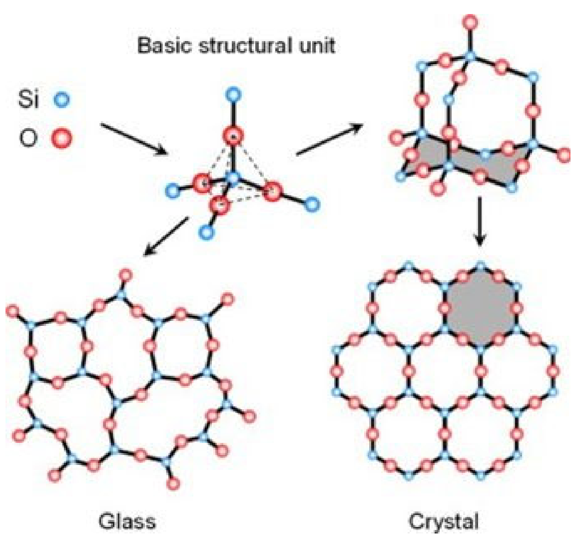
ENCH 615 Materials for Chemical Engineering

Lecture 6: Glasses

SILICON DIOXIDE

We last saw silicon dioxide as a crystalline material, quartz, in our section on piezoelectric materials. Quartz exists all over the world, but Silicon dioxide is also readily found as a glass.



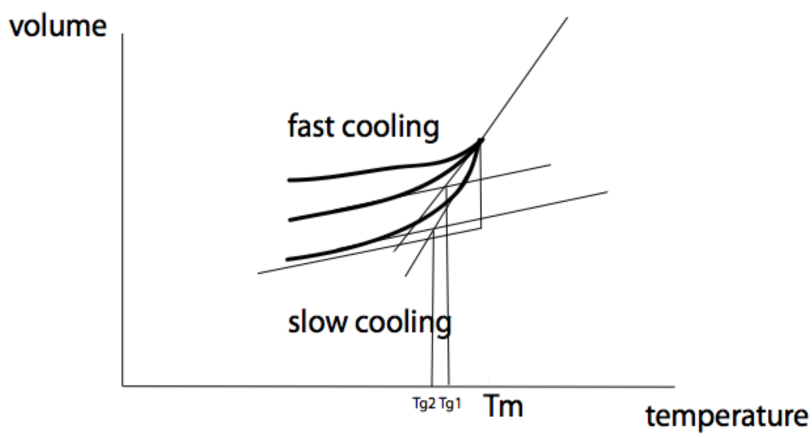
From: (Shioya and Kikutani 2015) Shioya, M. and T. Kikutani (2015). Chapter 7 - Synthetic Textile Fibres: Non-polymer Fibres. Textiles and Fashion. R. Sinclair, Woodhead Publishing: 139-155.

GLASSES: solids with short range order, but no long-range order

For silicon dioxide, this means that the atomic coordination is maintained, but the longer range structure such as the rings vary.
A glass is an amorphous version of the crystalline material. We briefly mentioned during metals that it was hard to make metallic glasses because it was challenging to cool them faster than the crystals formed. For ceramic materials that involve multiple elements, glasses are far more common.

Making glasses

If one cools a material fast enough, faster than the atoms can move into crystalline structures, one will get a glass.



Key points:

- The faster the cooling rate, the larger the volume of the final glass

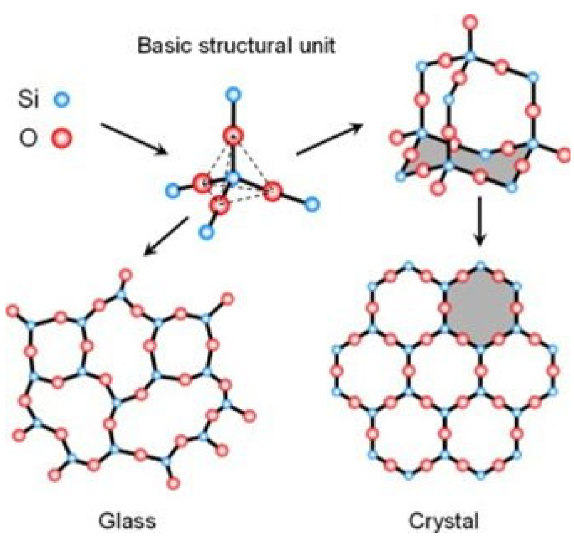
- The faster the cooling rate, the higher the Tg. The glass transition temperature is RATE DEPENDENT

