high-energy levels, the statistical average of the spacing will still be right in the center. So there's no thermal expansion.

However, this kind of energy curve typically is not symmetric. There's a little bit of so-called anharmonicity that's always getting introduced. In fact, usually, the curve will look more like this because you just simply cannot squeeze two atoms very close to each other. There's always a very strong repulsion force. But if you try to pull them away, the interaction actually weakens a little bit. So that's why it's a bit softer along this arm.

So now, if you heat it up, you start to access the higher energy levels. You find that the average position of your spacing will now get shifted to the right side. So what you are actually getting here is essentially like this. So as you go to higher, higher temperature, essentially, you start to get longer average spacing between the atoms. And that's why you have thermal expansion. Does that make sense? Now, what happens if you have a silica, for example, which have very strong chemical bonds? What does strong chemical bond do? You will have a--

AUDIENCE: It makes the walls really steep.

JUEJUN HU: You have like this, like that. So if it's really steep, it means that, of course, this variation is going to be pretty small. You don't get lots of thermal expansion versus, if you have some other glasses with softer bonds, you open up, then you have a large thermal expansion. So that's why, typically, if you have strong chemical bones, you tend to have a low coefficient of thermal expansion in a covalent solid. Polymers are a different animal.

And that's why silica, silica as a coefficient of thermal expansion is actually remarkably small. It's like 0.5 PPM per Kelvin. So it means that it expands 10 to the minus 7 in length per degree Celsius, which is really, really small. Now, to give you a comparison, if you think about window pane glasses-- these are soda lime glasses-- the typical coefficient of thermal expansion is like 10 PPM. So it's 20 times higher than silica.

Why is that important? Silica can be very good, for example, if you want something with very good thermal shock resistance, like if you have-- just say you have kitchenware. You want to remove it from the stove, immediately put it on a cold surface. Then you get a large temperature gradient. If you have a high-thermal coefficient of thermal expansion, it means that different regions of different temperature have different volume, essentially. So they build up very high stress, eventually cracks.

If you have a container made out of silica, nothing's going to happen. We're actually going to do a little demo, show you that silica is very, very, very resistant to any kind of thermal shock. Downside, why you are not using kitchenware made out of silica? Silica has a very high softening point. It means it's actually very difficult to process silica compared to other soda lime glasses. You need a furnaces that can go up to 2,000 degrees Celsius, which is why people are not using it.

So what do people do? If you want something that's a lot more easy to process, you have to add some network modifiers, which we're going to talk about in a second. Now, before I go to that, I just also want to mention one very peculiar thing about silica glasses. It's called volume anomaly. So for now, look at this plot. This is basically volume as a function of temperature, similar to what I showed you in the previous lecture.

Forget about everything on the left-hand side. Only focus on this one here. So if you look at only this part here, it looks actually quite normal. It's basically supercooled liquid. And if we're cooling it down, then at some point, you're going to go deviate from the supercooled liquid and then go to the glass line. That makes sense.

What's weird about silica is that if you-- at some temperature range, its thermal expansion coefficient is actually negative. So as you cool it down, it expands. That's why you see the curve actually goes back up. So if it goes back up, the glass line also will deviate from this curve there. Same thing, if you cool down faster, you will deviate from the supercooled liquid line earlier.

If you cool down slower, then it actually traces this supercooled liquid line for a longer period of time until it go to the glass line. But the consequence of that is that, in some region-- in some temperature regime, slow-cooled silica actually has a volume larger than fast-cooled silica. This is opposite to most glasses. Yes?

AUDIENCE: Do you know why?

JUEJUN HU: Great question. To be honest, I don't have an immediate answer here. People actually have done lots of, essentially, simulation studies. You can look into how to explore the glass structure, silica glass structure, and why it has this kind of negative coefficient of expansion. That's actually beyond my immediate knowledge. But I can refer you to some papers if you're interested about why they have this kind of weird behavior, yeah.

AUDIENCE: So is the main curve your supercooling?

JUEJUN HU: This curve, this line, is basically how the volume of the supercooled liquid changes as a function of temperature.

AUDIENCE: So that's the liquid.

JUEJUN HU: So this is a supercooled liquid, this line. Now, each of this little branch is the glass line that eventually deviates from supercooled liquid line, where you have different cooling rates. Yeah, so this is a fast cooling, slower, even slower, even slower. Yeah?

