MIT 3.071
Amorphous Materials

9: Glass Strengthening

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After-class reading list

- Fundamentals of Inorganic Glasses
  - Ch. 13.8, Ch. 18.12
- Introduction to Glass Science and Technology
  - Ch. 9, Section 4.4

Solar panels

Display

Architecture

Strengthened Glass

Defense

Automobile & aviation

Consumer product

Glass strengthening techniques

Engineer chemistry and microstructure (improve K_{Ic})

- Crystallization
- Composites
- **Engineer glass structures**

Reduce defect density or severity (decrease K_I)

- Fire polishing
- Surface etching
- Surface coating

Introduce surface compressive stress (increase σ_f)

- **Heat treatment / tempering**
- **Ion exchange**

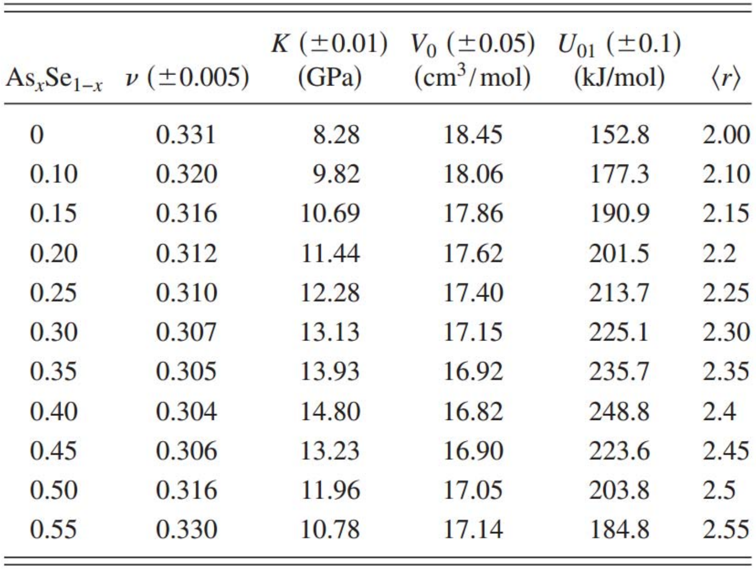
Mechanical property dependence on mean coordination number in network glasses

- In brittle materials, fracture toughness is determined by elastic modulus and bond energy

$$\left.\begin{aligned} \sigma_f &= \frac{1}{2}\sqrt{\frac{\gamma E}{a}} \\ K_{Ic} &= \sigma_f \sqrt{\pi a} \end{aligned}\right\} \Rightarrow K_{Ic} = \frac{1}{2}\sqrt{\pi \gamma E}$$

- Mechanical property evolution in As-Se glass

Figure removed due to copyright restrictions. See: G. Yang, et al. "Correlation between structure and physical properties of chalcogenide glasses in the AsxSe1−x system." *Phys. Rev. B* 82 (2010). [Complete article].



As_xSe_{1-x}	ν (±0.005)	K (±0.01) (GPa)	V_0 (±0.05) (cm^3/mol)	U_{01} (±0.1) (kJ/mol)	$\langle r \rangle$
0	0.331	8.28	18.45	152.8	2.00
0.10	0.320	9.82	18.06	177.3	2.10
0.15	0.316	10.69	17.86	190.9	2.15
0.20	0.312	11.44	17.62	201.5	2.2
0.25	0.310	12.28	17.40	213.7	2.25
0.30	0.307	13.13	17.15	225.1	2.30
0.35	0.305	13.93	16.92	235.7	2.35
0.40	0.304	14.80	16.82	248.8	2.4
0.45	0.306	13.23	16.90	223.6	2.45
0.50	0.316	11.96	17.05	203.8	2.5
0.55	0.330	10.78	17.14	184.8	2.55

Phys. Rev. B **82**, 195206 (2010)

Mechanical property dependence on mean coordination number in network glasses

- In brittle materials, fracture toughness is determined by elastic modulus and bond energy

$$\left.\begin{aligned} \sigma_f &= \frac{1}{2}\sqrt{\frac{\gamma E}{a}} \\ K_{Ic} &= \sigma_f \sqrt{\pi a} \end{aligned}\right\} \Rightarrow K_{Ic} = \frac{1}{2}\sqrt{\pi \gamma E}$$

- Mechanical property evolution in Ge-Se and Ge-Sb-Se glasses

Figures removed due to copyright restrictions. See Figures 1, 2: Varshneya, A.K., et al. "Deformation and Cracking in Ge–Sb–Se Chalcogenide Glasses During Indentation." *J. Am. Cer. Soc.* 90 (2007): 177-183.

