MIT 3.071
Amorphous Materials

9: Glass Strengthening

Juejun (JJ) Hu

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

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Glass strengthening techniques

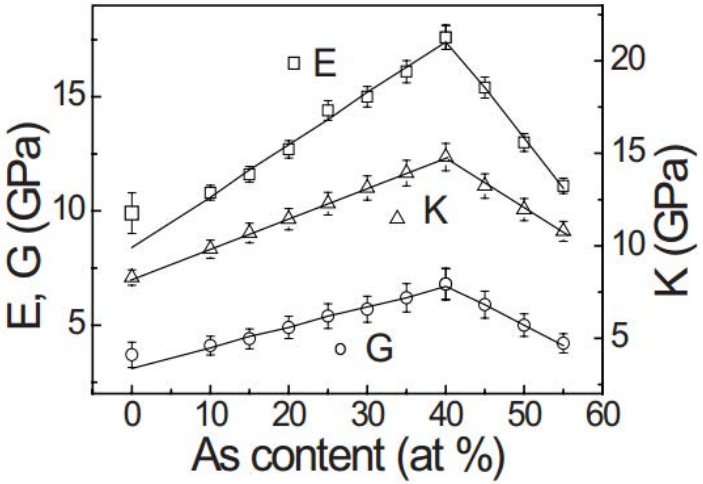
Engineer chemistry and microstructure (improve K_{Ic})	Reduce defect density or severity (decrease K_I)	Introduce surface compressive stress (increase σ_f)
Crystallization	Fire polishing	**Heat treatment / tempering**
Composites	Surface etching	**Ion exchange**
Engineer glass structures	Surface coating	

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



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

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

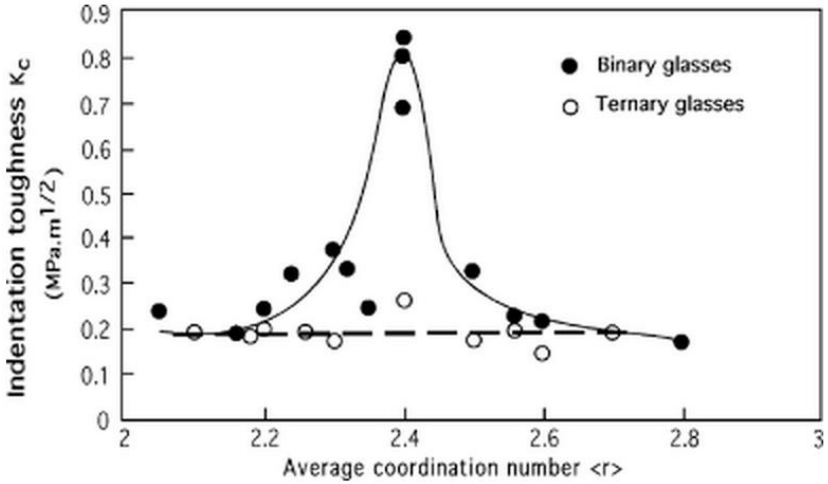
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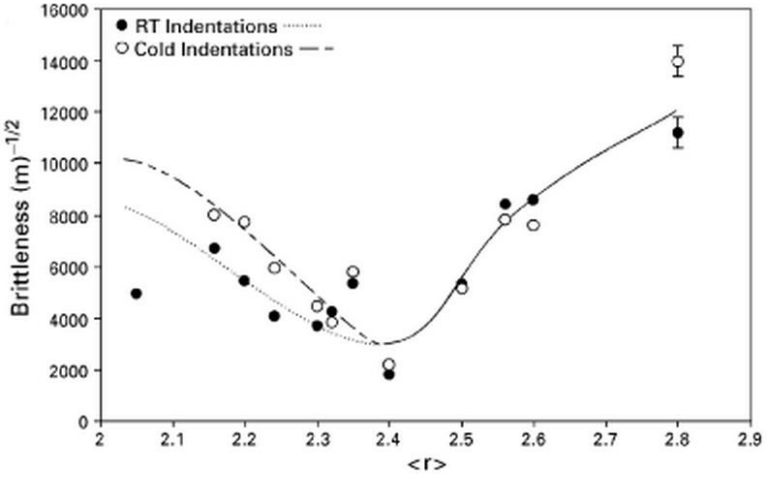
Mechanical property dependence on mean coordination number in network glasses

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

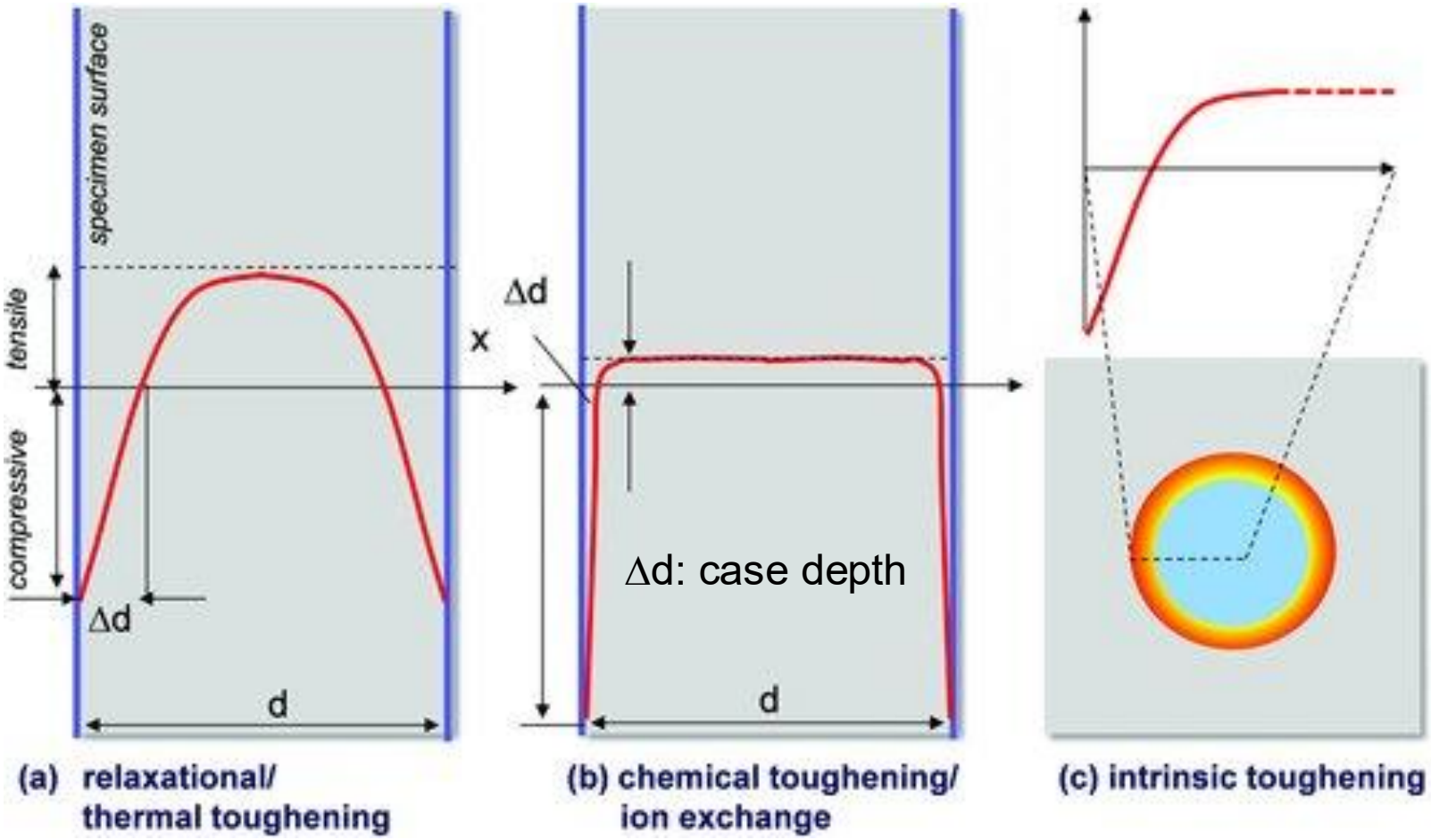




J. Am. Cer. Soc. **90**, 177 (2007)

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Thermal and chemical glass strengthening

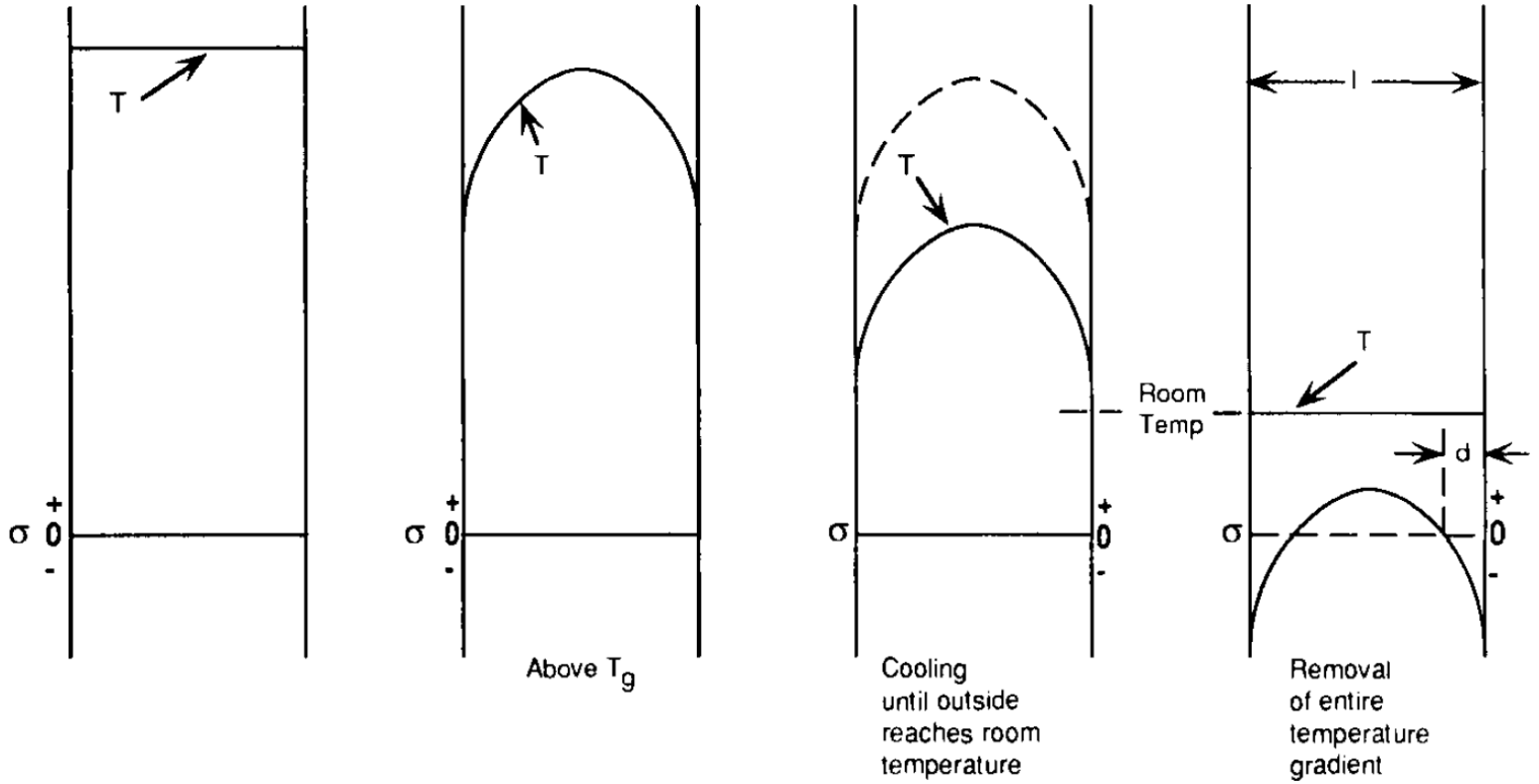


Adv. Mater. **23**, 4578 (2011)