AUDIENCE: So, essentially, if you want to minimize the volume, you have to-- yeah, [INAUDIBLE].

JUEJUN HU: Yeah, you can do that with silicon. Yeah, so that's why. In the last lecture, I was saying that the pro I showed you in the previous class, that's universal, which is enthalpy. Slow cooling always gives you a low enthalpy. But volume, not always. Usually, slow cooling gives you smaller volume, but not always because of silica.

AUDIENCE: So, presumably, it's like-- I guess, how do you prevent solidification at the higher temperatures if you, for some reason, wanted to explore?

JUEJUN HU: Like here.

AUDIENCE: Yeah, cooling.

JUEJUN HU: Cooling rate. Let's make it a knob you turn. The faster you cool, the-- essentially, if you cool down faster, you don't allow nearly as much time for the atoms to rearrange themselves and find a more stable structure. The supercooled liquid is the more stable structure that the glass is trying to relax to. So if you do cool down faster, you don't get the opportunity to actually relax to this line here. It has to deviate and go to the glass line.

AUDIENCE: So it has to be fast enough cooling not to crystallize, but slow enough cooling to cool it.

JUEJUN HU: Exactly, yeah. But for silica, practically, it will never crystallize it. It's like, the cooling rate you need to actually crystallize it, it's like 10 to the minus 10 degrees Celsius per second. Impossible. In fact, later on, I'm going to show you one example in large telescope mirrors. People take years to cool on, just so you don't develop any stress uniformly in the kind of large optical mirrors. Again, they don't crystallize. So there are some glasses that are really very, very, very, very stable, yeah. Any more questions about this?

All right, now, let's take a look at how we make glass more processable by lowering the softening temperature. So the way you do it, adding network modifiers. Simple one, one example is to do alkaline atoms, like sodium. As we have already mentioned, every time you're adding one alkaline ion, you basically create one non-bridging oxygen. You break up the network, decrease the network connectivity, which means that you now start to exhibit properties exactly opposite to what you have in silica.

You have a low viscosity because atoms is a lot easier to move past each other now you don't have a tightly connected network. You have a much higher diffusion coefficient because you're creating lots of spaces now. In between the clusters, you can essentially have smaller atoms to squeeze through. So you have a higher diffusion coefficient. You also have a higher coefficient of thermal expansion because of the weaker chemical bonds.

Now, the downside, though, if you go to alkaline silicate glass, the problem is the chemical durability. So, for example, let's suppose you have sodium. Let's just look at this simple silicon. You have oxygen, sodium. This is what happens if you put sodium into a silicate glass. Now, you put water in there.

What's going to happen is that water is going to break this very weak connection between sodium and oxygen. What you end up getting is SiOH plus NaOH. Now, to make things worse, producing an NaOH essentially means that you now have a basic solution. Glasses typically dissolves in a basic solution. NaOH can actually react with SiO2. What you end up getting would be, essentially, a sodium silicate plus water. And sodium silicate is soluble in water, by the way.

So what you're seeing here is that, if you put water into an alkaline silicate glass, you get preferential leaching of the sodium atoms into the solution, which turns it basic, which then allows you to actually attack the backbone of the glass network. So that's why actual alkali silica glasses, people simply don't use it because of this reason.

There are a few ways to improve the chemical resistance of these glass materials. One common strategy is called a fire polishing or flame polishing. What you would do is you have, essentially, your glass products. After you make it, you then use fire to essentially do a heat treatment on the surface. This allows you to essentially have this sodium ion, too essentially volatile, and leave the network.

So on the surface, you get the layer of glass that's actually depleted of the sodium ions. So that way, you can essentially prevent this kind of phenomena from happening and, therefore, improve the chemical longevity of the glass material. We're going to talk a bit more about these kind of strategies, how to improve the chemical durability later.

All right, but another very interesting thing I also want to mention here is that, when you add these sodium atoms into the glass network, as I said, every sodium atom creates one non-bridging oxygen. If you keep on adding sodium atoms, you create more and more non-bridging oxygen. At some point, you have so many long-bridging oxygen there, you can no longer sustain a 3D glass network. You simply don't have enough connectivity to bring all the atoms together.