**Why do ceramics (eg. SiO_2) form glasses more easily than metals?

**How can we make a metallic glass?

Structure and properties of glass

Glasses have short range order (SRO) (e.g. the bond angles of Si will be 109.5°), but they do not have long range order (LRO).



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This makes glasses isotropic (the same in all directions) and, by definition, amorphous.

So, what cool things are there about glasses? What are the properties of them we tend to embrace?

Many of the glasses we're interested in are transparent, at least to part of the visible spectrum. They are also excellent electronic insulators, they have high tensile strength, and they are good thermal insulators. The last seems deeply questionable as I write this next to the window that feels very cold, but compared to other materials, glass is a great thermal insulator. Glass tends to be chemically resistant, too, which is hugely helpful.

The major glass we all encounter most days is soda-lime-glass.

SODA-LIME GLASS

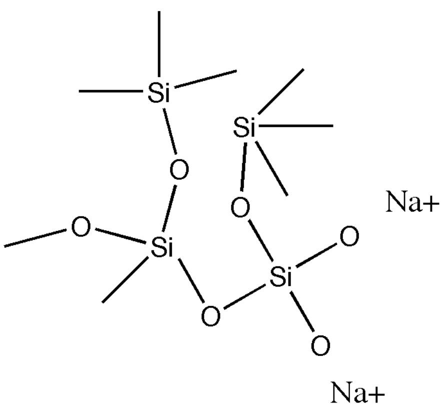
Another name for soda lime glass is flint glass, though that name is not used very often outside of optics circles. The name comes from flint in chalk deposits that were used to extract silica. Flint glass has a strong optical clarity.

Silica glass is a network. The glass transition temperature is approximately 1000 ˚C. It is difficult to keep a furnace at this temperature over a large hotzone as is needed for glass blowing and processing. It is very expensive to work at these temperatures.

However, if one breaks up the network, the Tg will decrease which makes it easier to process.

SODA-LIME-GLASS
$Na_2O+CaO+SiO_2$

Na_2O is a network breaker
CaO helps with chemical stability



Soda interrupts the network. It is an additive that makes a huge difference in the properties of the material. However, it also makes silica glass more chemically vulnerable. The addition of lime helps to counteract this.

One of the big challenges with soda-lime glass beyond the fact that it is slightly chemically vulnerable (have you ever seen your drinking glasses get cloudy with time—they are getting etched) is that silica glass does not tolerate changes in temperature well. If you forget and put a regular glass on the stove, for example, you may find that the glass expands and the bottom pops off catastrophically. I don't recommend doing this if you can help it. You can end up with a lot of broken glass around you.

PYREX OR SODIUM BOROSILICATE GLASS

There is a need for glass that is transparent, chemically resistant, and can be cycled through hot and cold temperatures.