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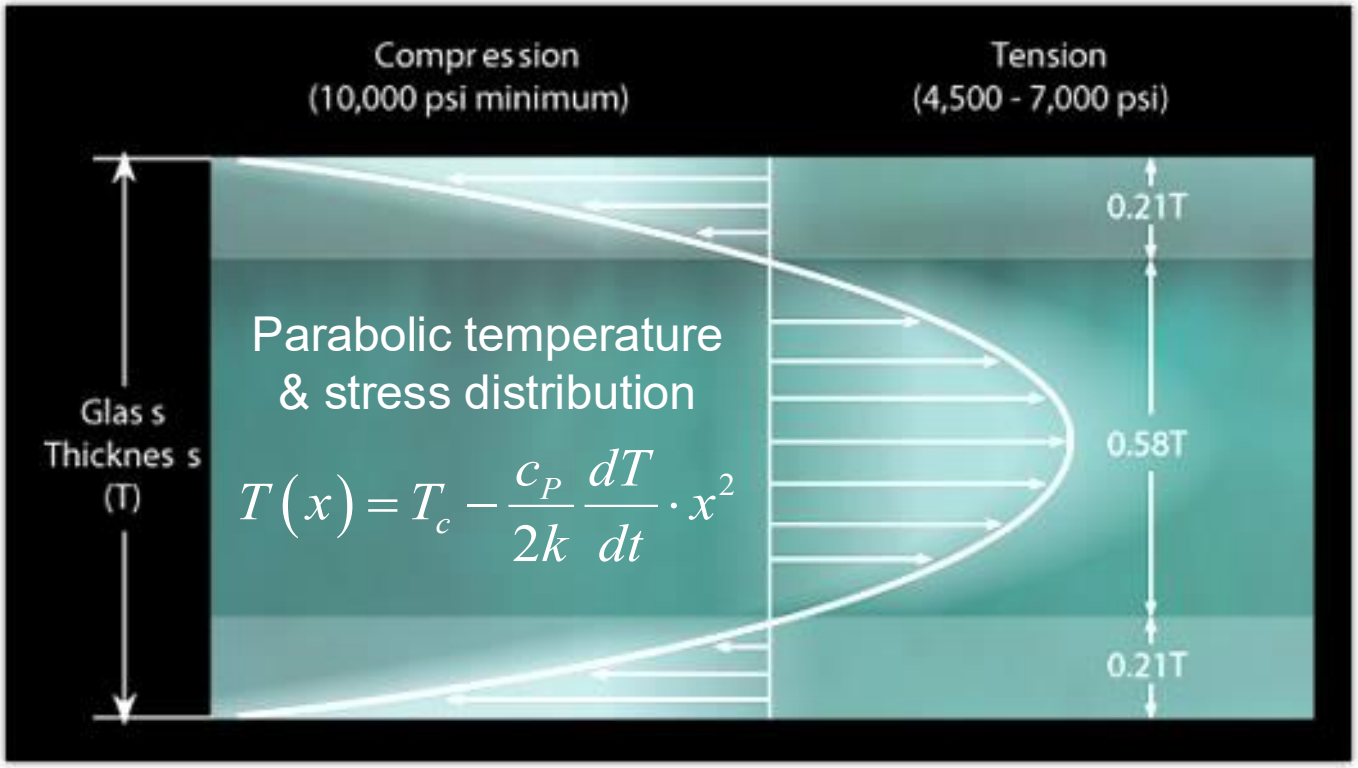
Heat-strengthened / tempered glass

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



Heat-strengthened / tempered glass

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



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Heat-strengthened / tempered glass

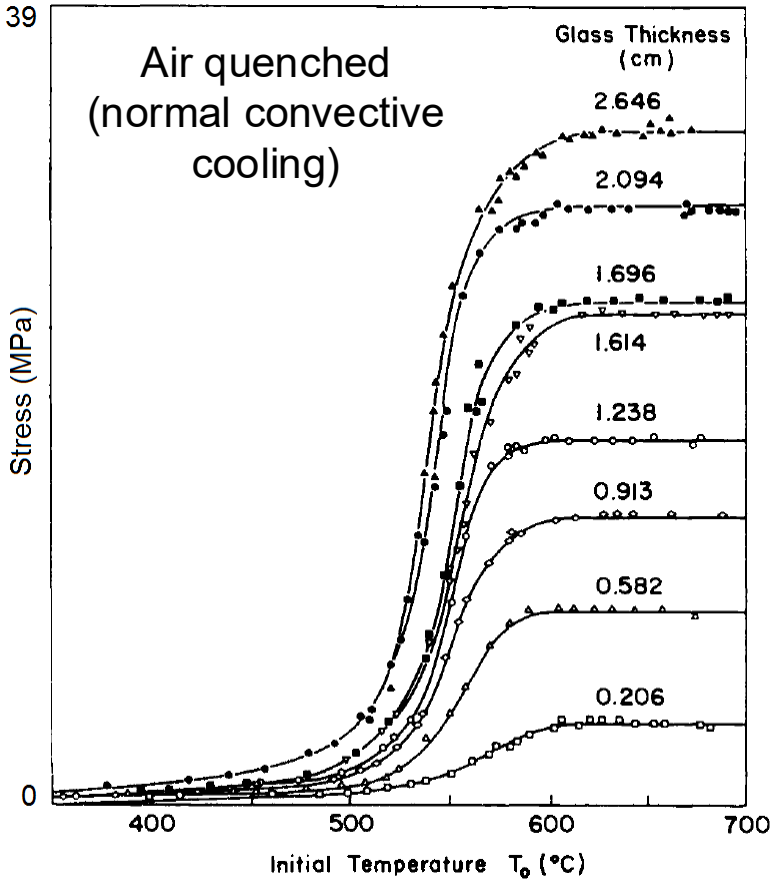
- Glass heated to 600 – 650 °C and force-cooled to generate surface compression

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

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

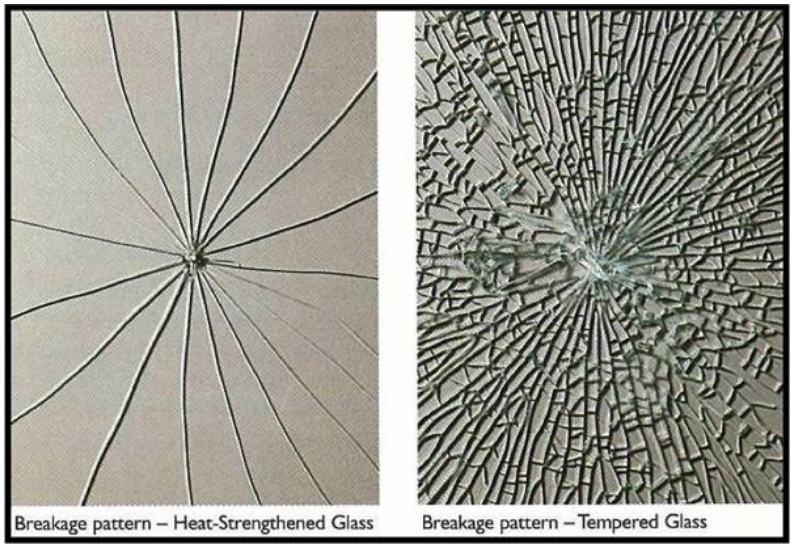
D : glass thickness

- 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

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Glass goes ballistic: Bullet vs. Prince Rupert's Drop



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Quantifying the strength of Prince Rupert's drops

TABLE I. Collective data from residual stress measurements of all the four PRDs' heads.

Drop No.	Drop's head diameter (mm)	Center stress (MPa) (tensile)	Surface stress (MPa) (compressive)	Ratio of maximum compressive stress to maximum tensile stress	Thickness of surface compressive layer (mm)
PRD1	7.4	400	−525	1.30	0.75
PRD2	6.5	225	−700	3.1	0.50
PRD3	6.5	360	−450	1.25	0.75
PRD4	6.5	230	−400	1.80	0.85

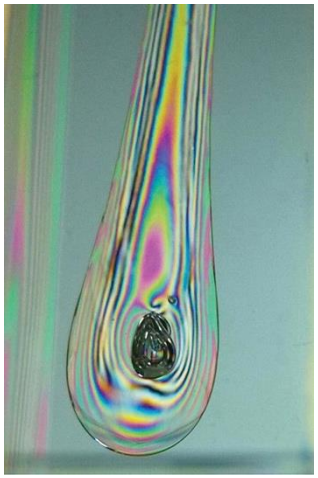


TABLE II. The response of four PRDs when compressed between tungsten carbide platens to high loads.

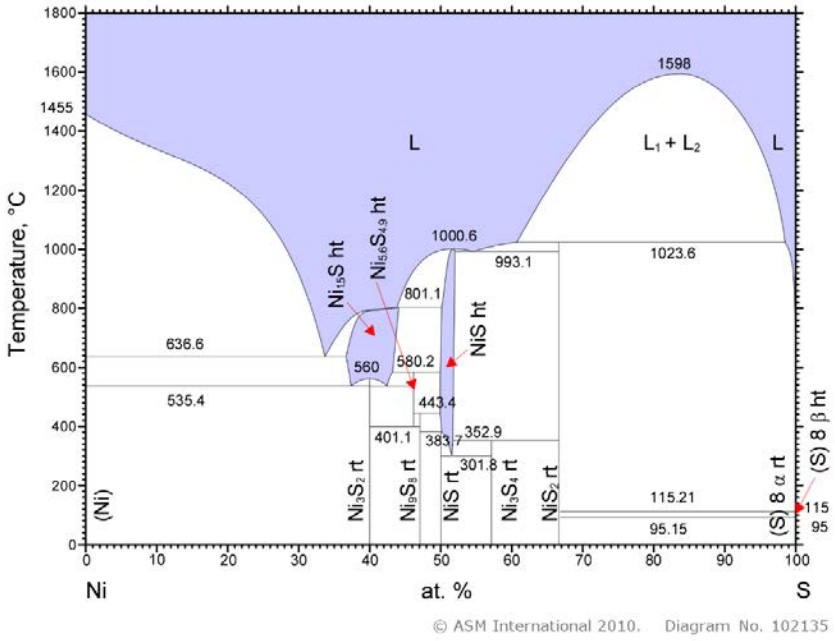
PRD No.	PRD's head diameter/mm	Maximum compressive load/N	Remarks
5	7.83	11 000	Broke at the maximum load
6	7.35	19 000	Broke at the maximum load
7	7.20	10 000	Did not break
8	~7.5	18 000	Broke during unloading

Appl. Phys. Lett. **109**, 231903 (2016)

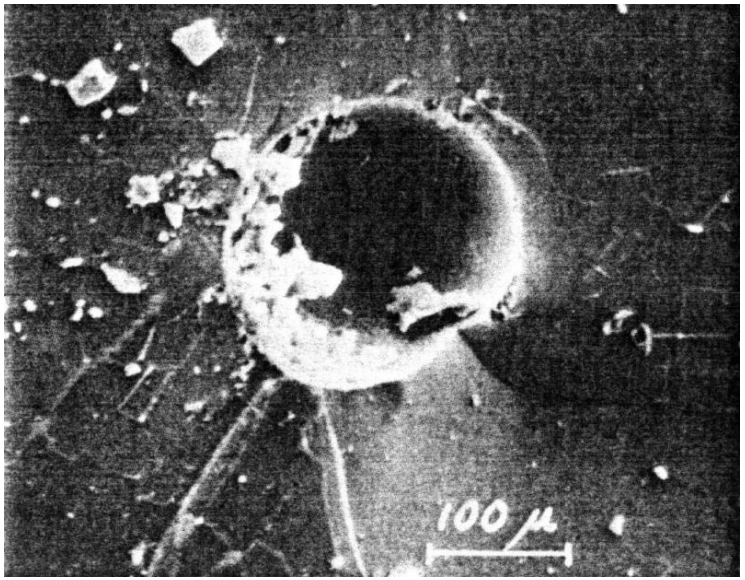
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Premature fracture of tempered glass

- 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
- Heat soaking: a destructive test to trigger NiS phase change