Then what happens is you go to this new regime called the invert glass. So what I'm schematically representing here, each of this little triangle is basically one SIO4 tetrahedra. Now, because you have broken so many chemical bonds, you can no longer link them together to form a continuous network. Instead, what you get is small fragments of this tetrahedra linked together.

These fragments are actually attracted to each other through electrostatic interaction with the sodium ion in between. And then, eventually, the whole thing is bound together through, essentially, van der Waals force. So this is also amorphous solid, but sort of the main bonding mechanism is actually quite different from what you get here, which is purely covalent bond, more or less.

This invert glass also exhibits a very different trend in terms of how the property evolves with the concentration of alkali ion. So for this regime here, for this initial regime, you can imagine that, if you put more alkaline, you get decreased hardness. It becomes softer. You have low-glass transition temperature. You have high-diffusion coefficient and such.

But when you go to the invert glass, because the force, the chemical force that binds everything together, is basically the interaction between the sodium ion and these tetrahedral fragments, so the more sodium ion we add in there, the stronger the connection actually becomes. So you see that the property actually starts to work, essentially, to change to evolve in opposite direction. As you put more sodium in the invert glass, the hardness actually increases. The glass transition temperature also starts to rise. Diffusion coefficient starts to drop. It's the exactly opposite trend.

So now, one very interesting exercise is to see, can we quantitatively predict, at what specific composition do we have this transition from a non-regular network glass to an invert glass? So I will show you one example, how to actually do a structured determination in this kind of alkaline silica glass. So to do that, let's introduce one parameter here, Y.

Y is what we call the average number of corners shared per SiO4 tetrahedra. So normally, in a silica glass without sodium, this number, Y, should be equal to 4 because all four corners should be connected to some other neighbor in a tetrahedra. So now, what if we start to add sodium? Let's assume we have a glass with this kind of molar competition here.

So then what we want to determine here is, what is Y? How does Y changes with x, the amount of sodium you add in there? So the way you do it is you start by looking at the total number of oxygen. Total oxygen in one mole of glass, how much oxygen do you have? So you have oxygen coming from the SiO2 layer, which is 2 minus 2x. You also have x oxygen coming from sodium oxide, which gives you 2 minus x. This is the amount of oxygen in one mole of this glass.

Next thing, we have two kinds of oxygen here. We have non-bridging oxygen. We have bridging oxygen. Let's take a look at the amount of non-bridging oxygen we have. So every time you add one sodium atom, you create one non-bridging oxygen. So the amount of non-bridging oxygen should just equal to the amount of sodium, which is the 2x.

Without bridging oxygen, well, that would be pretty straightforward. It's basically a total amount of oxygen minus non-bridging oxygen. It would be 2 minus 3x. We also notice that each bridging oxygen creates two shared corners of the tetrahedra. Why? Because each bridging oxygen is always shared between two tetrahedra. So, effectively, each bridging oxygen creates two shared corners. So the total number of shared corners, corners that are shared will be 2 times that of bridging oxygen. So it's going to be 4 minus 6x.

Last step, we can now define Y. Y, by our definition, is the number of corners shared, which is 4 minus 6x, divided by the number of tetrahedra. Each tetrahedra has one silicon sitting in the center. So the number of tetrahedra is basically the number of silicon we have, which is basically a 1 minus x.

All right, so now the next question is, what is the y value that will correspond to the onset of the transition from a network glass to invert glass? How many corners need to be shared in order to form 3D network? At least two. In fact, you have to be above two. If you only have two corners shared between each tetrahedra, you can form a non-linear shape, which is not really 3D. You need a little bit above two in order to have interconnects or cross-linking between different chains to get 3D network.

So we argue that Y equals to 2 would be the threshold going from a network glass to invert glass. You can solve that pretty straightforwardly. Basically, it will tell you that x basically equals to 0.5. And that's something people have actually verified experimentally. So what I'm plotting in this plot here, this is actually experimentally-measured viscosity inside these glass materials at different temperatures.

The horizontal axis is basically Y, as we defined. Vertical axis is the logarithm of viscosity. What you see here is that, for all the temperature ranges, you always see this kind of change of how the viscosity depends on glass condition. Y, essentially, is the glass composition. So you always see that viscosity reach a minimum right at Y equals 2.

On this side, this is, basically, you're adding more sodium from a glass. You essentially decrease network connectivity, so you have a lower viscosity. And then above this end, this is when you go to invert glass. You start to put more and more sodium atom, you actually link the network more closer together through this electrostatic interaction. And that's why you see a decrease of the viscosity there. So this is one example to show that this is a very simple geometric determination allows us to predict quantitatively, the glass property change.