J. Am. Cer. Soc. **90**, 177 (2007)

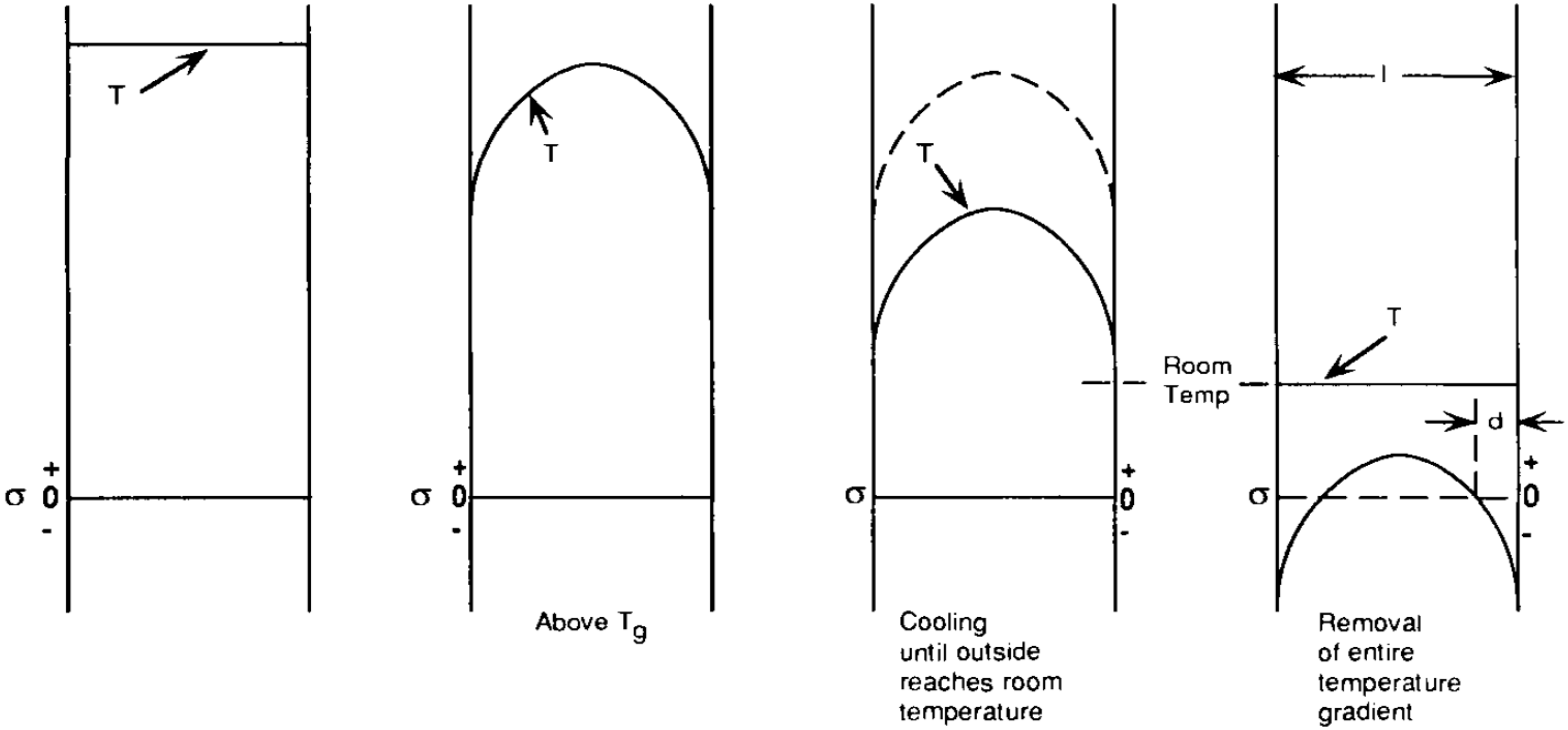
Thermal and chemical glass strengthening

Figure removed due to copyright restrictions. See Figure 8: Wondraczek, L., et al. "Towards Ultrastrong Glasses." *Adv. Mater.* 23 (2011): 4578-4586.

Adv. Mater. **23**, 4578 (2011)