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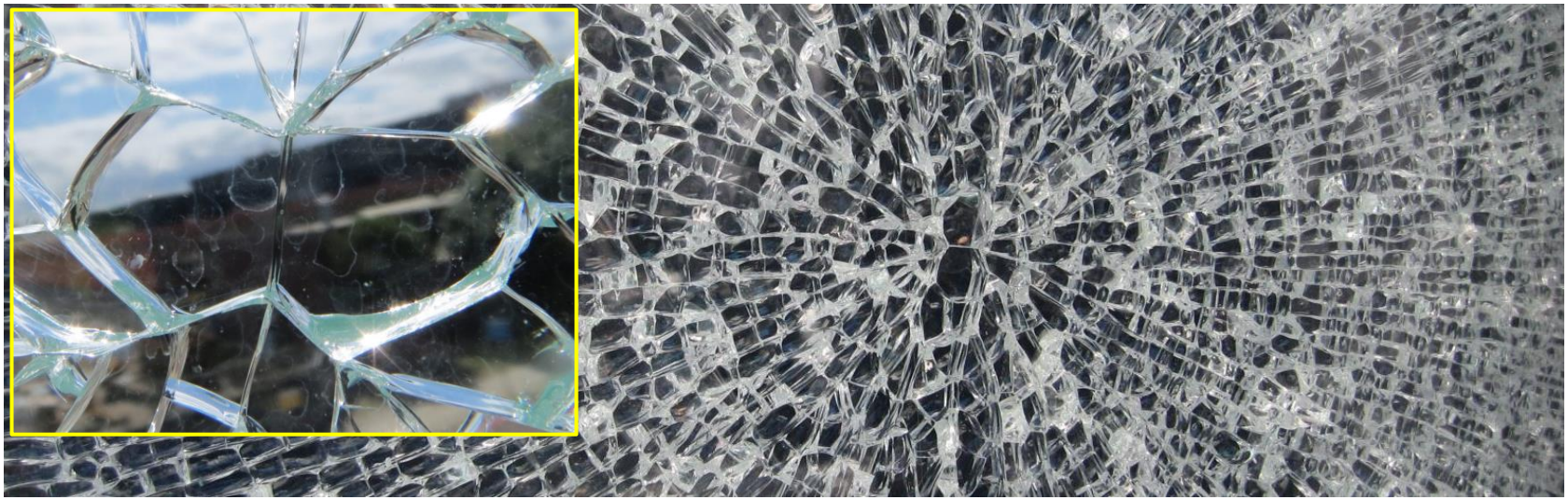


Fracture **3**, 985 (1977)

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The “butterfly” pattern often associated with NiS-induced breakage

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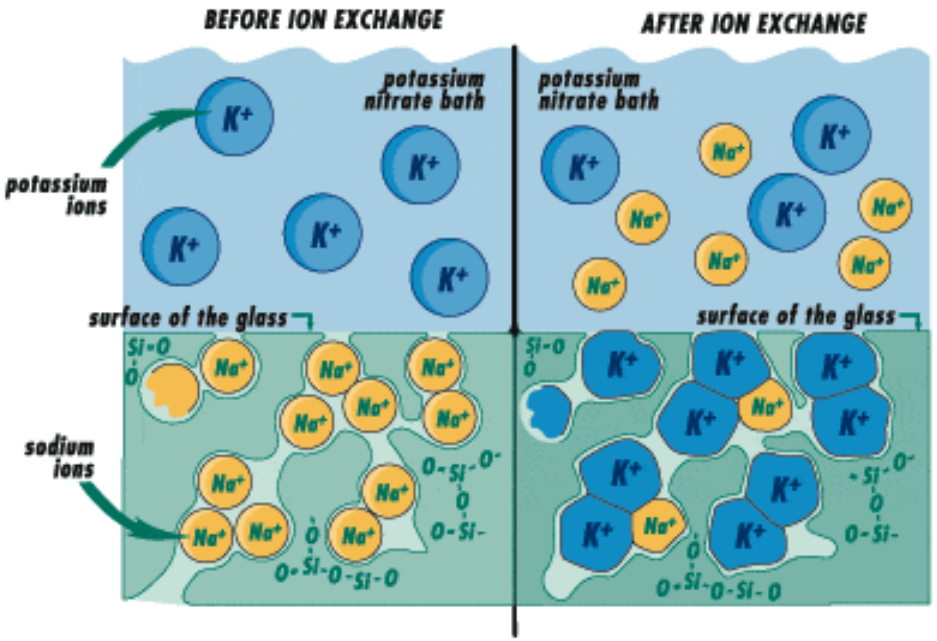
Chemical strengthening

- 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



- Only applies to alkali/alkali earth glasses
- Typical case depth in soda-lime glass: 25 to 35 μm

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

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INTERNATIONAL JOURNAL OF Applied Glass SCIENCE

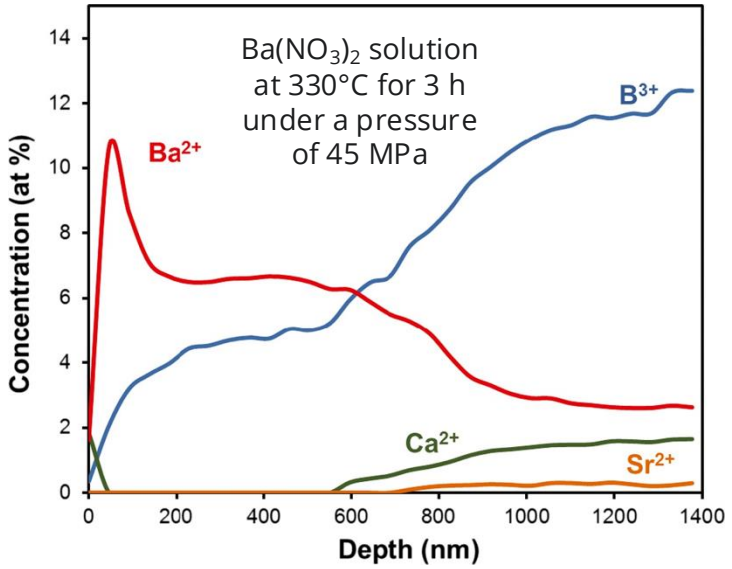
Communication

Chemical Strengthening of Alkali-Free Glass via Pressure Vessel Ion Exchange

John C. Mauro ✉, Carlton M. Truesdale, Kaveh Adib, Alana M. Whittier, Arthur W. Martin

First published: 10 November 2016 | https://doi.org/10.1111/ijag.12249

- Thermal tempering is not applicable to thin glass
- Alkaline earth salts have high melting points, tend to decompose into oxides, and are highly corrosive
- Ion exchange in subcritical aqueous solutions



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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 6 (sodium aluminosilicate glass)

Viscosity

Softening Point ($10^{7.6}$ poises)	884.9 °C
Annealing Point ($10^{13.2}$ poises)	624 °C
Strain Point ($10^{14.7}$ poises)	572 °C

Addition of aluminum increases softening temperature and T_g

Properties

Density	2.40 g/cm^3
Young's Modulus	77 GPa
Poisson's Ratio	0.21
Shear Modulus	31.9 GPa
Vickers Hardness (200g load)	
Unstrengthened	611 kgf/mm^2
Strengthened	678 kgf/mm^2
Fracture Toughness	0.7 MPa m$^{0.5}$
Coefficient of Expansion (0-300°C)	75.2 x 10^{-7}/°C

$$B = \frac{E}{3(1-2\nu)} = 44.3 \text{ GPa}$$

$G/B = 0.72 > 0.42$ brittle

Increased surface hardness and minor impact on fracture toughness

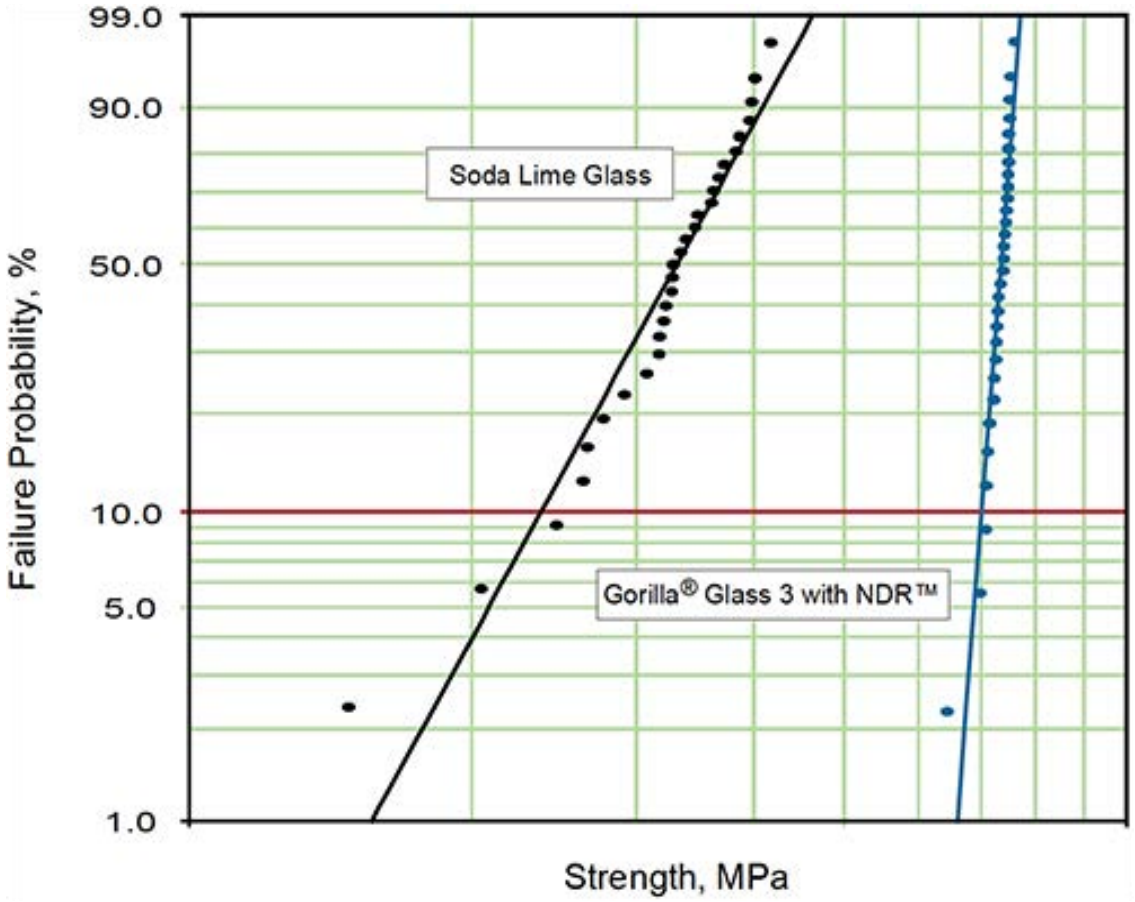
Chemical Strengthening

Compressive Stress Capability	≥ 900 MPa
Depth of Compression Capability	≥ 80 µm

Increasing stress & larger case depth compared to prior generations

Data from Corning product information

Weibull analysis on Gorilla glass



- Enhanced mean strength
- Larger Weibull modulus: improved consistency

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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 GPa
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:

GT ASF Sapphire Cover; Schott Sapphire Glass; Corning Gorilla 6 Glass; Schott Xensation Cover Glass; Asahi Dragontrail Glass

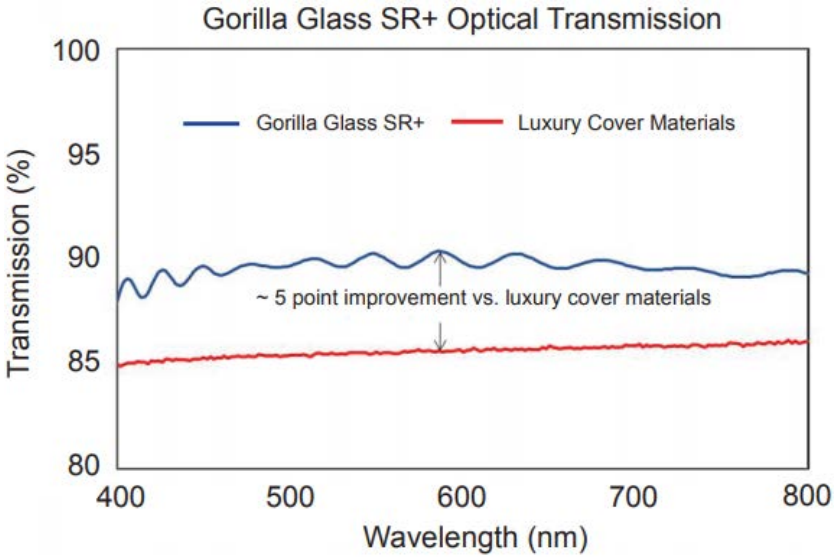
Glass still has more to offer: scratch resistance



Figure 1 - Gorilla Glass SR+ scratch performance vs. other materials (150 grit garnet sandpaper scratch test, 1 cycle under 1, 2 and 4 kg loads)

