# 2. Optical properties of glasses

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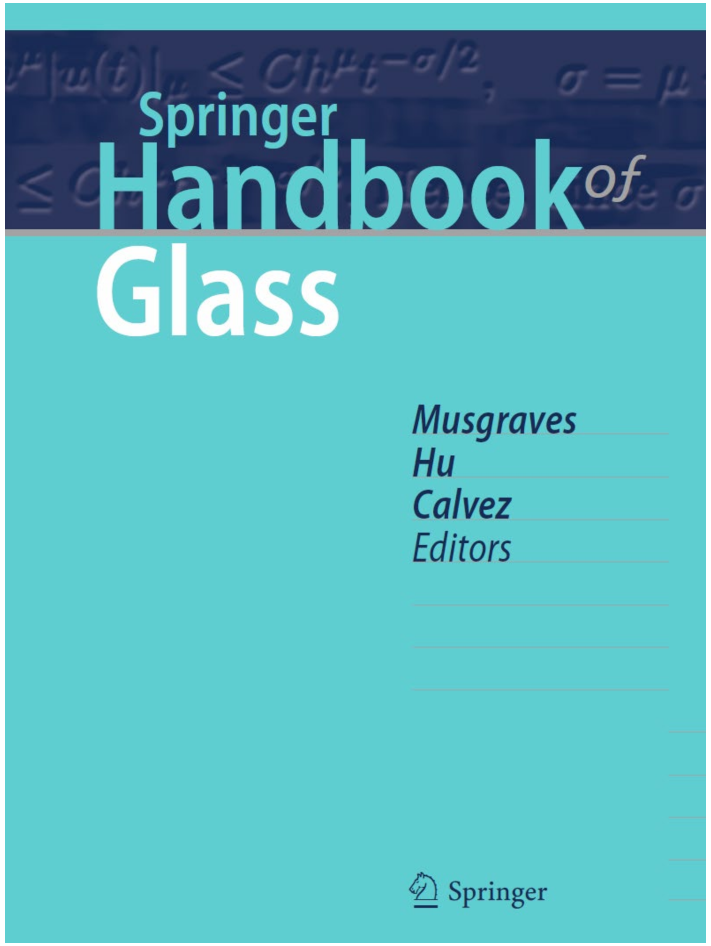



Springer Handbook of glass, J. David Musgraves, Juejun Hu, Laurent Calvez (Eds.), Springer, Nature, Switzerland, 2019

# Obsidian tools during the stone-ages (7000-30000 BC)


*Obsidian arrowheads (Ainu Stone Age from Hokkaido)*

# 2.1 Historical perspectives

Egyptian faience vase (glazing is made of $Na_2CO_3$ and $NaHCO_3$. Around 1400 B.C.)

Chinese Dragonfly Eye (lead, barium, silicate glass beads. Around 260 B.C.)

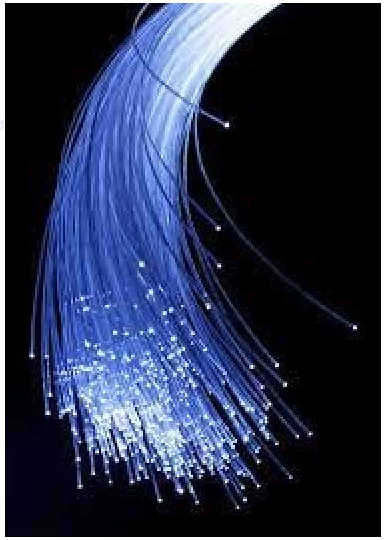
Roman glass technology started around A.D. (silicate and $NaCO_3$ from Egypt). With the invention of glass blowing (Egypt 2700 B.C. and Romans 100 A.D.) a new area of glass manufacturing started

World famous Murano glass started its production in the 13th century on the Venetian island of Murano. It also became famous for its fine mirrors. Still today, Murano is home to several glass factories and artists' ateliers. Of course it is also a tourist attraction.


Bohemian decorative glass from the region of Boehemia and Silesia (now Czcech republic has a centuries long history starting from the 13$^{th}$ century. Still today, the prestigious bohemian glasses are world famous and are a major tourist attraction.

Today, glass has become a material of major technological importance and is widely used in construction, transportation, electronics, optics, medical, energy, containers and homeware products. It is a cyclic materials «par excellence».