Heat-strengthened / tempered glass

- Glass heated to 600 – 650 °C and force-cooled to generate surface compression



Heat-strengthened / tempered glass

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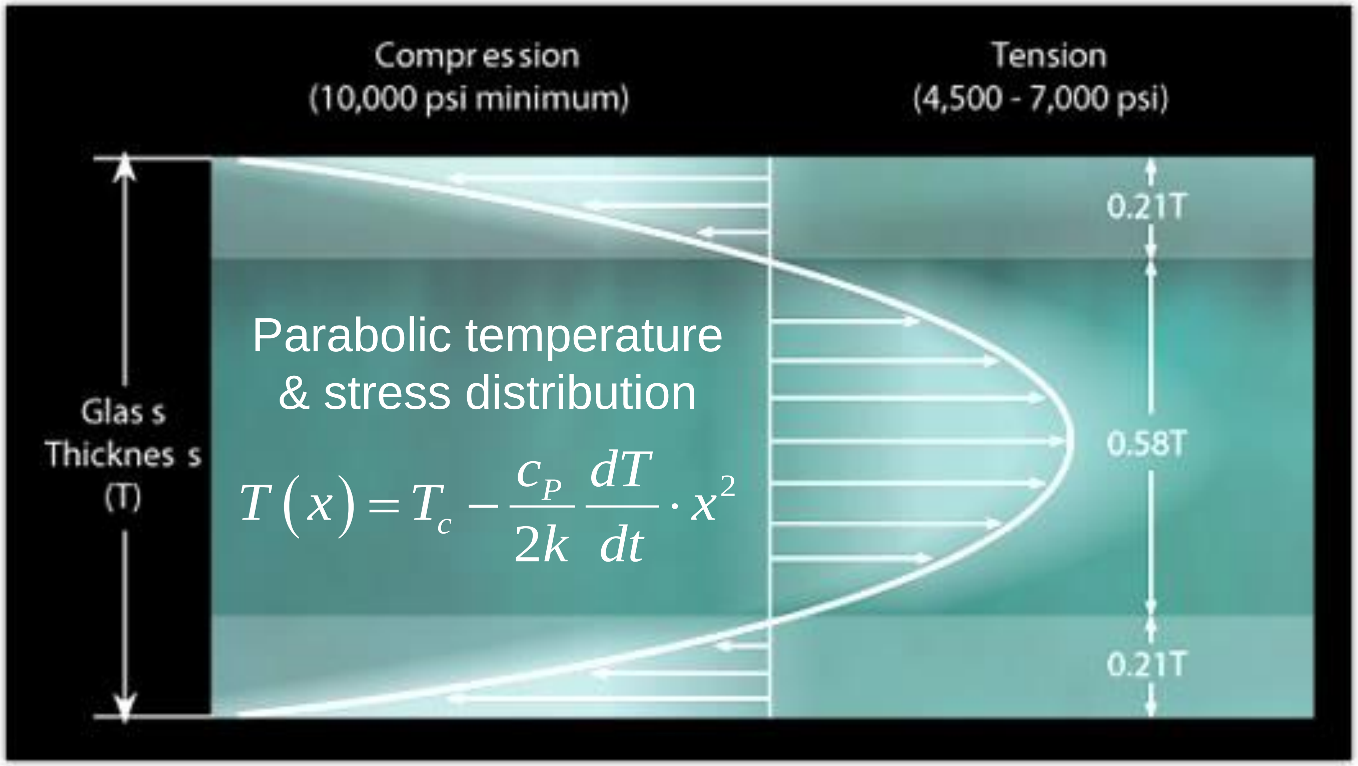