** Alternative Luxury Cover Materials*

Data from Corning product information



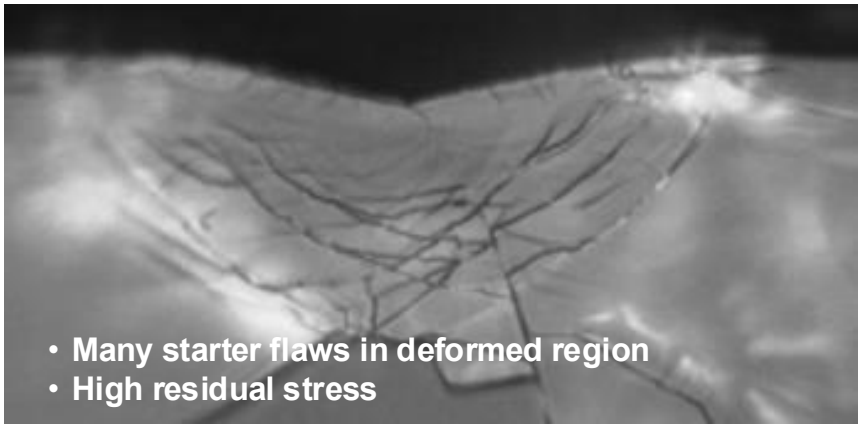
Gorilla Glass SR+ transmission in the visible spectrum

? A surface coating layer with ~ 2.25 μm thickness and an index 0.03 higher (or lower) than the substrate glass at 600 nm wavelength

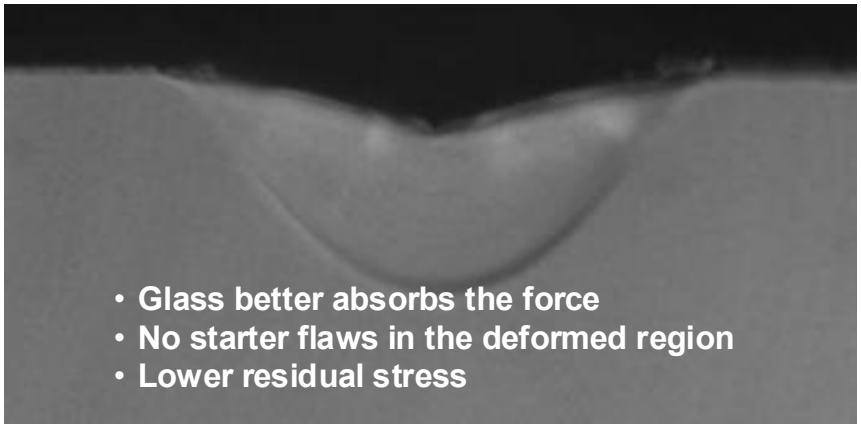
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Glass still has more to offer: native damage resistance (NDR)

Alternative cover glass experiences Lateral Cracking

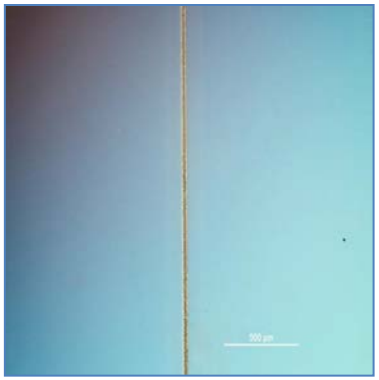


Glass with NDR better absorbs the force with Densification



Competitive Aluminosilicate Glass After Ion Exchange 7 Newton Scratch



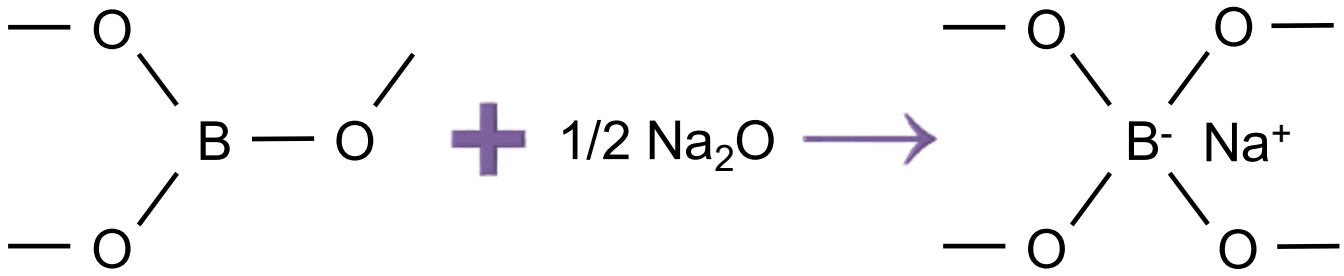


Glass with NDR 7 Newton Scratch

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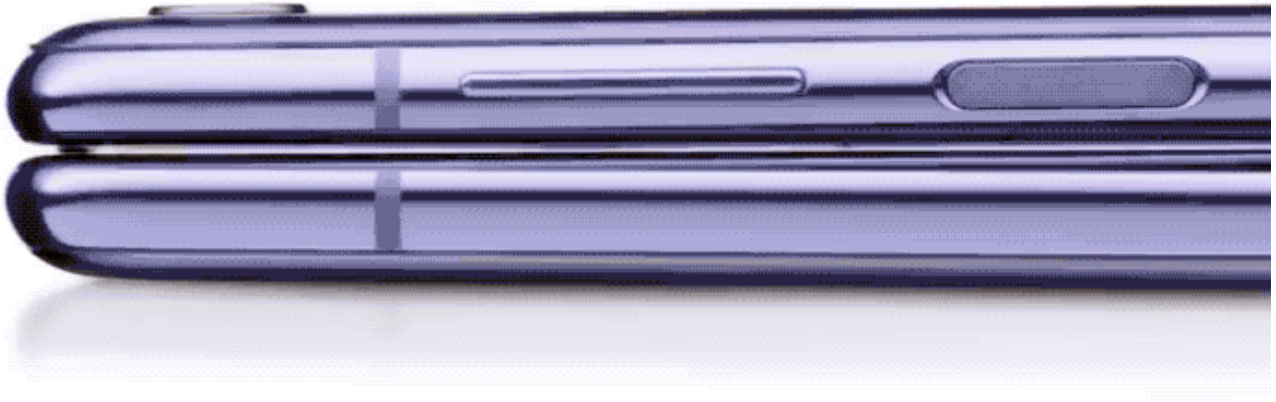
$B_3 \rightarrow B_4$ conversion



Trigonal boron creates a more open glass structure that is able to densify via plastic deformation upon mechanical compression to avoid crack initiation

Chem. Mater. **28**, 4267-4277 (2016)

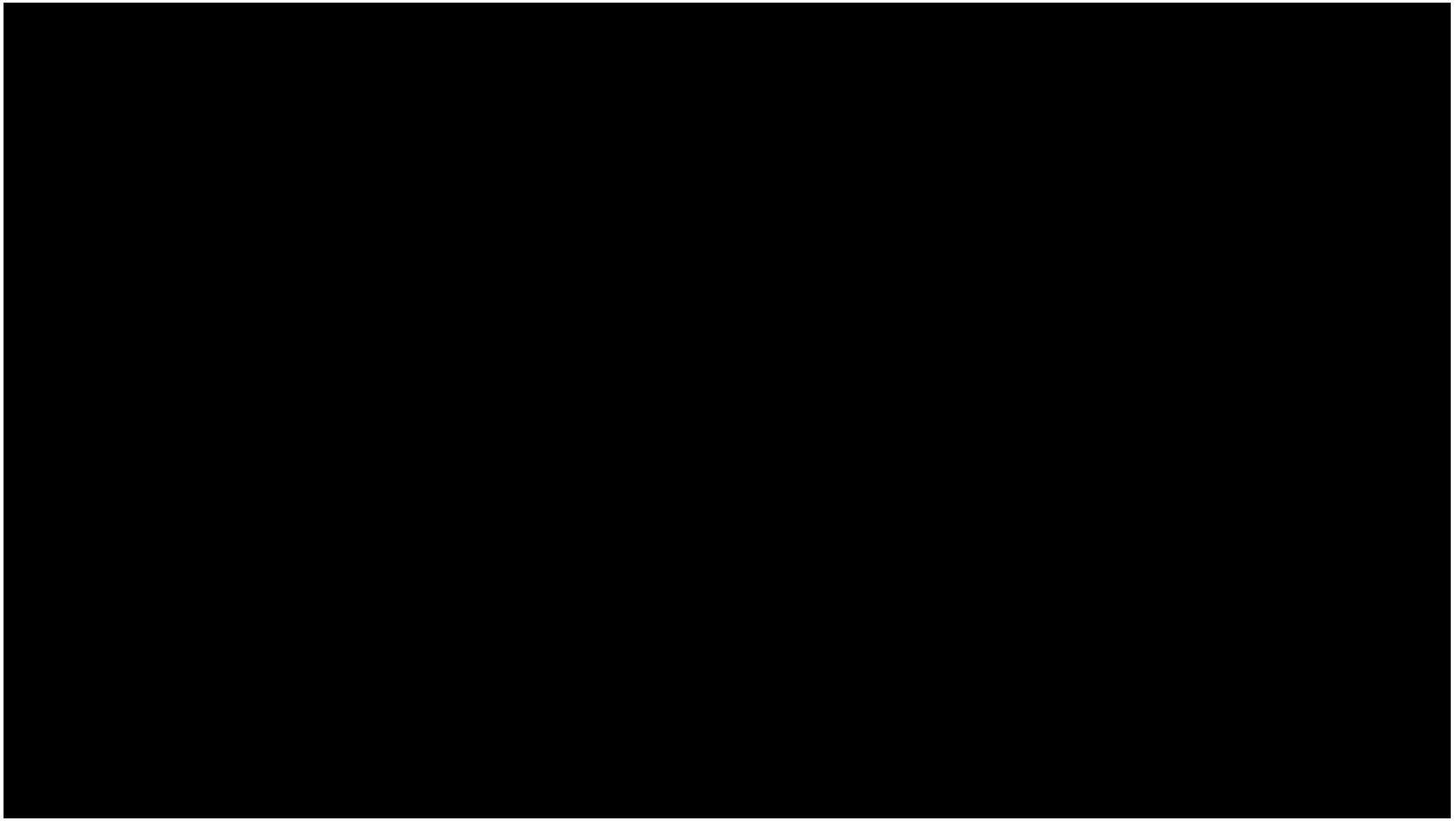
The first foldable phone with a glass screen