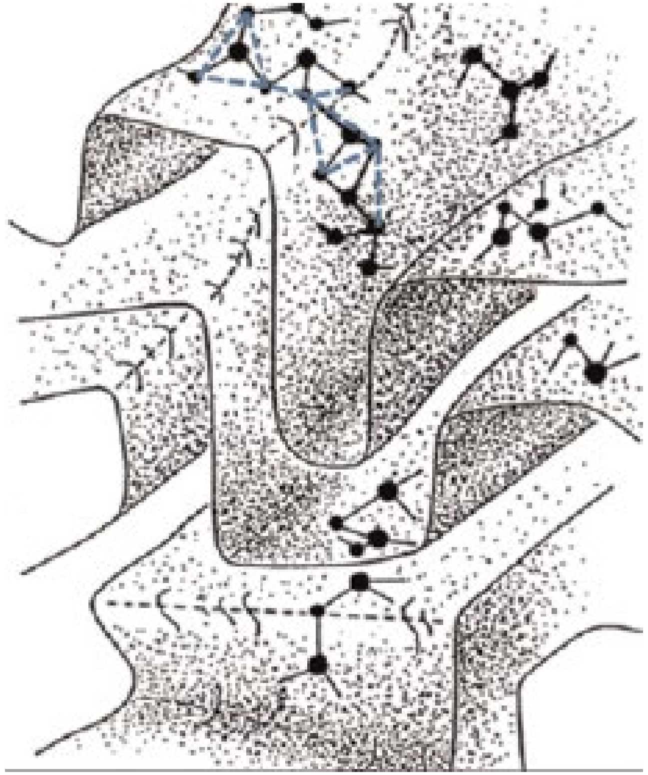
Global flat glass market is going to reach 153 billion $ by 2024. Top players are St. Gobain, PPG, Corning, AGC, Kyocera, Nippon Sheet, Guardian, Fuyao, Vitro etc.