Parabolic temperature & stress distribution

$$T(x) = T_c - \frac{c_P}{2k}\frac{dT}{dt}\cdot x^2$$

http://www.cardinalst.com/

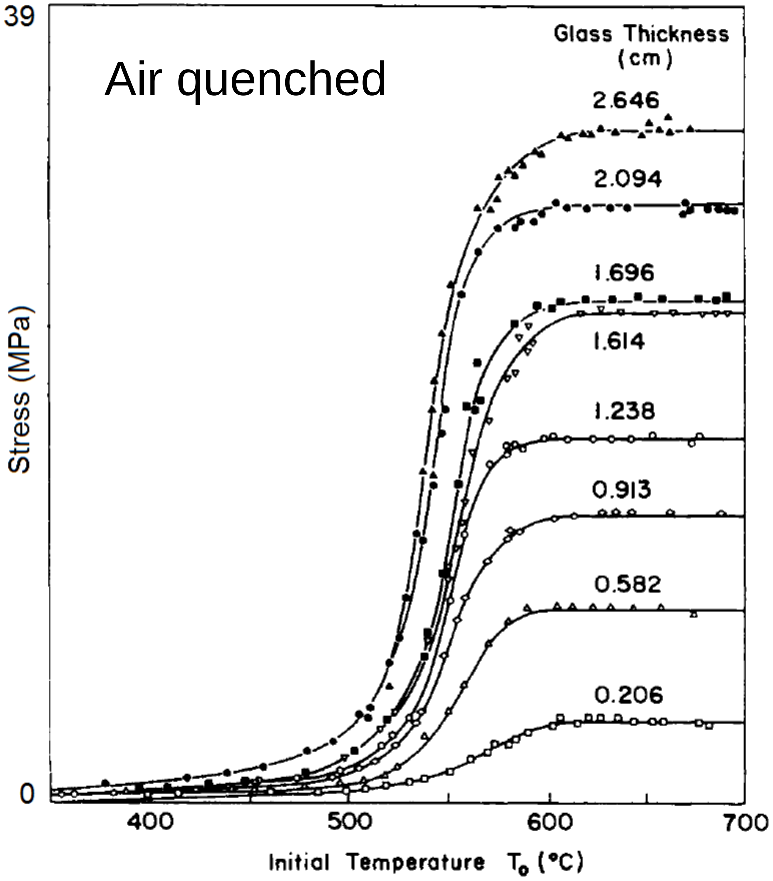
Heat-strengthened / tempered glass

- Glass heated to 600 – 650 °C and force-cooled to generate surface compression

$$\sigma(x)=\sigma_c-\frac{E}{1-\nu}\cdot\frac{\alpha c_P}{2k}\frac{dT}{dt}\cdot x^2$$

$$\sigma_s=-\frac{2}{3}\frac{E}{1-\nu}\cdot\frac{\alpha c_P}{2k}\frac{dT}{dt}\cdot\left(\frac{D}{2}\right)^2$$

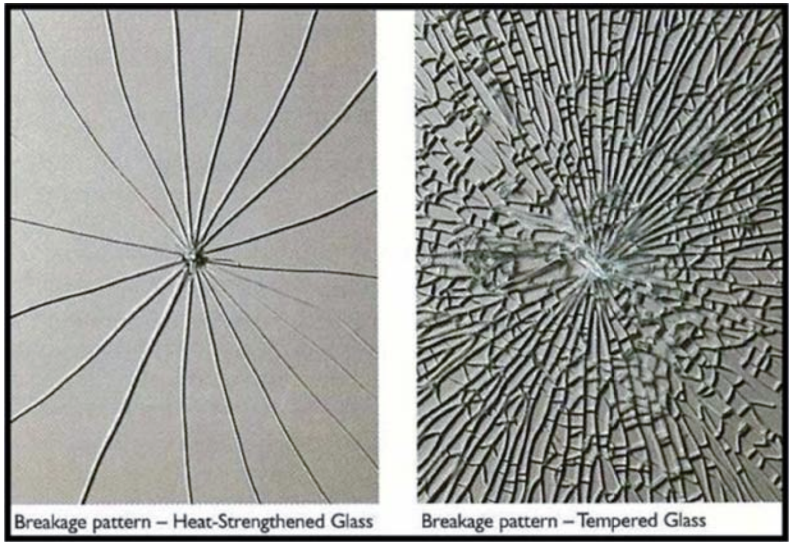
D: glass thickness



- Additional stress contributions
  - Fictive temperature gradient
  - Viscoelastic relaxation

Heat-strengthened / tempered glass

- Glass heated to 600 – 650 °C and force-cooled to generate surface compression
- ASTM C1048 standard
  - Heat-strengthened glass: surface stress between 24 – 52 MPa, about twice stronger than annealed (untreated) glass
  - Tempered glass: surface stress > 69 MPa (10,000 Psi), 4 to 5 times stronger than untreated glass



http://www.legardien.com/architectural-products

Premature fracture of tempered glass

- Nickel sulfide inclusion induced subcritical crack growth
- Sulfur is introduced in a fining agent (Na_2S) in glass making
- The origin of nickel is unclear but likely due to contamination

Nickel-Sulfur Binary Alloy Phase Diagram removed due to copyright restrictions. See Diagram No. 102135 on the ASM International website.

Figures removed due to copyright restrictions. See Figures 2, 5: Hsiao, C.C. "Spontaneous Fracture of Tempered Glass." Fractures 3, (1977): 985-992. [Preview in Google Books].

Fracture **3**, 985 (1977)