Samsung Galaxy Z Flip

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Ultra-thin flexible glass

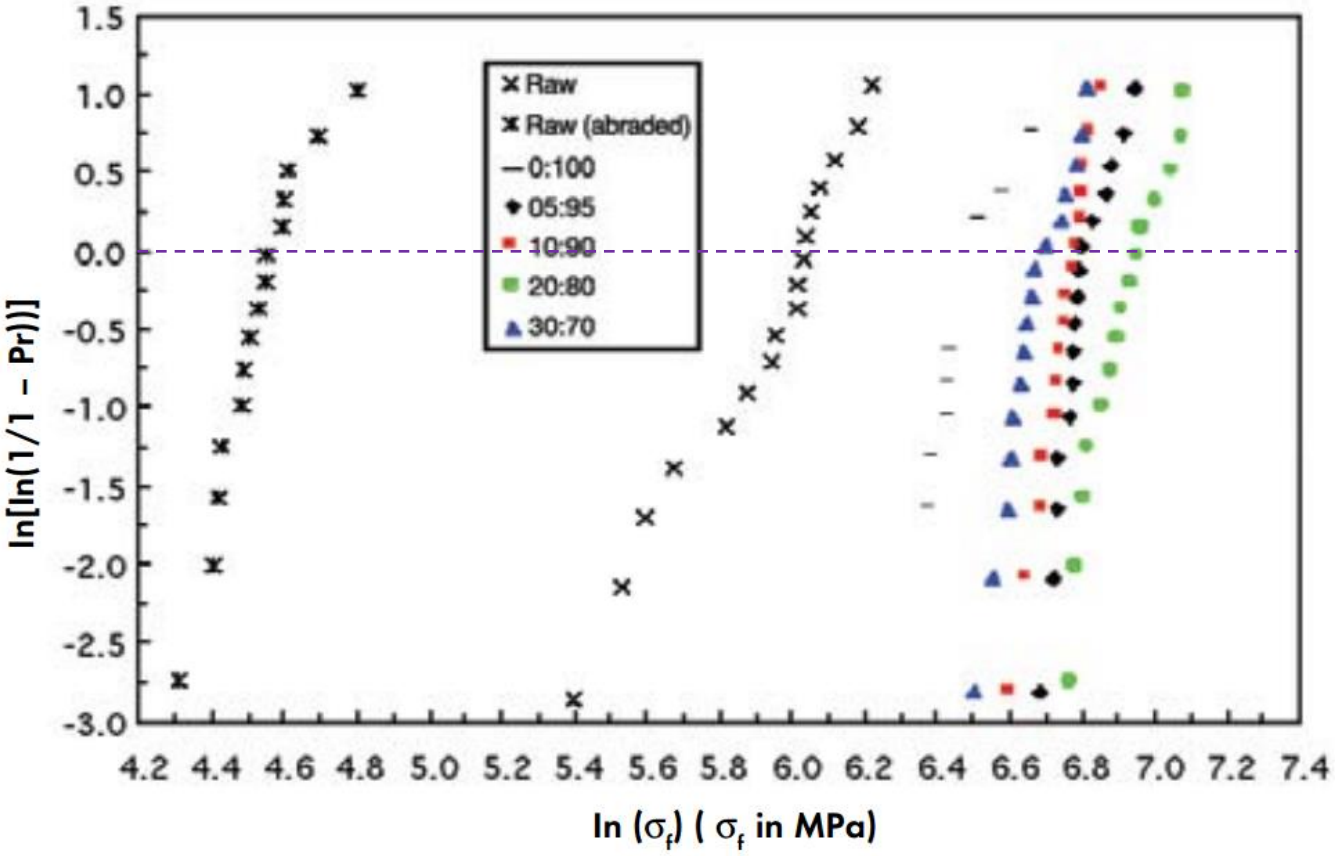


Glass compositions for deep ion exchange and high MOR†

	PPG Shelestak 20050090377	Corning 0317	Pilkington 6 518 211 Feb. 11, 2003	St. Gobain 5 773 148 June 30, 1998	St. Gobain 6 333 285 Dec. 25, 2001	Schott 5 895 768 Apr. 20, 1999	Schott Robax	Saxon Ion-Armor™ NEG N-11	Saxon Ion-Armor™ NEG Narumi
Composition (%)									
SiO_2	60–75	62.3	58–70	65–76	55–71	63–67.5	67.2	65.7	65.1
Al_2O_3	18–29	16.4	5–15	1.5–5	>2	9.5–12	20.1	22	22.6
Li_2O	3–9						3.2	4.5	4.2
MgO	0–2.6	3.3	4–10	4–8	4–11	3–9	1.1	0.5	0.5
CaO	0–1.27	0.3		0–4.5			0.05		
BaO							0.9		
ZnO							1.7		
Na_2O	0.39–2.39	12.8	12–18	10–18	9–16.5	8.5–15.5	0.4	0.5	0.6
K_2O	0.07–0.1	3.5	0.1–5	1–7.5	4–10	2.5–4	0.23	0.3	0.3
B_2O_3				0–4					
TiO_2		0.75				0.5–1.5	2.7	2	2
ZrO_2	0–3						1.7	2.5	2.9
Fluorine									0.1
Properties									
Invading ion	K^+	K^+	K^+	K^+	K^+	K^+	K^+	K^+ and Na^+	K^+ and Na^+
Surface compression (MPa)	830	600	400	500	600	900‡	550/850	1,000	800
Temperature (°C)	≤425	500	430	415	380	520	500/500	450–475	450–475
Time (day)	~1	1	4	18	2	0.83	8/2	0.33	1
Case depth (µm)	≤420	225	500	265	90	220	80/40	600	1,000

†Glasses are identified by manufacturer, trade name and patent number (and date) or patent application number on a "best information available" basis. ‡MOR.

Chemical strengthening of lithium aluminosilicate glass



Weibull plot after strengthening in varying ratios of $NaNO_3$ + KNO_3 baths

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

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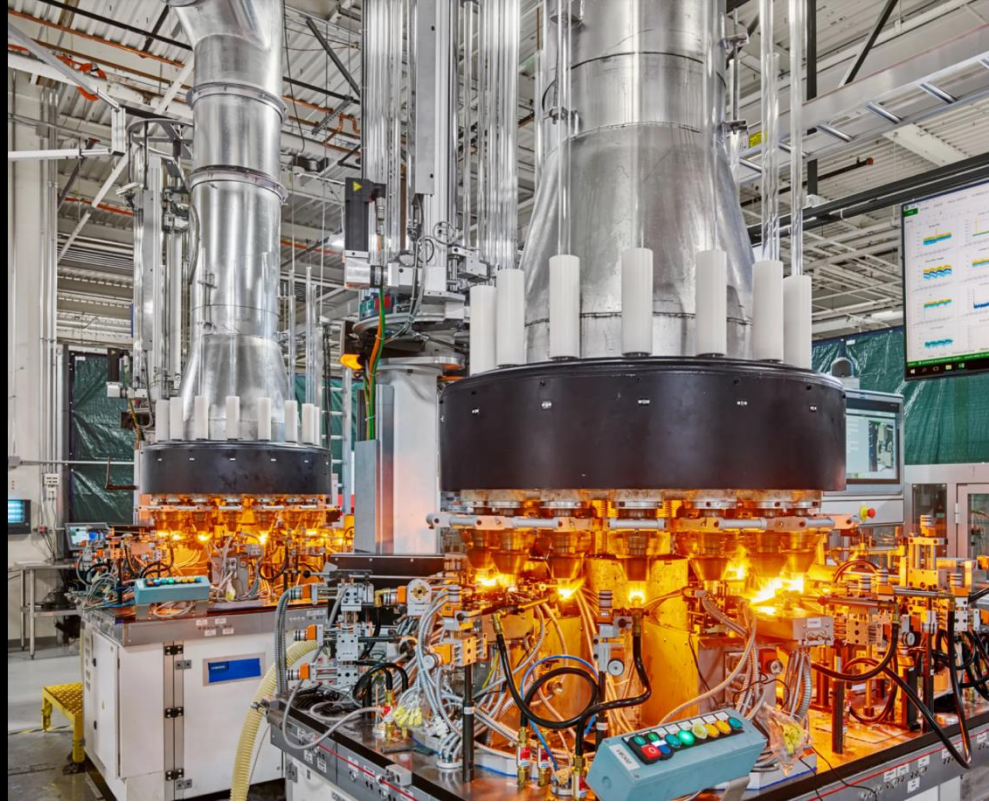
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THE RACE TO MAKE VIALS FOR CORONAVIRUS VACCINES

A Corning factory in upstate New York is running around the clock to help meet the urgent demand.

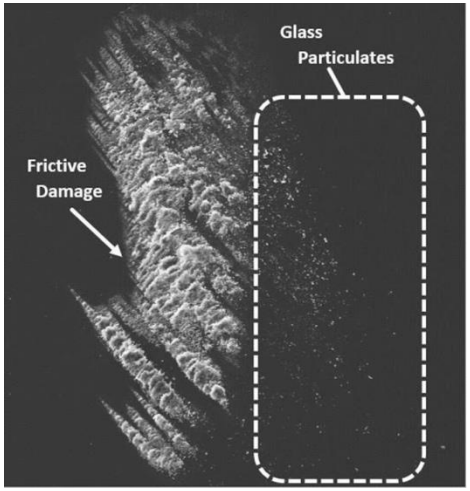
Photography by Christopher Payne

November 30, 2020



CORNING
Valor™ Glass

- Boron-free formulation to minimize delamination
- Surface coating to reduce friction and wear
- Ion exchange to boost mechanical strength



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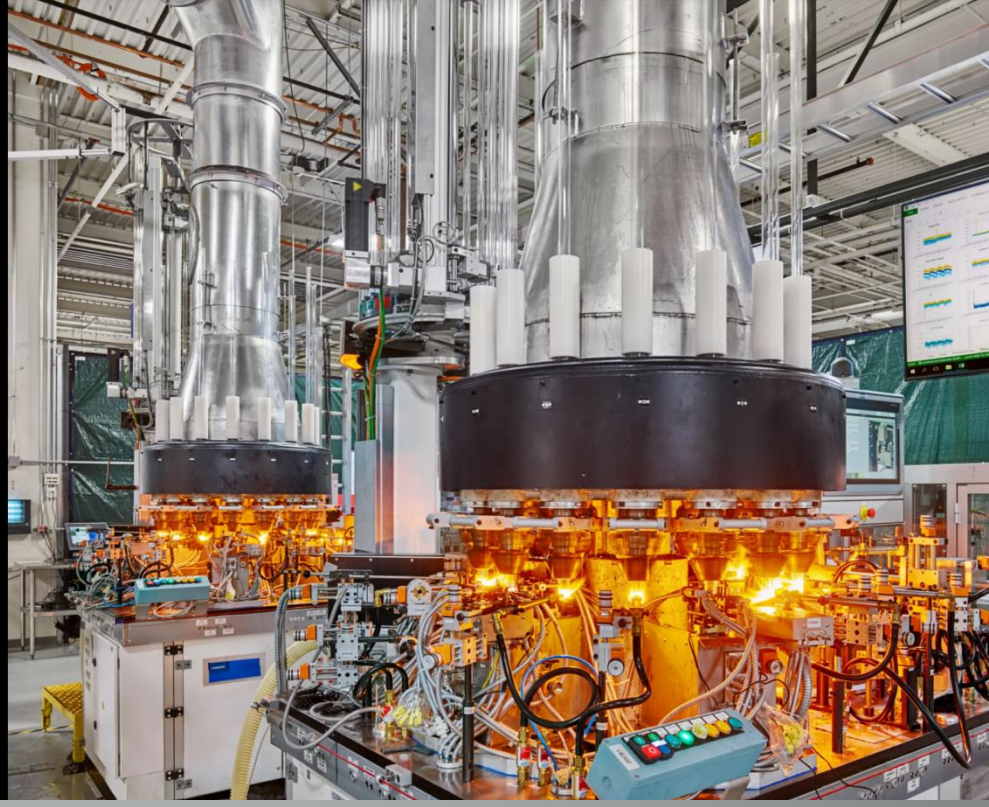
PORTFOLIO DECEMBER 7, 2020 ISSUE

THE RACE TO MAKE VIALS FOR CORONAVIRUS VACCINES

A Corning factory in upstate New York is running around the clock to help meet the urgent demand.