# 2.2 Physical properties of glasses

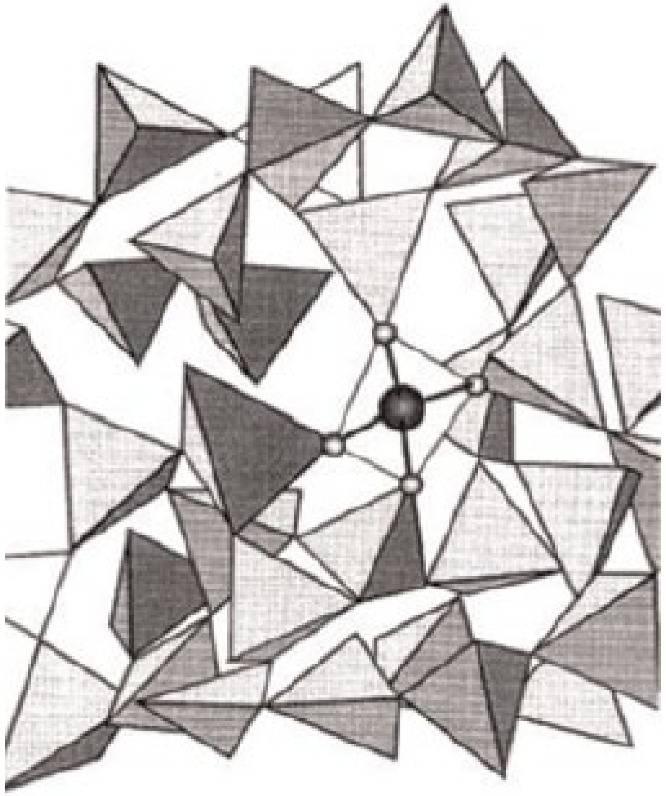
*Glass-forming* structures

Compared to crystalline solids, translational symmetry is missing

Polymers, Se, S glasses showing wormlike chains

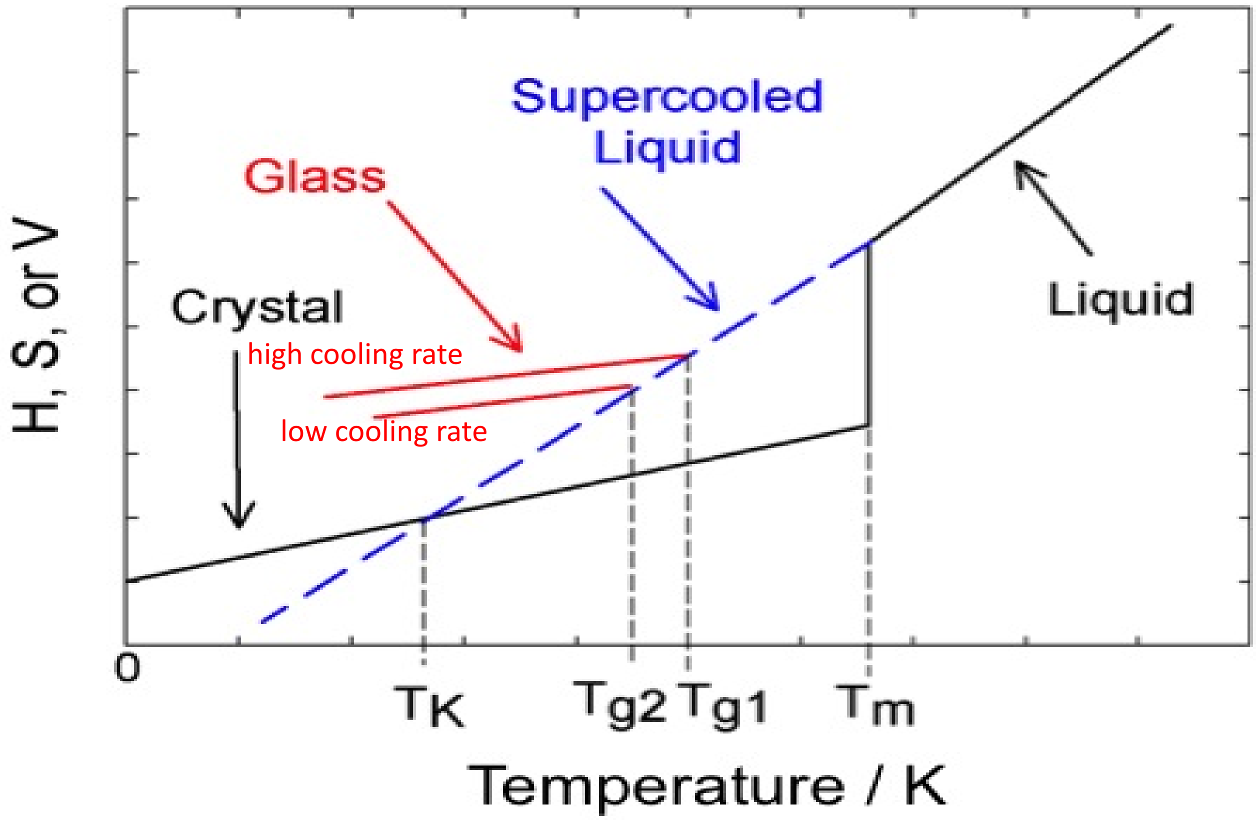


$AsS(Se)_3$ glass. The three-and the two-fold coordinated circles represent As and S(Se) atoms, which form $AsS(Se)_3$ trigonal pyramids (dashed lines), which produce corner-and edge-shared connections and extend to distorted layer-like clusters.



$SiO_2$ glass. Tetrahedra represent $SiO_{4/2}$ units, which are connected by the corners, producing three-dimensional continuous random networks.