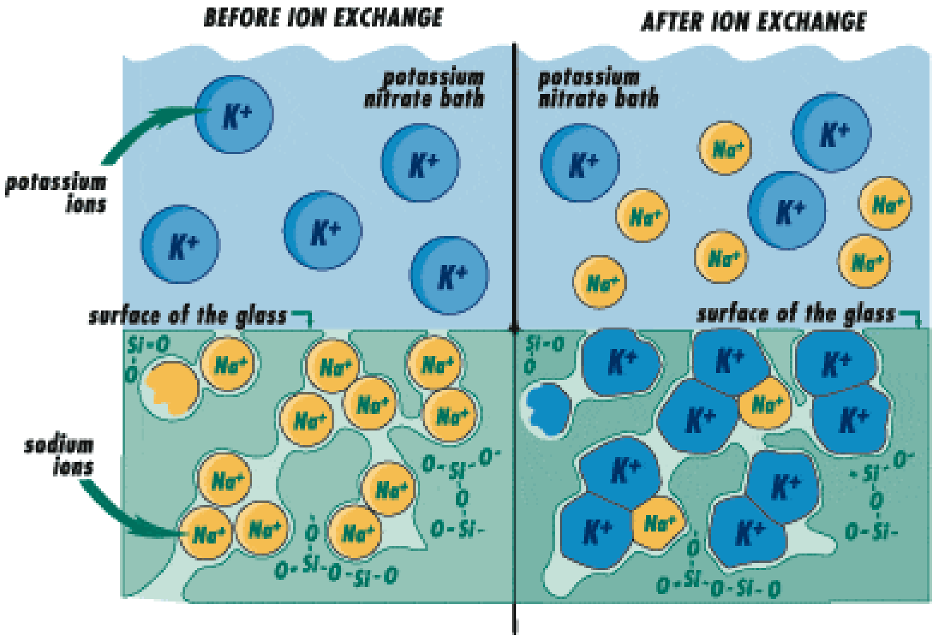
Chemical strengthening

- Ion exchange in salt bath
- Interdiffusion process

$$\overline{D} = \frac{D_{Na} D_K}{D_{Na} N_{Na} + D_K N_K}$$

$$\Delta d \approx \sqrt{\tau \overline{D}}$$

  - ☐ Kinetics limited by slow-moving ion species
  - ☐ Compressive strain impedes diffusion
- Typical case depth in soda-lime glass: 25 to 35 μm
- Only applies to alkali glasses



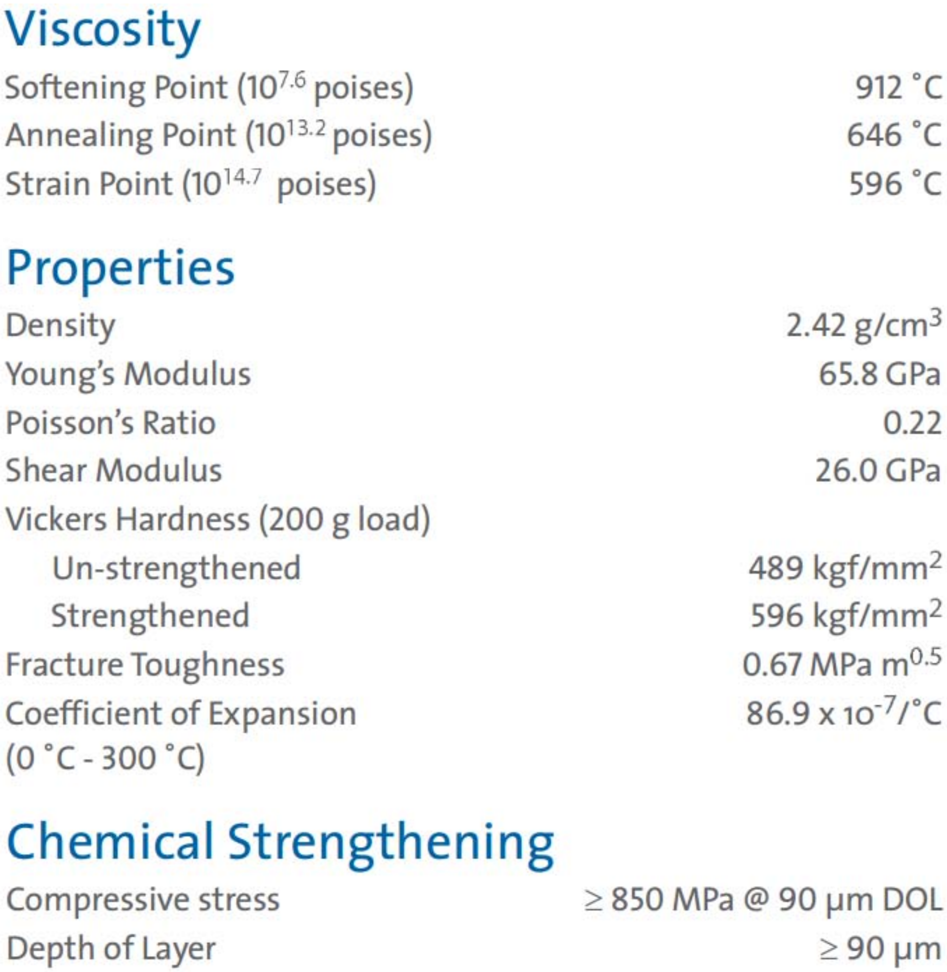
Int. J. Appl. Glass Sci. **1**, 131 (2010)

Methods to increase case depth

- Electric field, sonic or microwave assisted ion exchange
- Use alkali aluminosilicate glasses with an alkali/alumina ratio of ~ 1
- Use lesser size-disparity alkali pair for exchange: e.g. Li^+ / Na^+ instead of Na^+ / K^+
- Add minor quantities of MgO or CaO in glass
- Use mixed salt bath