All right, so I have already mentioned that people don't like alkaline silicate glass because it has poor chemical durability So one kind of a modification people have made is to-- besides alkaline, you also get alkaline earth into a glass network. So alkaline earth would be something like calcium plus 2 valence state.

If it's calcium, you put it in the network, it's still a network modifier. Each calcium creates, actually, two non-bridging oxygen because of the plus 2 valence state. So similar to alkaline silicate glasses, alkaline earth silicate glasses can also decrease the network connectivity. And you have all the similar kind of a property evolution [INAUDIBLE], but to a much lesser extent compared to alkaline silicate glass because calcium is two-fold coordinated.

So it means that you still have some connection between these two oxygen atoms through electrostatic interaction. So you break up the network, but not fully. You still maintain some connectivity there. And that's why this kind of alkaline, alkaline earth glasses, they tend to have a better chemical durability compared to just pure alkaline silicate glass.

But it also inherits the same advantage, that you don't need a very high-process temperature, such as in the case of pure silica. And that's why the everyday glasses we use, they pretty much all fall in this category, alkaline, alkaline earth silicate glass. You can strike this balance between chemical durability and processability. Yes?

AUDIENCE: Why or what's the benefit of having alkali as well as alkaline earth versus just alkaline?

JUEJUN HU: Alkaline is more effective in lowering the processing temperature.

AUDIENCE: Oh.

JUEJUN HU: Yeah, that's the idea. Yeah, and that's what actually allows people to actually utilize this glass material back from Ancient Roman times because, at that time, people were not able to reach very high temperature. And, again, the origin of where glass comes from, nobody really knows. But accidentally, I think people just mixed some of these oxides together with sand. And they found that they can actually melt sand, which, otherwise, we would not be able to do. And that transparent substance you get in the end is actually glass.

AUDIENCE: So does the oxygen-calcium-oxygen bridge create any of the lower effectivity?

JUEJUN HU: Yeah.

AUDIENCE: Is it just like an alternative to the unstable regular alkaline?

JUEJUN HU: Basically, yes. It's sort of like-- they are still connected together.

AUDIENCE: Yeah.

JUEJUN HU: It's just weaker connection. It's no longer a very strong SiO covalent bond. It's this kind of electrostatic attraction. It's weaker, but it's still connected together.

AUDIENCE: Do you can get crazier angles or something?

JUEJUN HU: Actually, you can because, again the two tetrahedra are not really connected together. This ionic interaction is electrostatic. So it's not directional. So you can actually twist it at all angles, yeah. Yes?

AUDIENCE: Well, look at the chemical formula.

JUEJUN HU: Yes.

AUDIENCE: And thinking about the 3D structure, should we think about, more or less, it's that ratio in a single area, or just like it's a ratio or--

JUEJUN HU: It's an average.

AUDIENCE: Oh.

JUEJUN HU: It's an average, yeah. If you zoom in to every location, obviously, you get fluctuations of a structure, and also a little bit of chemical composition as well, yeah. Yeah, I'm going to talk about this one. So this is the typical glass you will get. This is called soda lime glass. This guy is soda. This is a lime. So this is called soda lime glass.

Now, what's quite remarkable, you may see, this is a very weird composition. It's not any integer numbers. And what's even more remarkable is, if you go around the world, you look at glasses of different applications, whether it's windowpane glasses, whether it's container glasses. Or you go to Ancient Roman times or you go to Medieval Venetians, they more or less all converge on this composition, a few percent around their composition.

Later on, we're going to show you that this composition is actually quite remarkable. It corresponds to the most stable glass composition, specifically for this ratio I'm showing here. All right, I'm going to leave it as a little question that we're going to address later when we talk about glass stability, why you get these kind of very weird numbers there. So now I will actually try to do a little bit of demo here. I promise you that I'm going to show you that silica glasses--

AUDIENCE: Excuse me, folks.

JUEJUN HU: Yes?

AUDIENCE: [INAUDIBLE] oh. Yeah, excuse me.