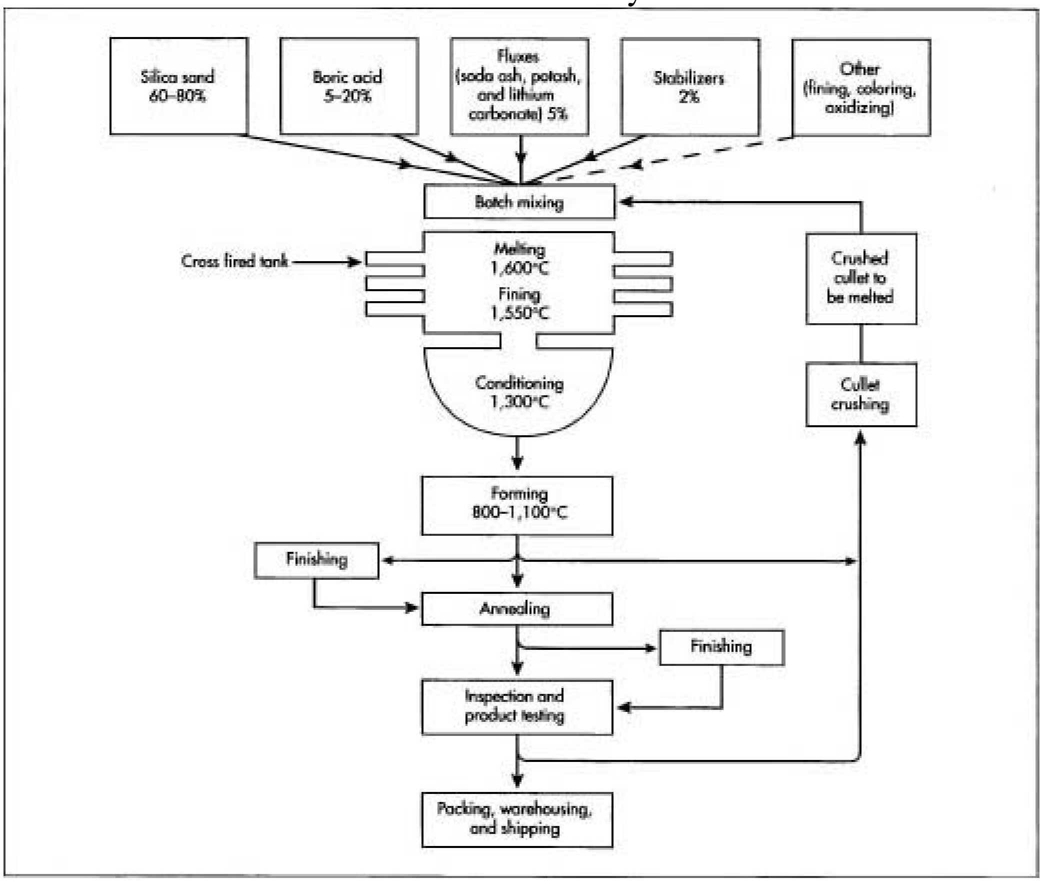
Labs, cooking, baking…. Art (bear with me on this but I promise we'll figure it out.)

The killer for thermal cycling is thermal expansion. If one can suppress thermal expansion, one can cycle to one's heart's content.

Pyrex is silica glass with boric acid. Boron is a network former. Pyrex is, essentially, silica with droplets of borate throughout the structure. Borate, it turns out, also imparts a strong chemical resistance. This was known before the thermal expansion behavior was studied. The first use of silica-borate glass was for battery jars that were used by the telegraph.

The inventor of Pyrex, Eugene Sullivan (Corning) first invented Nonex which was a no expansion glass. Pyrex is very similar but does not have the lead of nonex which, as you might imagine, makes it far safer to make and use.

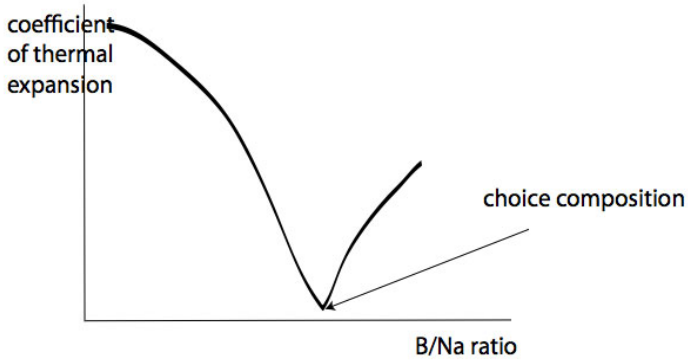
Fluxes are used to help make Pyrex processable, but they can also make it less chemically robust.