Int. J. Appl. Glass Sci. **1**, 131 (2010)

Example: Corning Gorilla 4 (sodium aluminosilicate glass)



Viscosity

Softening Point ($10^{7.6}$ poises)	912 °C
Annealing Point ($10^{13.2}$ poises)	646 °C
Strain Point ($10^{14.7}$ poises)	596 °C

Properties

Density	2.42 g/cm^3
Young's Modulus	65.8 GPa
Poisson's Ratio	0.22
Shear Modulus	26.0 GPa
Vickers Hardness (200 g load)	
Un-strengthened	489 kgf/mm^2
Strengthened	596 kgf/mm^2
Fracture Toughness	0.67 MPa m$^{0.5}$
Coefficient of Expansion (0 °C - 300 °C)	86.9 x 10^{-7}/°C

Chemical Strengthening

Compressive stress	≥ 850 MPa @ 90 µm DOL
Depth of Layer	≥ 90 µm

Data from Corning product information

Addition of aluminum increases softening temperature and T_g

$$K = \frac{E}{3\left(1-2\nu\right)} = 39.2\ \text{GPa}$$

$$G/K = 0.66 > 0.42$$ brittle

Increased surface hardness and minor impact on fracture toughness

Larger case depth than that of soda lime glass

Sapphire vs. strengthened glass

	Sapphire	Strengthened glass
Density	3.97 g/cm^3	2.4 – 2.5 g/cm^3
Tensile strength	0.27 – 0.41 GPa	N/A
Flexural strength	0.9 GPa	> 0.8 GPa
Vickers Hardness	21.5 GPa	5.8 – 7 GPa
Fracture toughness	2.3 MPa·m$^{0.5}$	0.7 MPa·m$^{0.5}$
Young's modulus	345 GPa	60 – 75 MPa
Shear modulus	145 GPa	26 – 30 GPa
Refractive index (633 nm wavelength)	1.75 – 1.77	1.50 – 1.52

Data compiled based on specifications of the following products (retrieved online 10/10/2015):
GT ASF Sapphire Cover; Schott Sapphire Glass; Corning Gorilla 4 Glass; Schott Xensation Cover Glass; Asahi Dragontrail Glass

Table: Glass compositions for deep ion exchange and high MOR removed due to copyright restrictions. See p. 30: *American Ceramic Society Bulletin*, Vol. 88, No. 5.

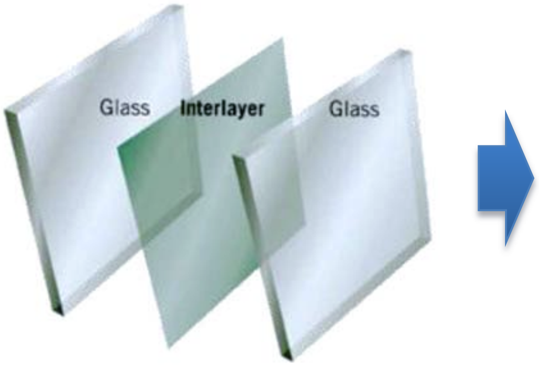
Chemical strengthening of lithium aluminosilicate glass

Figure on Weibull plot after strengthening in varying ratios of NaNO3 + KNO3 baths removed due to copyright restrictions. See: *American Ceramics Society Bulletin* 88 (2009): 27.

Am. Cer. Soc. Bull. **88**, 27 (2009)

Configurational design: laminated glass

- Two or more layers of glass (annealed, heat-strengthened or tempered) bonded together by polymer interlayer(s)



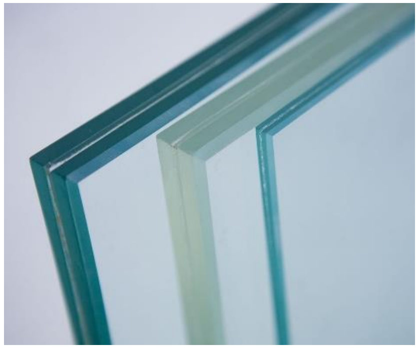


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Image of bulletproof glass removed due to copyright restrictions.