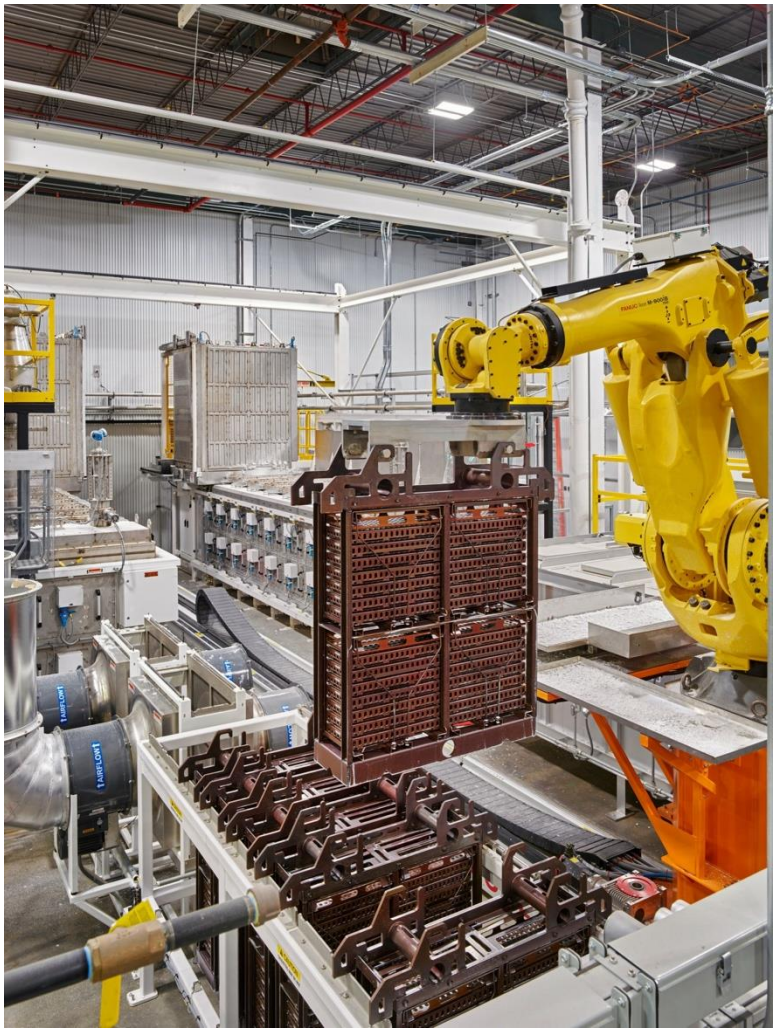
Photography by Christopher Payne

November 30, 2020

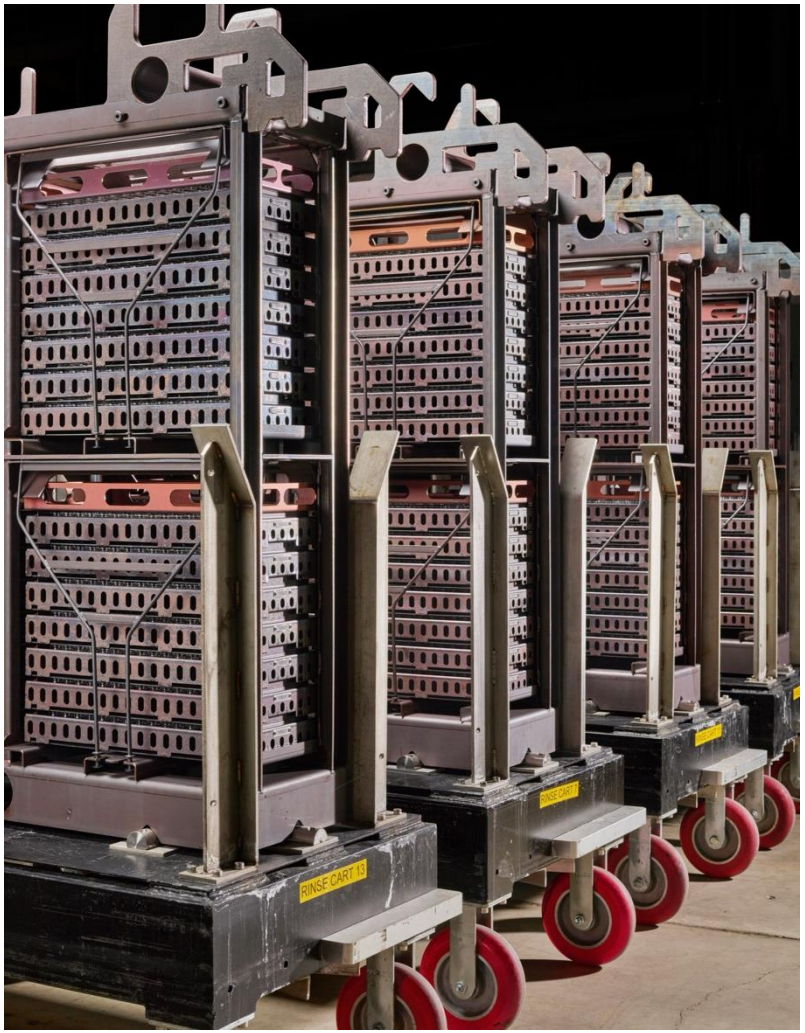




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A robotic arm dunks racks of vials into molten salt to strengthen the glass.

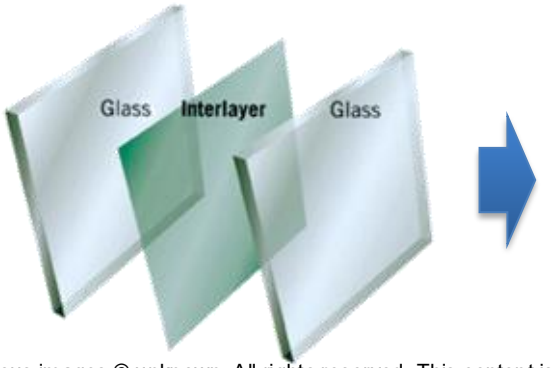


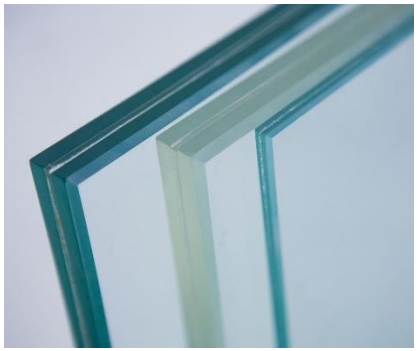
After removal from the salt bath, the vials are submerged in water for an initial rinse.

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Configurational design: laminated glass

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





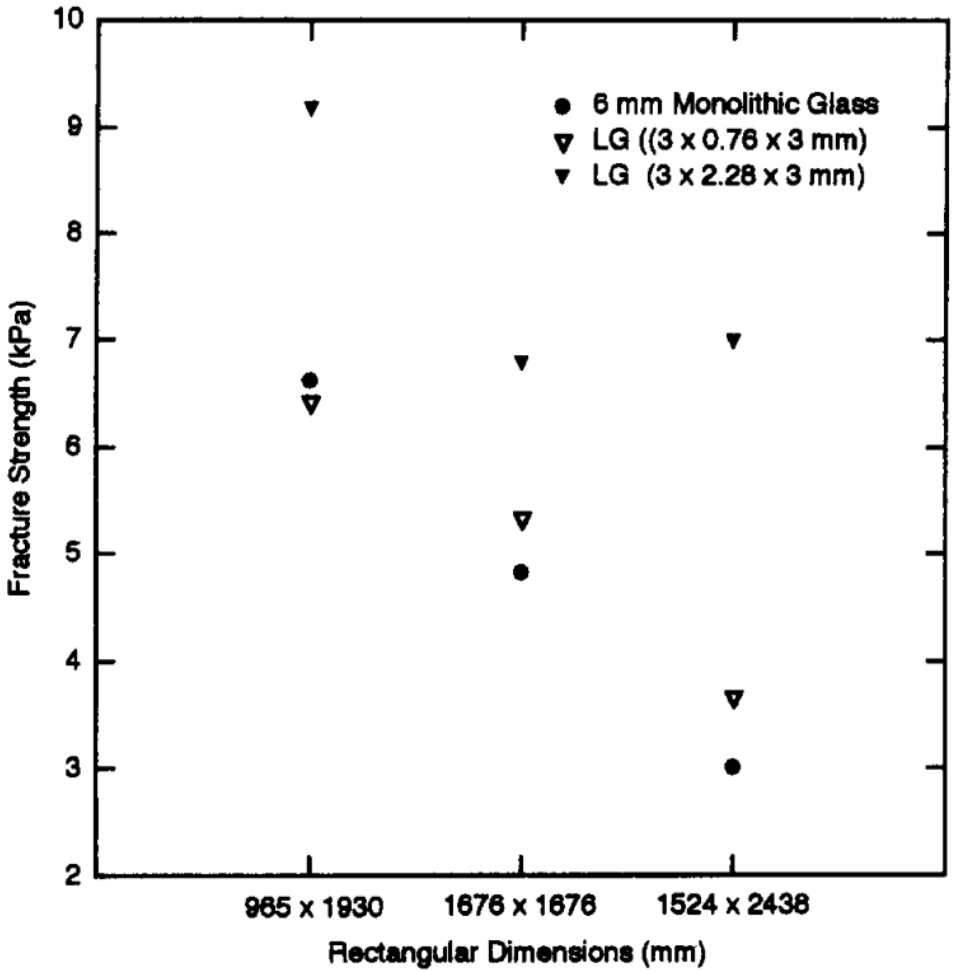


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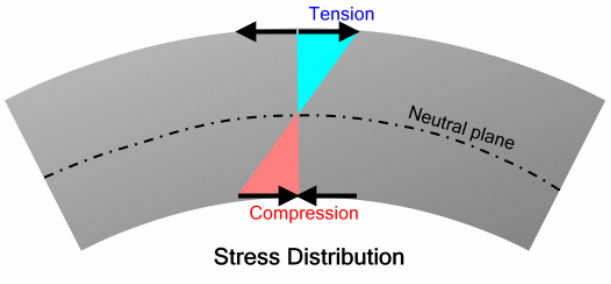
Facture toughness of laminated glass

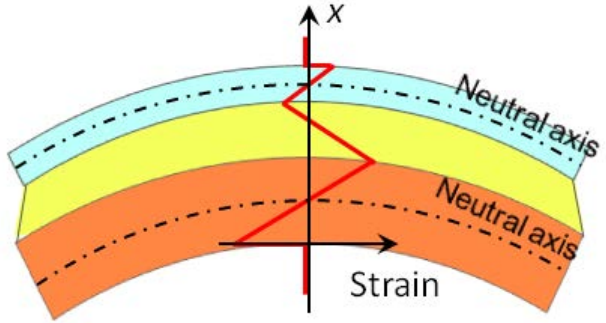


Laminated glass is tougher than monolithic glass sheets

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

Properly design laminated structures are tougher than monolithic glass



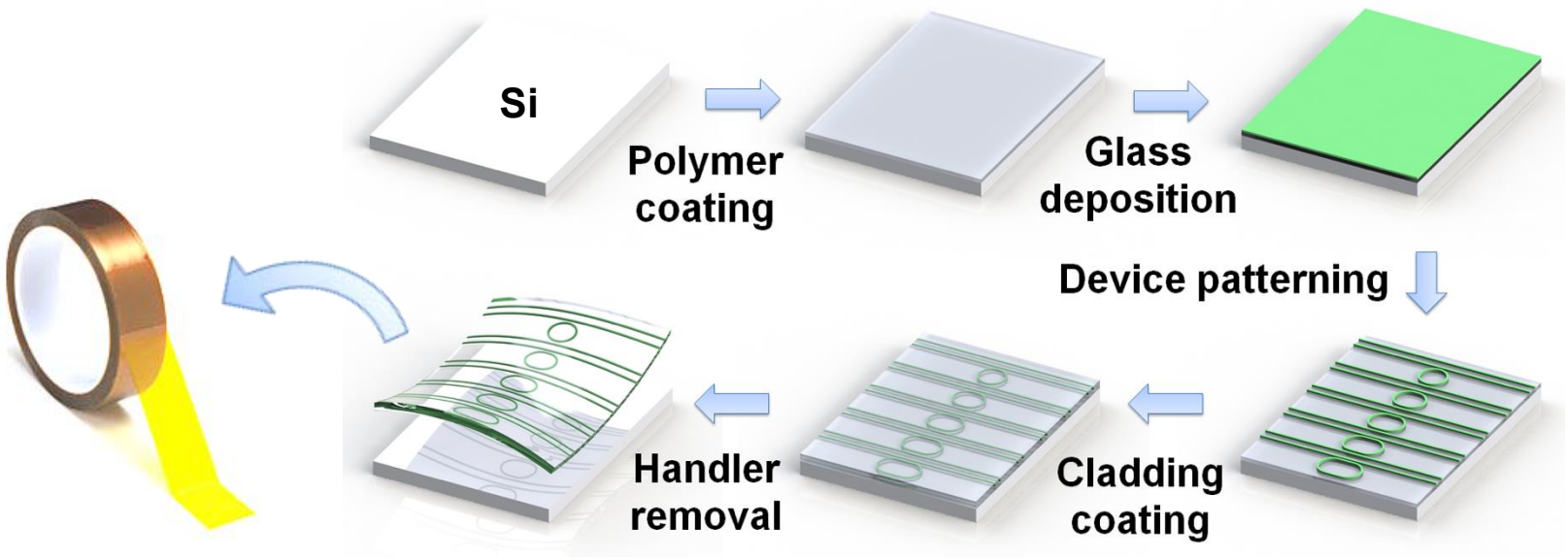


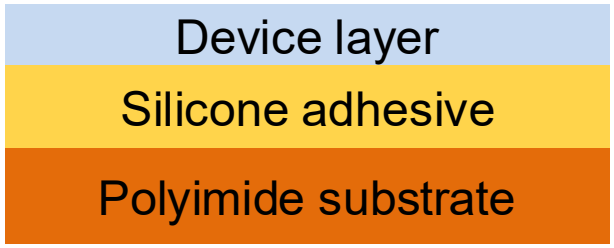
	Classical multilayer bending theory	The new multi-neutral-axis theory
Formulation	$z(\varepsilon=0)=\sum_{i=1}^{n}E_i d_i\left[\left(\sum_{j=1}^{i}d_j\right)-\frac{d_i}{2}\right]\Big/\sum_{i=1}^{n}E_i d_i$	$\sum_i \bar{E}_i \int_{-h_i/2}^{h_i/2}(a y_i + b)dy_i = 0$
Assumption	No shear strain	The soft 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)

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Flexible glass photonic device fabrication