From: http://www.madehow.com/Volume-7/Pyrex.html#:~:text=Pyrex%20glass%20is%20a%20borosilicate,into%20different%20types%20of%20glassware.

Low thermal expansion → high thermal shock resistance

Boron is a network former. By having more Boron, one tightens up the structure. It's also chemically reactive, so we add other components for chemical stability



BO_3 increases connectivity and density. → decreases thermal expansion. By matching the B to the Na (which increases thermal expansion, one can get a matrix with little to no thermal expansion) The ratio of the two also means that one can process the material. Remember, we already add disruptors so we can process silica at temperatures that are achievable without tons of energy.

Evelyn Roberts

From the Corning Museum website:
https://blog.cmog.org/2020/08/20/women-in-glasshouses-women-in-science/

Evelyn Roberts (1893-1991) obtained her bachelor's in math from U. Michigan. She joined Corning and worked on the early generations of Pyrex where she specialized in materials testing. She published with her mentor, Jesse Littleton (who identified that Nonex, the batter case, might be a good baking dish material). Littleton and Roberts published "A Method for Determining the Annealing Temperature of Glass" in J. Optical Society of America in 1920. Roberts then completed her Master's in Physics at. U. Michigan.

Early CGW lab, ca 1917, i.e. Physical Lab. Making measurements in the Physical Lab. Corning Incorporated Department of Archives and Records Management.

Image of Corning Glass Works laboratory physicist Evelyn Roberts, in 1917 or 1918, pouring boiling water from a teapot onto a Pyrex pie plate as it rests atop block of ice on the roof of a Corning Glass Works building to demonstrate Pyrex ware's thermal endurance. From Corning Incorporated Department of Archives and Records Management.

Pyrex is famous for it's amazing thermal shock resistance.

In the end, this photo was recreated for an entirely different purpose. After the Oklahoma City bombing, there was a desire to build a memorial to the victims. The design called for copper seats on glass bottoms.

The challenge was that this in an outdoor memorial in Oklahoma City where it can be incredibly hot and then a rapid storm can form with cold water.

The original design involved one of two different glasses, but both seemed prone to cracking in the extreme conditions. Prof. Yet Ming Chiang was invited to consult, and prototype chairs were brought to MIT.

Ben, an amazing grad. student and former wrestler, got the job of hauling the prototypes to the roof of the building. (No elevator went up to the roof.) He and Yet recreated Roberts's experiment of many years ago.

In the end, a variant of Pyrex ended up being the only glass that would last long term in the extreme conditions of Oklahoma.


Yet Ming Chiang and his team recreating her experiment with prototype chairs.
https://news.mit.edu/1998/oklahoma
Ben Hellweg was the key grad. student on the project. He is on the right. He was the only member of the research team who could carry the glass block up to the roof.

http://johnlewisglass.com/our-work/for-architects/oklahoma-city-memorial/
Design by Butzer Design Partnership Images by Ted Betz

Description: 168 chairs consist of hollow glass cubes that are illuminated from inside, with the victims' names etched on the front

The CORELLE PLATE

Corning also created Corelle plates. I have promised my family that I will stop destroying our dishes, but I highly recommend trying it some time.

The Corelle plate consists of a ceramic core. Ceramics are very weak in tension (they crack) but very strong in compression. The ceramic is dipped in glass and the glass is cooled quickly so it puts the core in compression.

You can bang the pants off corelle plates without failure, but if you drop it on its side, it can delaminate and will essentially explode like a prince rubert drop. 😊

How Correlle dishes are made:
https://www.youtube.com/watch?v=eW8egUCzw-k

Prince Rubert drop:
https://www.youtube.com/watch?v=xe-f4gokRBs