JUEJUN HU: I mentioned that silica glasses has a very low-thermal expansion coefficient. So it's extremely thermal shock resistant versus other glasses, like soda lime, because of the lower network connectivity, you now have a much higher thermal expansion coefficient, about 20 times higher. So what I have here, I actually have some silica glass slides. Let me open it up. Oh. Any of you have scissors or something?

AUDIENCE: Yeah.

[LAUGHTER]

AUDIENCE: I'll take this one.

AUDIENCE: [LAUGHS]

JUEJUN HU: Just cut it open.

AUDIENCE: It's so easy [INAUDIBLE].

AUDIENCE: You can also reach for a knife.

[CHUCKLING]

This is my third one.

JUEJUN HU: There we go.

AUDIENCE: What was it? The compass? [LAUGHS] No, the caliper. This is so much--

[INTERPOSING VOICES]

AUDIENCE: Should we--

AUDIENCE: We have a good class. And Kurt was like, how was it [INAUDIBLE] caliper.

JUEJUN HU: All right, now we have it.

AUDIENCE: Four people pulled out [INAUDIBLE].

JUEJUN HU: You don't really see a difference. They look all the same. This is silica, soda lime. Let me see when the temperature gets there. So what I do, I set the hot plate to 400 degrees Celsius. I'm just going to place it here for-- you can even-- any of you want to time it? Let's be a bit more consistent. I'll put it there for 30 seconds, throw it into water, and let's see what happens. I can already smell something. I don't know what they put here.

AUDIENCE: You can see the surface is smoking.

JUEJUN HU: I just grab it from my lab. I really don't know what my student is using them for to heat it up. So I assume it's not something harmful.

AUDIENCE: [LAUGHS]

JUEJUN HU: Otherwise, EHS is going to come and chase me.

AUDIENCE: Oh, [INAUDIBLE].

AUDIENCE: No, you're the most honest woman.

AUDIENCE: [CHUCKLES]

JUEJUN HU: All right, so I think it's coming up, if you want to-- I think 300, probably, is enough. Let me try to stabilize it here. Just do 350, all right? All right, 330. We're right there. So any of you want to count? I'll try to put it in the same position, 30 seconds, 1, 2, 3.

AUDIENCE: And this one is silica or silicate?

JUEJUN HU: Soda lime. So it's going to be quite dramatic.

AUDIENCE: [LAUGHS]

AUDIENCE: [INAUDIBLE]

JUEJUN HU: Countdown. Give me a countdown because I need time to grab it.

AUDIENCE: 10, 9, 8, 7, 6, 5, 4, 3, 2, 1.

[PHONE RINGING]

AUDIENCE: Oh, it's so [INAUDIBLE].

JUEJUN HU: All right. Maybe I should go to a bit-- oh, you can already see it.

AUDIENCE: Oh.

AUDIENCE: Oh.

JUEJUN HU: You can already see it. I'm going to pass it around. I don't know if the camera can see it, but it's full of cracks.

AUDIENCE: Yeah.

JUEJUN HU: I will pass it around, take a look. Yeah, it hasn't break yet.

AUDIENCE: But industrial thing.

AUDIENCE: I'll be so worried if my thing--

JUEJUN HU: All right, now, this guy, soda lime. Go.

AUDIENCE: Oh. Burgers space is a great name because I like this department. We just break things.

JUEJUN HU: We are going to break more things later on in the semester, so don't worry. There are more.

AUDIENCE: You'll need a hotplate.

AUDIENCE: [INAUDIBLE] put stuff together. I just want to--

JUEJUN HU: Give me the countdown?

AUDIENCE: 8, 7, 6, 5, 4, 3, 2, 1. Oh.

[PHONE RINGING]

JUEJUN HU: All right.

AUDIENCE: Can I see it for a sec?

JUEJUN HU: It's perfectly intact. There's some water. I probably need to wipe it up a little bit. I should come with a--

AUDIENCE: Looks fine to me.

JUEJUN HU: It's perfectly intact.

AUDIENCE: It looks very safe.

JUEJUN HU: Nothing. Absolutely nothing.

AUDIENCE: It smells a little bit burnt. Other than that.

[LAUGHTER]

There's no reason--

JUEJUN HU: That's a chemical problem we are not going to address in the class.

AUDIENCE: [INAUDIBLE]

JUEJUN HU: Yeah, you can clearly see a difference. I know. Maybe we can-- later on, we can show it under the camera.

AUDIENCE: Yeah.