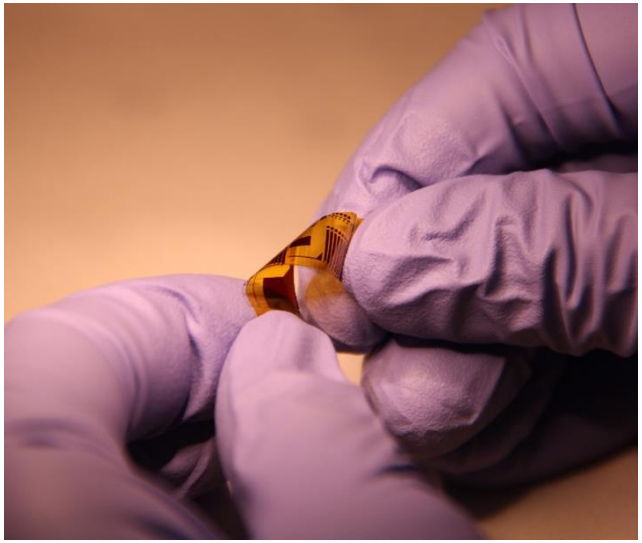
} Tape

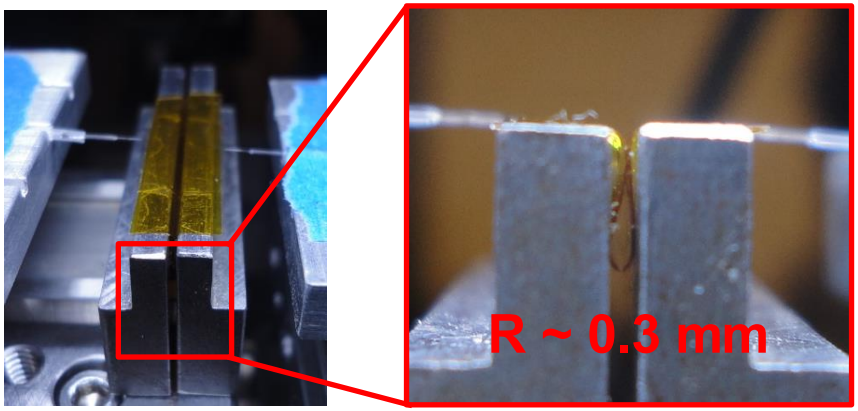
Sandwiched “Oreo” structure for stress relaxation

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

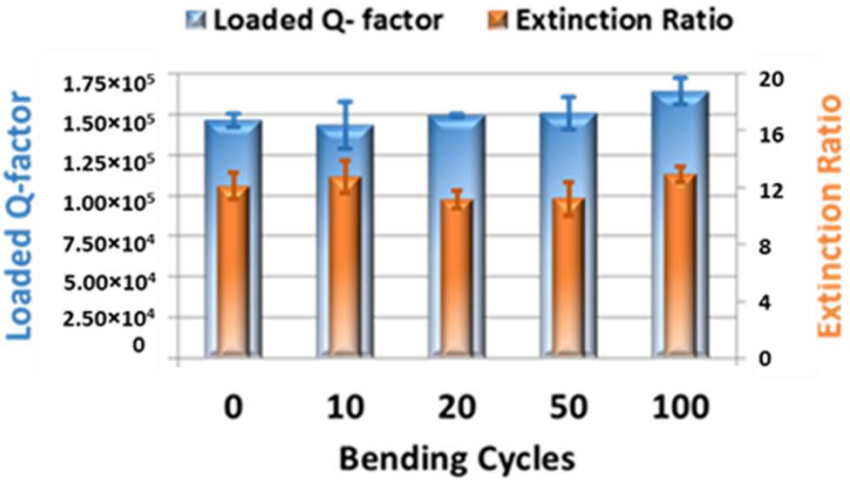
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Bend… but don't break!

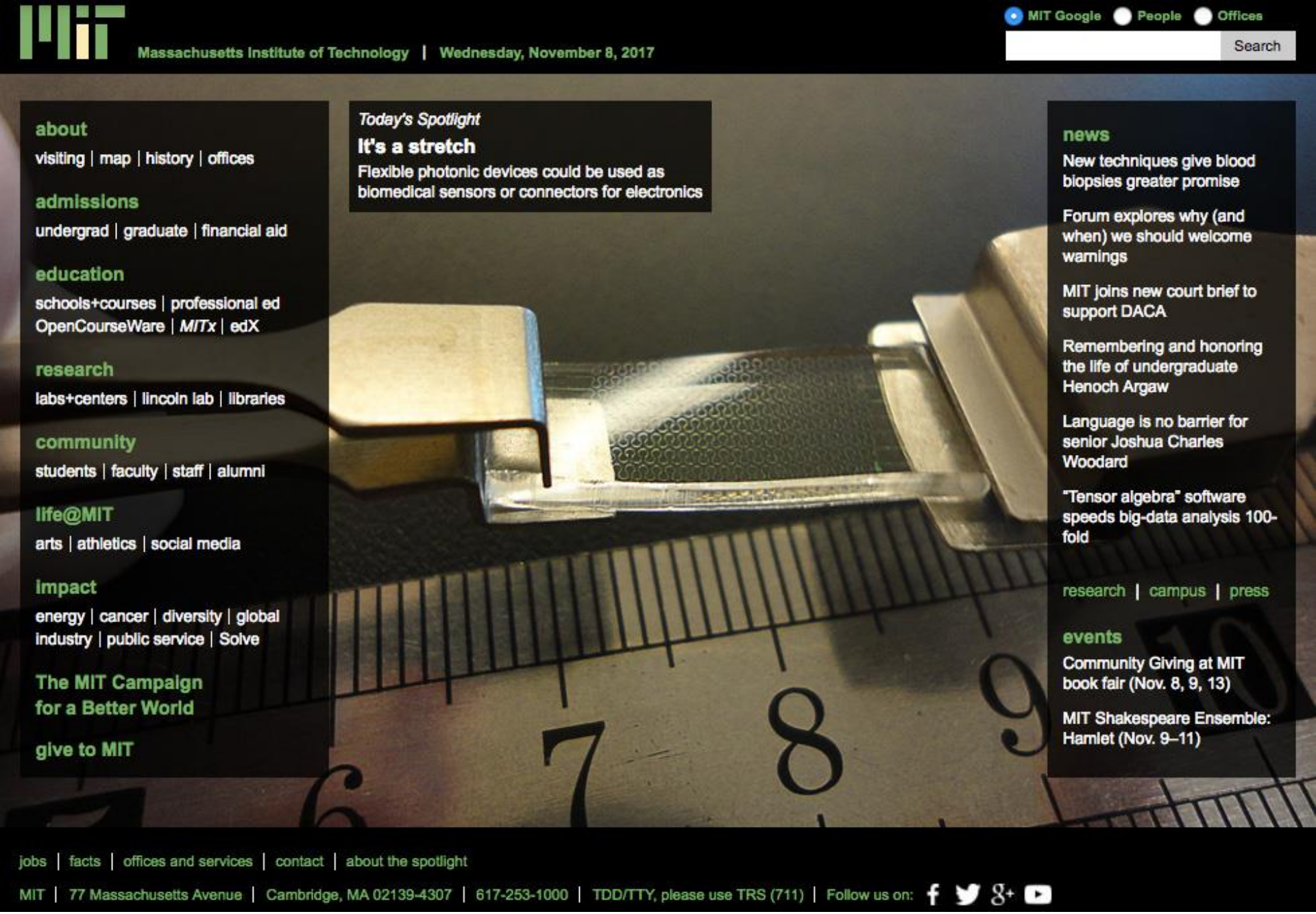




The multi-neutral axis design enables foldable, robust photonic circuits



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

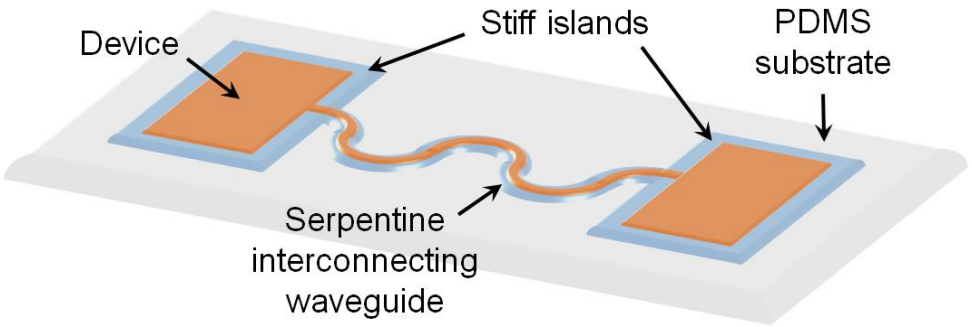


Light Sci. Appl. **7**, e17138 (2018)

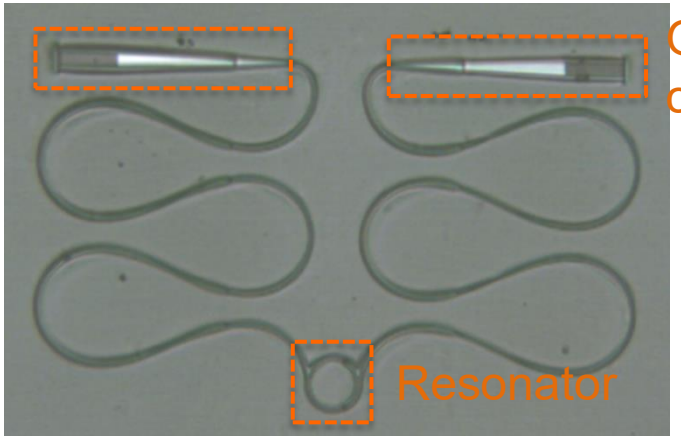
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Making stretchable photonics out of rigid glass





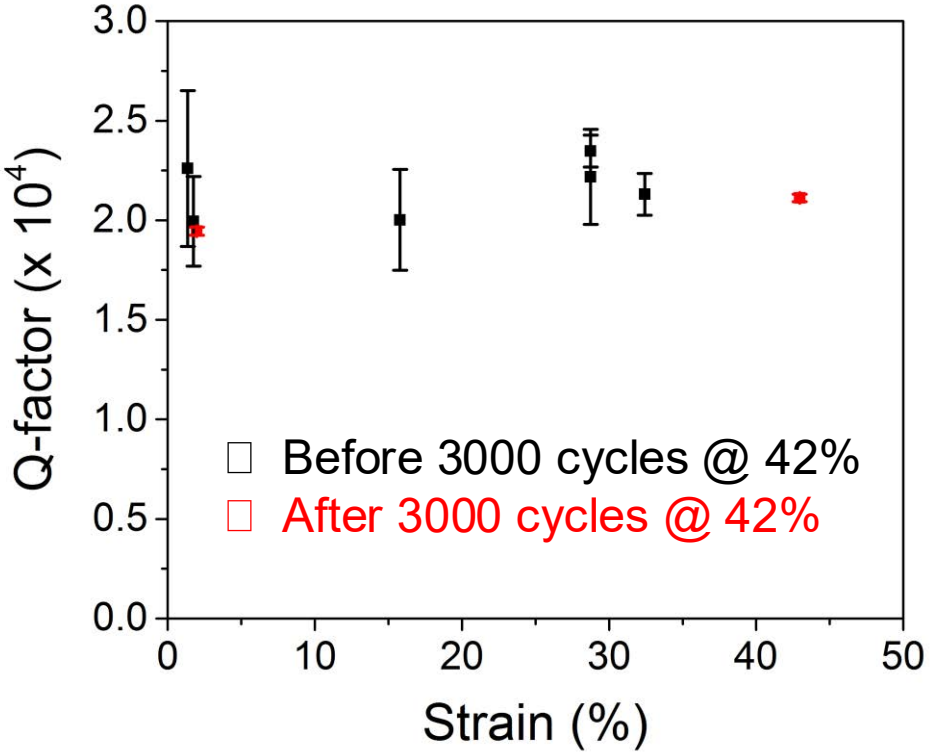
Devices on locally stiffened islands interconnected by serpentine waveguides

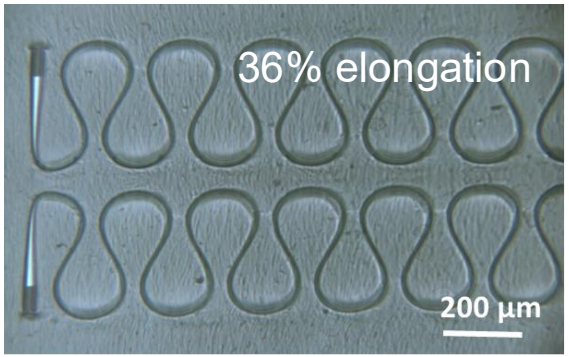


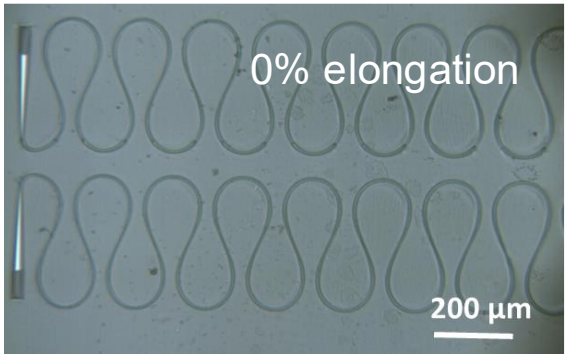
Light Sci. Appl. **7**, e17138 (2018)