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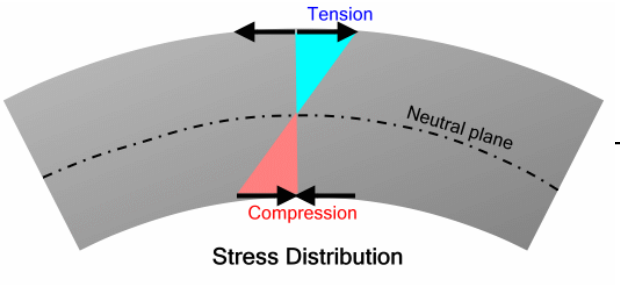
Facture toughness of laminated glass

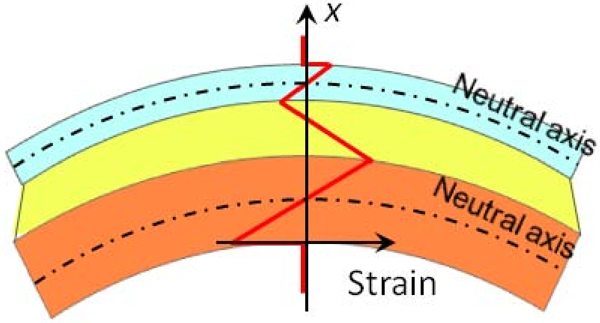
Figure of Breaking Strengths of Monolithic and LG Lites removed due to copyright restrictions. See Figure 7: Norville, H., K. King, and J. Swofford. "Behavior and Strength of Laminated Glass." J. Eng. Mech. 124, no. 1 (1998): 46-53.

Laminated glass is tougher than monolithic glass sheets

J. Eng. Mech. **124**, 46 (1998).

Properly design laminated structures are tougher than monolithic glass

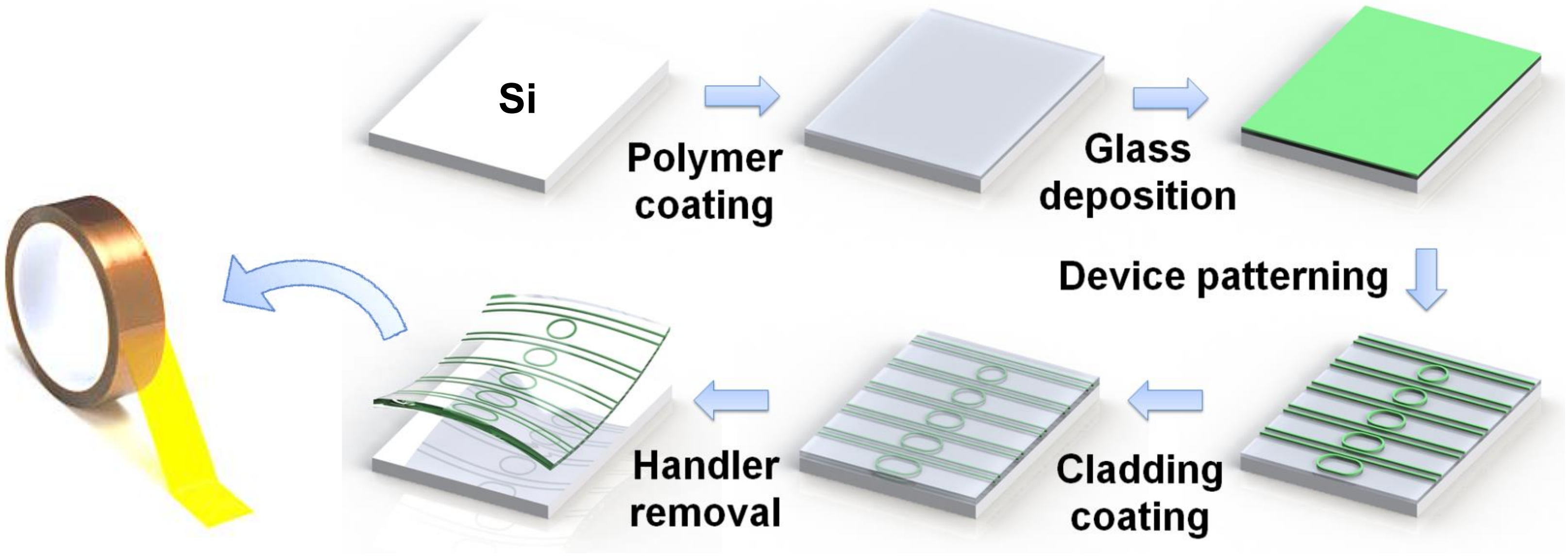




	Classical multilayer bending theory	The new multi-neutral-axis theory
Formulation	$z(\varepsilon=0)=\sum_{i=1}^{n}E_i d_i\left[\left(\sum_{j=1}^{i}d_j\right)-\frac{d_i}{2}\right]\Big/\sum_{i=1}^{n}E_i d_i$	$\sum_i \bar{E}_i \int_{-h_i/2}^{h_i/2}(ay_i+b)dy_i=0$
Assumption	No shear strain	The soft layer relieves the strain by shear deformation
Device Placement	Fixed near the substrate center	Readily tuned by adjusting the elastic contrast

Nat. Photonics **8**, 643-649 (2014)