JUEJUN HU: Yeah.

AUDIENCE: Can you just put it behind like--

JUEJUN HU: A sheet of paper or something, yeah.

AUDIENCE: [INAUDIBLE]

JUEJUN HU: It'll probably take a separate quick shot there.

AUDIENCE: Can you hold the first one, please?

JUEJUN HU: First one?

AUDIENCE: Yeah.

JUEJUN HU: This is soda lime.

AUDIENCE: This is [INAUDIBLE].

JUEJUN HU: Can you see it? Soda lime has lots of cracks.

AUDIENCE: Yeah, it does.

JUEJUN HU: You can see a difference?

AUDIENCE: Yes.

JUEJUN HU: OK, great.

AUDIENCE: We should [INAUDIBLE].

JUEJUN HU: All right, so now you see that. Well, that's why silica is great for these kind of applications there. So now let me switch over from silicate to something else. Let's talk about borate. So boron, boron oxide can also form glass in itself. It's basically B_2O_3. The basic structural unit is quite simple. It's one boron in the center, three oxygens surrounding it. You form this center, BO_3 kind of structure unit, interlinked to each other to form glass.

Now, one thing I want to mention there is that previously, in the lecture, I was talking about this fictitious glass, A_2O_3, where you form this 2D glass. I did not mention it as boron because the structure of boron oxide is actually non-planar. You still have this kind of BO_3 units. But when they are linked together, they actually warp out of plane to form this kind of 3D structure there.

So, basically, that's just boron oxide. Now, we like to talk about boron oxide because it has this very unique behavior. When you start to put alkaline into it, you can have two kind of structural moieties. You can have a normal one. Sodium goes in there, create non-bridging oxygen, decrease network connectivity, lower processing temperature, higher diffusion coefficient, all the same.

But you can also have another structural transformation there. If you think about boron atom, boron have three outer shell electrons. You can form three chemical bonds with oxygen, but this still leaves behind an empty orbit. Now, sodium is an atom that really likes to give away electrons. So the electron can actually be taken up by the boron.

So now boron has one excess electron. And then this boron, this excess electron can allow this boron atom to form another chemical bond with the neighboring oxygen. In this process, the boron, obviously, becomes negatively charged. So there's some electrostatic interaction that then attracts the sodium ion.

But what you end up getting here is that you now have a four-fold coordinated boron atom because of the addition of sodium. And in the process, you increase the network connectivity instead of decreasing it. So this is really what's peculiar about boron here. If you have boron in the network, sodium can do two things, form NBO. Or it can induce this, what's called a B3 to B4 conversion. And they have a completely opposite impact on the glass property. One decrease network connectivity. One increase network connectivity. Yes?

AUDIENCE: How do you control for [INAUDIBLE]?

JUEJUN HU: Next slide.

[LAUGHTER]

Basically, the composition. So what I'm showing you here, this is basically just-- in this case, this is a different kind of a sodium oxide. We're all putting them into borate, B_2O_3. And what we're seeing here, you follow this kind of pretty general trend. Initially, when you start to put sodium in there, you're introducing B3 to B4 conversion.

So that's why, on the vertical axis, I'm showing you the fraction of fourfold-coordinated boron. It monotonically increases initially. So all the sodium atom you put in there initially, always introducing this B3 to B4 conversion. No non-bridging oxygen. Now, beyond a certain point, then any additional sodium atom in there or any additional alkaline atom in there, you're now introducing non-bridging oxygen.

So you can essentially control these two structural moieties just by changing the composition of the alkaline atom in there. You first form B3 to B4. Beyond some point, it becomes NBO. And that's why now, if you look into all the different properties of the glass material as to how it depends on the fraction of your alkaline oxide in there.

What I'm plotting here, this is a refractive index, density, glass transition temperature. This is actually a thermal expansion coefficient. You notice that they all exhibit some extreme behavior somewhere in between. So, for example, if you think about, say, density, initially, when you start to add in lithium oxide, in this case, you create this B3 to B4 conversion. You increase network connectivity. You have a more tightly bound network. So you actually increase in density.

At some point, you start to now trigger this NBO formation. Then you see a decrease in the network connectivity, enhanced density. Same thing with refractive index. Refractive index is actually almost synonymous as density. It's basically characterized, how polarizable the electrons are when they respond to the oscillating electromagnetic field or incident light. So if it's more polarizable, you tend to have higher refractive index. So if you have a glass network with high density, in the same volume, you essentially have more electrons, so it's more polarizable. Therefore, higher refractive index.