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Stretching serpentine glass waveguides





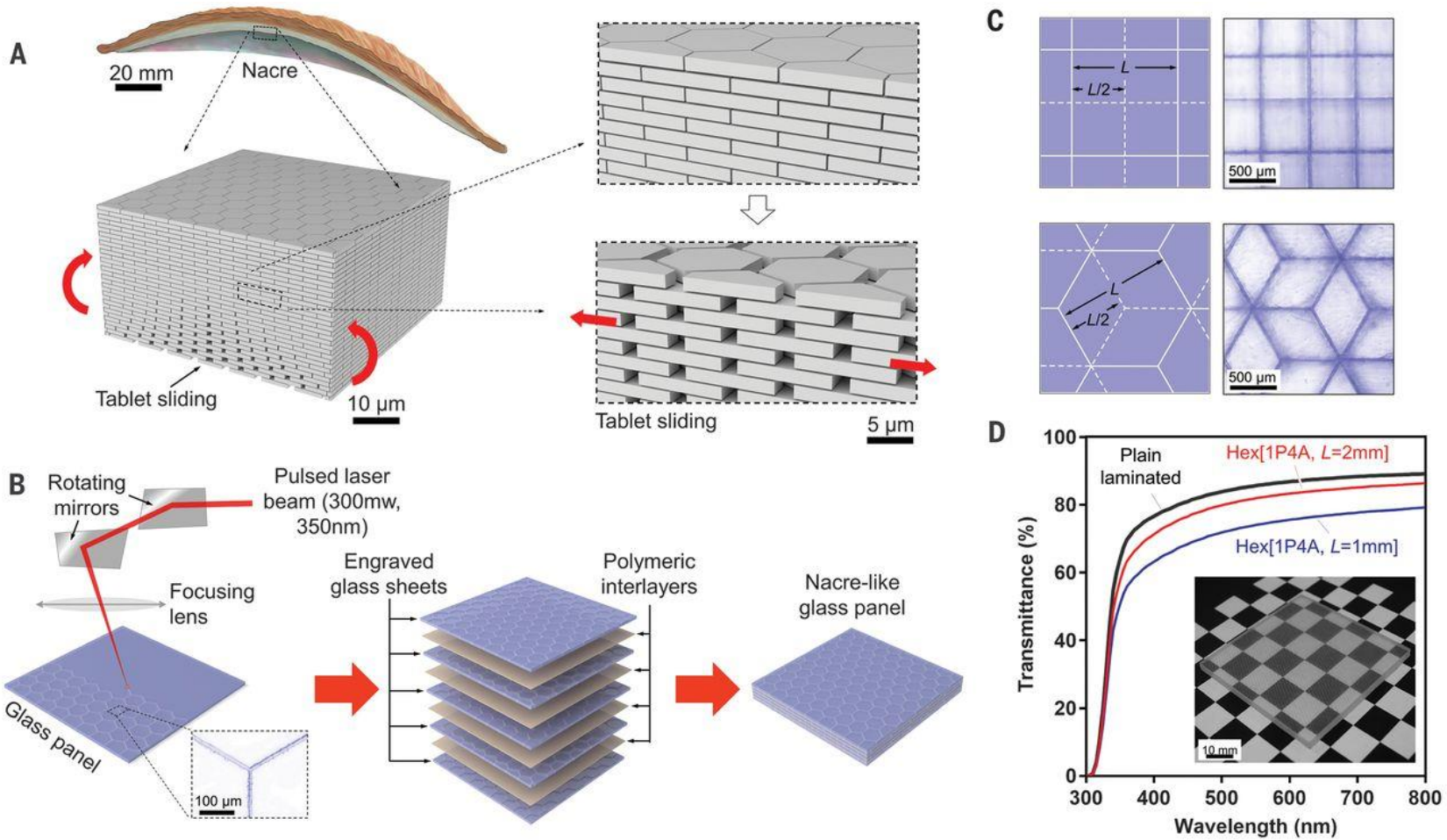


Serpentine waveguides are robust against repeated stretching

Light Sci. Appl. **7**, e17138 (2018)

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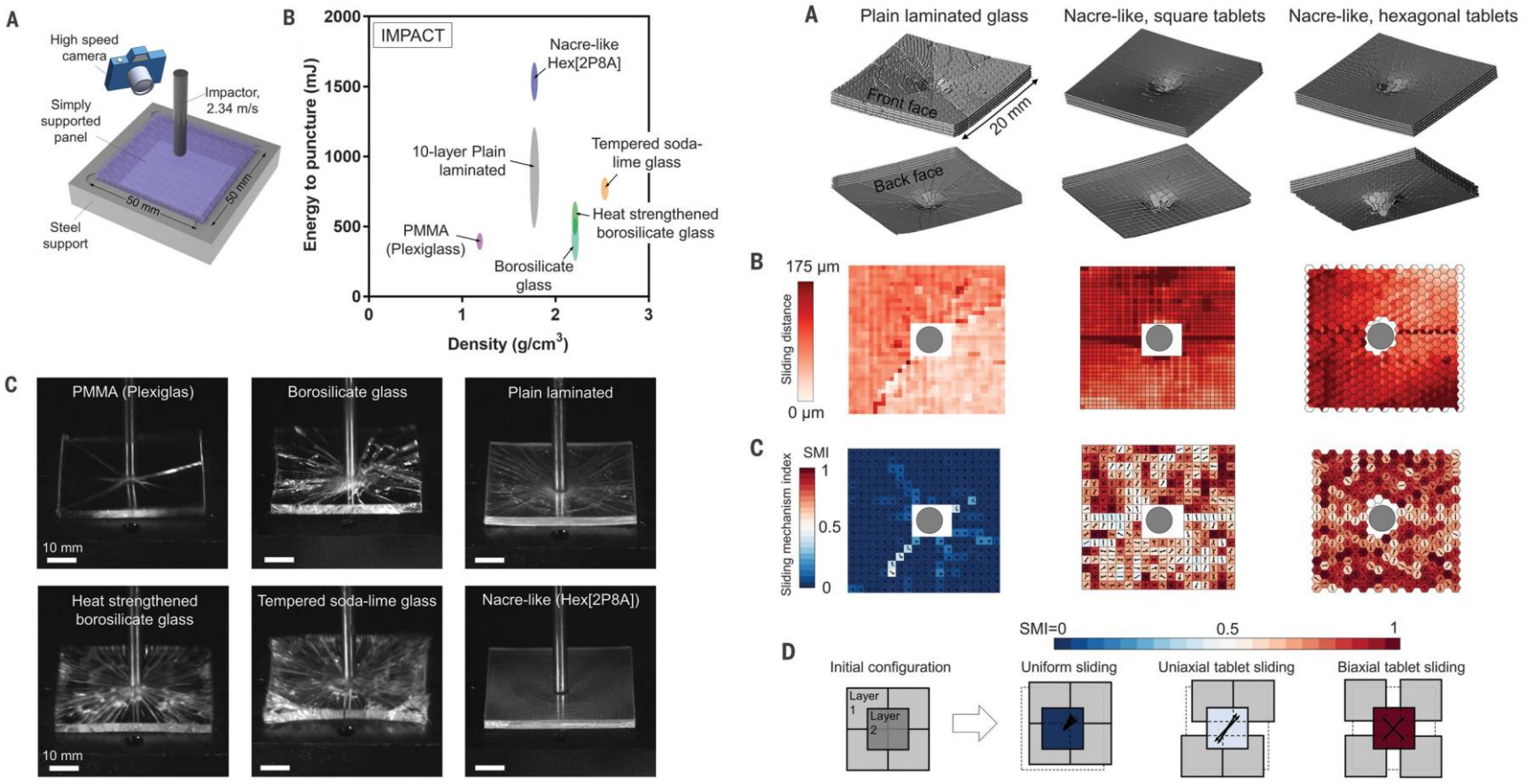
Nacre-inspired toughened glass



Science **364**, 1260 (2019)

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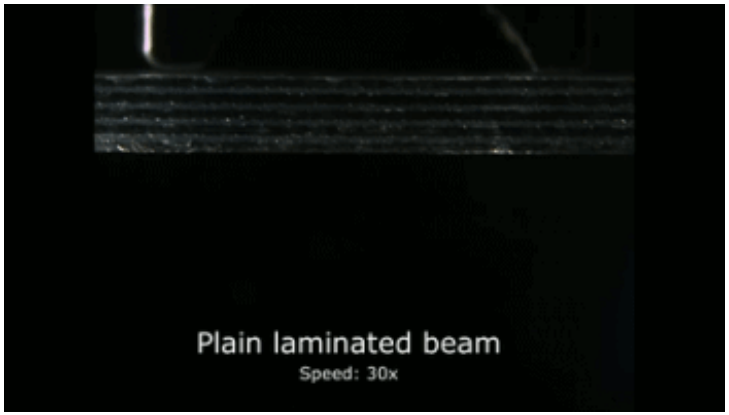
Nacre-inspired toughened glass

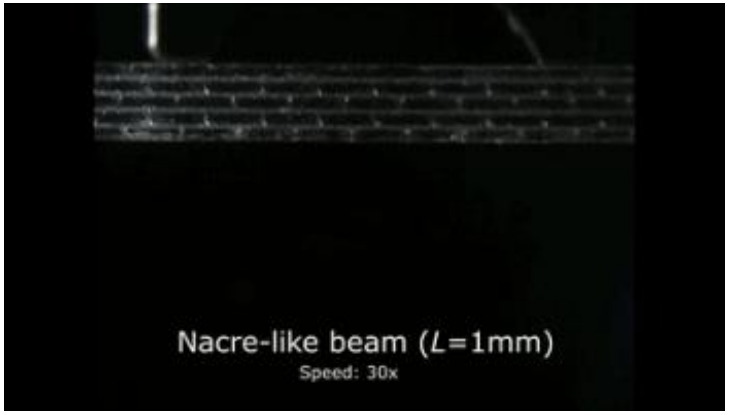


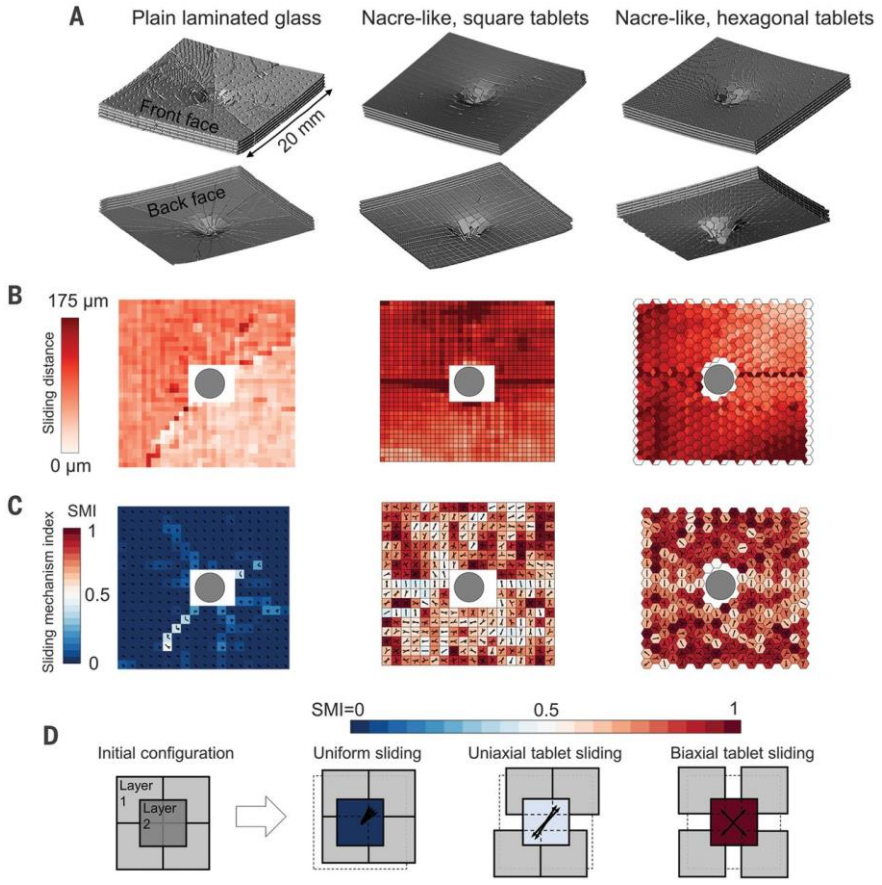
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Nacre-inspired toughened glass







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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

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3.071 Amorphous Materials
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