Flexible glass photonic device fabrication



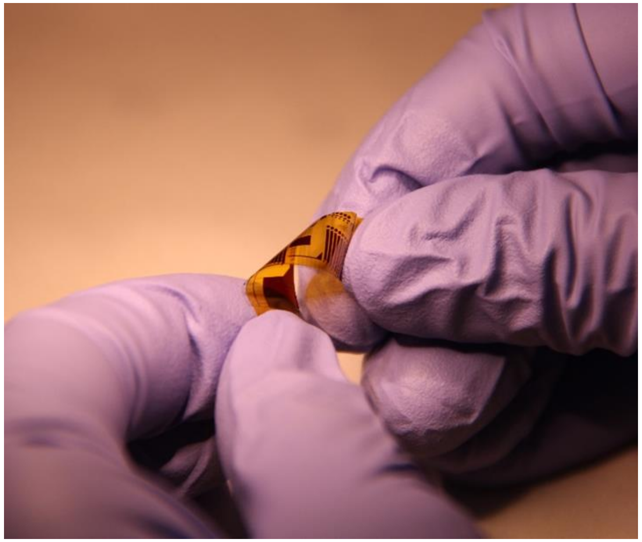
Device layer
Silicone adhesive
Polyimide substrate

} Tape

Sandwiched “Oreo” structure for stress relaxation

“Integrated flexible chalcogenide glass photonic devices,” *Nat. Photonics* **8**, 643 (2014)

Bend… but don't break!



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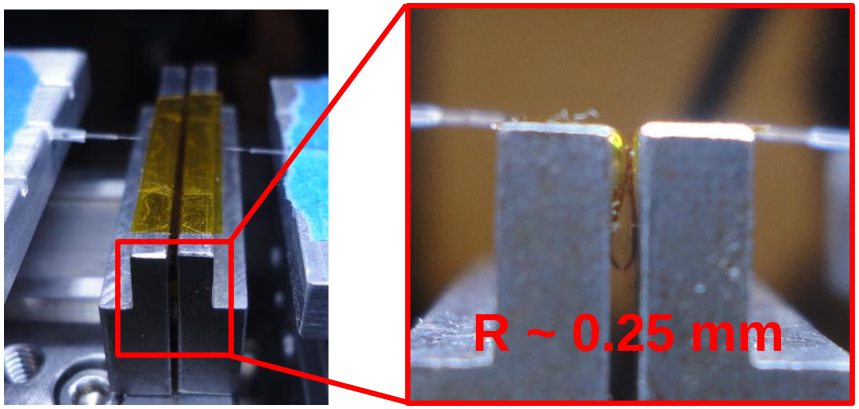

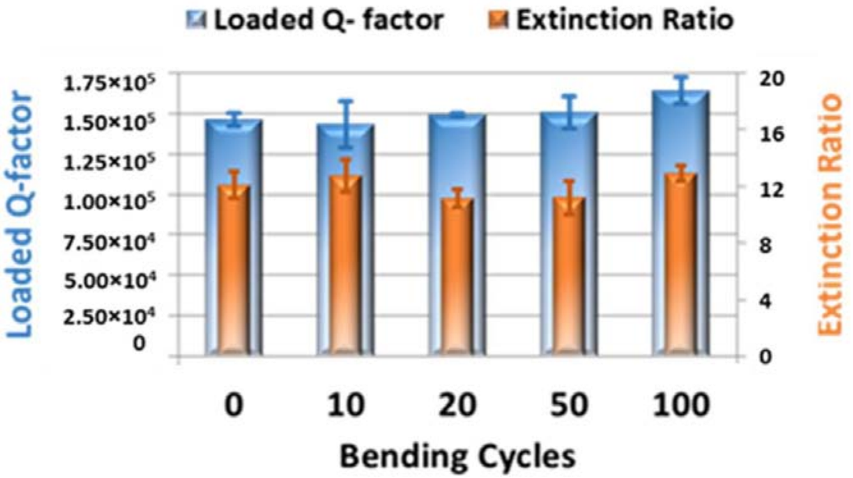

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Source: Li, L. et al. "Integrated Flexible Chalcogenide Glass Photonic Devices." *Nature Photonics* 8 (2014): 643-649.

The multi-neutral axis design enables foldable, robust photonic circuits

Nat. Photonics **8**, 643-649 (2014)

Summary

- In many cases, glasses with critically connected network possess high modulus and toughness
- Strengthening methods capitalizing on surface compressive stress
- Configurational design can further enhance mechanical properties

	Heat strengthened glass	**Tempered glass**	**Chemically strengthened glass**
Surface stress	24 – 52 MPa	> 69 MPa	Up to 1 GPa
Compressive stress depth	~ 20% pane thickness	~ 20% pane thickness	~ 100 μm
Heat treatment temperature T	$T_g < T < T_{soft}$	$T_g < T < T_{soft}$	$T < T_g$
Risk of premature failure	N	Y	N

3.071 Amorphous Materials
Fall 2015