Similarly, for Tg, again, higher network connectivity gives you a more thermally-stable network. So you have a higher Tg. Thermal expansion coefficient, exactly opposite. More connected network, then you have less room for thermal expansion. So you have a lower thermal expansion coefficient. Now, if you look into this plot carefully, you do notice one thing. The extremum point for these different properties, they occur at different points.

For thermal expansion coefficient, for example, the minimum is 20%. For density, the maximum is somewhere around 40%. So what this indicates is that the actual structural transformation is actually a lot more complicated than the simplified picture I'm giving you here. Besides this B3 to B4 conversion and then the NBO formation, thee actually are more than two structural moieties that's actually introduced when you put alkaline atoms into a borate network.

The detailed explanation is beyond the scope of this class. If you're interested, you can read the book by Shelby, Chapter 5. He essentially introduces about, there are multiple structural transformation that actually takes place in borate glasses. But for now, for the sake of this class, what you need to know is that there are, essentially, these two kinds of structural formations that give rise to opposite property chains.

Now, one more thing I also want to mention here is that, if you look at this one, by tailoring the amount of sodium in there, you can actually get to some composition with very low-thermal expansion coefficient compared to the parent glass. This is one attractive properties. That's why people like to add boron into different kinds of glasses.

So pure boron glasses, people actually don't use it quite a lot. But borosilicate glasses is what people use quite frequently. So borosilicate glasses, essentially, you have two glass networm formers. You have boron. You have silicon. Both form the glass network together. You can then add a little bit alkaline in there. And what I'm showing in the first bullet point is how the different chemical compositions affect the structural transformation.

It's basically controlled by this ratio here, the ratio between the amount of alkaline oxide and the boron oxide. So depending on composition, you may get B3 to B4 or you may get NBO. Same. But the idea is that, with some specific combination, you can introduce a maximum amount of B3 to B4 conversion, such that you can have a very low-thermal expansion coefficient. But at the same time, these glasses can also be a lot more easier to process compared to silica.

So that's what made this kind of an alkali borosilicate glass attractive. It's like a low-cost replacement of silica when you have applications, where you don't want any thermal expansion. It also provided improved chemical resistance. Similarly, because of the better network connectivity, it means that the network is also more stable. So it's also more resistant to any kind of chemical corrosion.

So one salient example of this kind of a borosilicate glass is actually Pyrex. This is a formulation that was developed initially by Corning about almost a century ago. And you probably have seen this in labs. All the lab beakers, you see this one. I can actually turn around. You see Pyrex right there. So these are all made of borosilicate glasses for obvious reasons. You need chemical resistance. You want it to be thermal shock resistant.

People also use it to make high-quality optical elements, like this one. This is a large telescope mirror they make out of borosilicate glass because they don't want the thermal expansion or temperature fluctuation to cause any thermal stress and distort optical properties. By the way, this is the mirror. It takes a year to cool down, just to ensure it's perfectly uniform. People also use them for space shuttle, the tiles, to essentially do a thermal shield. This little black coating on top is actually borosilicate glass. They mix it with a little bit of carbon to increase thermal emissivity, so that heat can escape more efficiently.

But same idea. You want to minimize any kind of thermal stress if you don't want to have a-- that's why you want to eliminate thermal expansion. Now, speaking of Pyrex, any of you have this Pyrex ware at home? They are not borosilicate. Now you have to be careful here when you get Pyrex. This one, this is all capital or uppercase PYREX, as you can see.

What you have in your kitchen is all lowercase. Lowercase Pyrex is soda lime glass. It's just basically tempered soda lime glass. If you search online, you'll find lots of YouTube videos, like Pyrex explosion. That's all lowercase Pyrex. If you want a real, real borosilicate glass, you have to be all uppercase PYREX. Basically, Corning, at some point, sold a brand to Work Kitchens. And then they start to make it out of other kinds of glasses. So I'm not going to get into that.

But bottom line, not all Pyrex is borosilicate. If you go to Amazon, some vendors claim they sell borosilicate stuff. It may not be true. I actually have left angry comments like, this is not borosilicate. That's just me ranting about people using the term for incorrect competitions. All right, any more questions about borosilicate?

So then I can also quickly talk about this, another one, aluminum silicate. Aluminum silicate is actually quite important for later on, especially when we talk about applications where you need good mechanical properties. All the carbon glasses for smartphones, for mobile electronic devices, they probably all contain aluminum.

So aluminum is also three-fold coordinated. It has similar properties-- although, similar to a boron there-- in that it can either be a metal. So introducing each aluminum atom, actually, introducing three non-bridging oxygen. But under certain circumstances, aluminum can also become a glass former. You can basically have this kind of a four-fold coordinate aluminum similar to the B4 structural unit, so that you actually increase the network connectivity.

And that's, again, entirely controlled by the stoichiometry of the glass. So that's why I'm showing this property chain here, basically, how the activation energy of conductivity varies as a function of ratio. You see a minimum there, which corresponds to the transition. You are going from, essentially, there's an aluminum foil connection now transitioning into forming NBO. So that's why there's an inflection point there. Good?

All right, so in the next five minutes-- we still have five minutes-- I'm going to talk about, start talking about, now non-oxide glasses. So whether it's silica, borates, or aluminosilicate, these all has oxygen in their glass network. For some applications, you can actually replace oxygen with other non-metal atoms. The simple example would be, you do isoelectronic substitution of oxygen with other group six elements, so sulfur, selenium, or tellurium.

The resulting glasses is what's called chalcogenide glasses, or chalcogenide glasses, depending on who you ask. The main difference here is that these atoms are a lot bigger and heavier compared to oxygen. So bigger atoms means that the interaction between the atomic nuclei and the outer shell electron is going to be weaker. So when you form chemical bonds, chemical bonds formed by these chalcogenide atoms tend to be a lot weaker compared to the counterpart, where you contain oxygen. So immediate consequence is that they tend to have lower mechanical strength.

So if you recall in the first lecture, I actually sent around a little piece of infrared transparent glass. I have told you that, be careful with that one because it's quite fragile. That's a chalcogenide glass They also tend to have a lower softening temperature. So you can actually process these glasses at much lower temperature, which can be an advantage.

People use them a lot for molded optics. You can actually mold it into different kinds of geometries by, essentially, apply some heat to introduce viscous flow. And the temperature you need to actually process that is actually a lot lower. So the wear and tear, for example, for the other kind of molds is actually a lot lower as compared to when you try to mold oxide glasses.

The reason they attract a lot of attention mostly is for the optical properties. They have much lower phonon energy and, therefore, they are transparent to infrared radiation. So the reason it's transparent, basically, if you think about, essentially, atomic network, you have chemical bonds. You have atoms. You can approximate it essentially as like you have masses attached to the end of the spring. That's a very simple model of chemical bonds.

So if you imagine it's attached to the end of the spring, you have a characteristic vibrational frequency. And if your instant electromagnetic wave has a frequency that coincides with the characteristic vibrational frequency of chemical bonds, then you can actually convert this optical energy into the vibrational energy of chemical bonds, which essentially means the absorption. The vibrational energy is basically thermal energy. So you convert, essentially, light into heat.

So for trochozonites, because they have a much heavier atom, so mass increases. You also have weaker chemical bonds. So it means that your spring constant is smaller. So for simple mechanics, you know that the characteristic vibrational frequency of this kind of harmonic oscillator basically scales with square root of mass divided by spring constant.

So larger mass, smaller spring constant. Both point to the fact that they have a much lower vibrational frequency there. So as a result, for oxide glasses, you typically have the absorption somewhere in the mid-infrared regime. But for these glasses, the absorption actually can extend to much longer wavelengths. They are transparent to thermal infrared wavelengths.

So that's why they are actually quite important for, essentially, infrared imaging applications, like night vision. You're looking at, essentially, thermal blackbody radiation from low-temperature bodies, like human body. Their wavelength is a lot longer compared to visible light. So that correspond to lower vibrational frequency, where it will get absorbed in oxide glasses, but it remains transparent for chalcogenide glasses.

They also have enhanced optical nonlinearity, which we are not going to really talk about. But that also has to do with the fact that they have a lot more outer shell electrons. So those outer shell electrons give rise to much higher probability and nonlinear optical properties as well. So I'm actually going to stop here. And in the next lecture, we are going to wrap up different classes of amorphous solids and start to talk about glass forming.