# *Vitrification via a supercooled liquid phase*



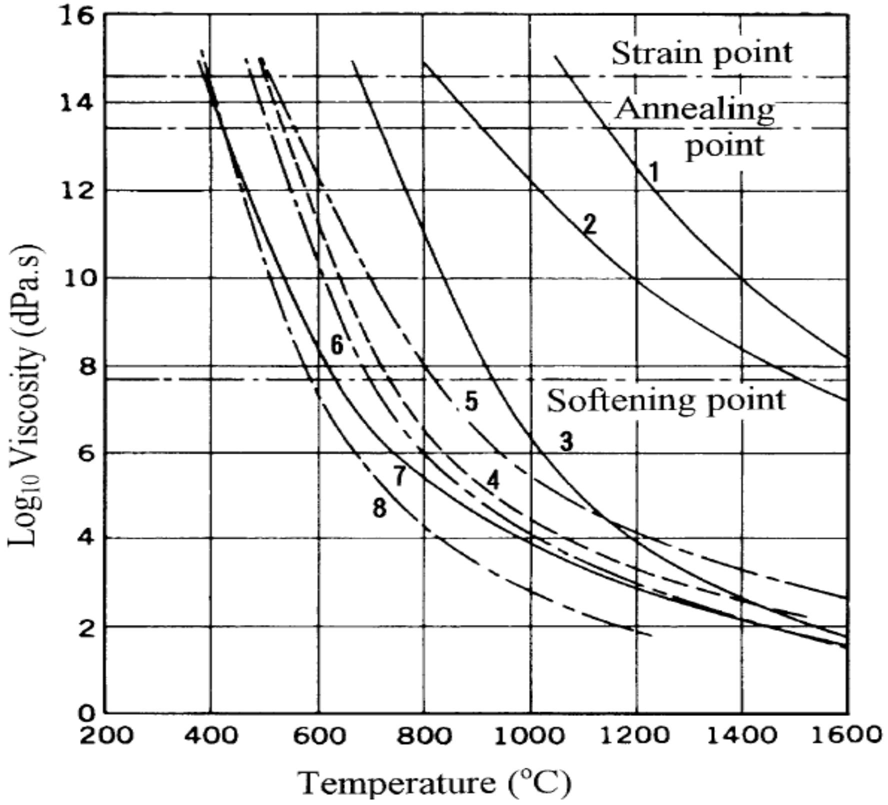

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{c_p}{T}$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

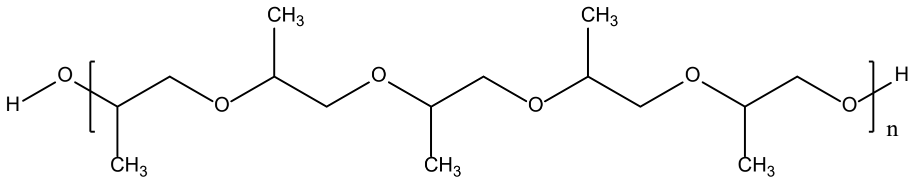
$$\left(\frac{\partial^2 G}{\partial T^2}\right)_p = -\left(\frac{\partial S}{\partial T}\right)_p = -\frac{c_p}{T}$$

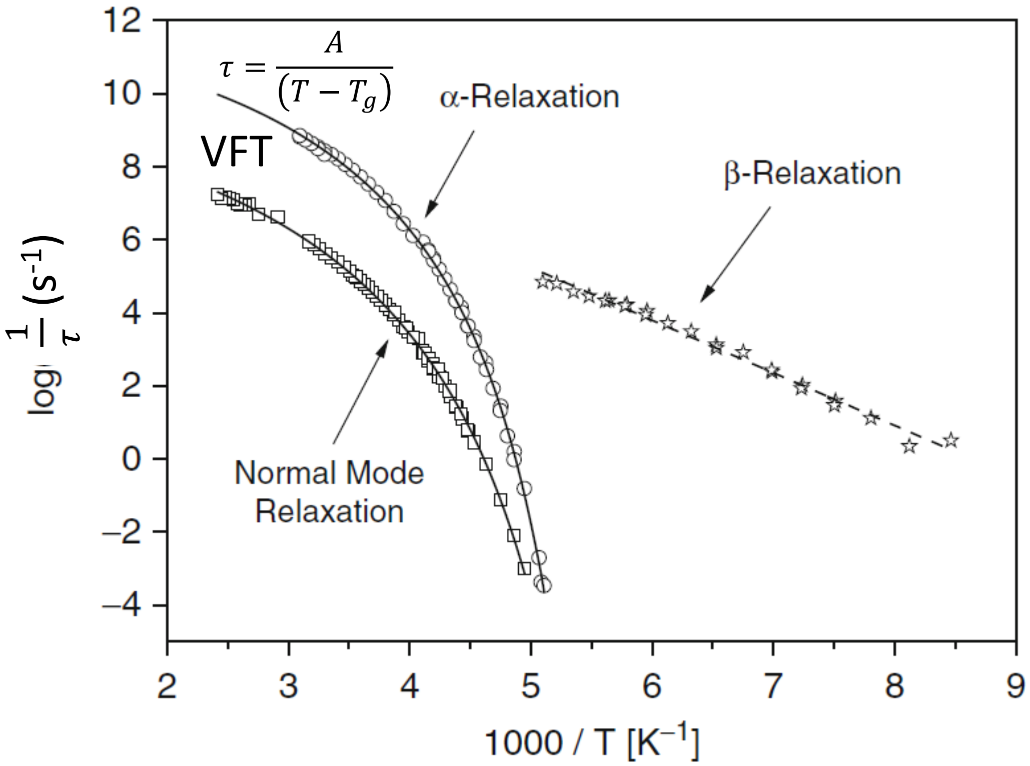
The glass transition temperature is dependent on the cooling rate (also on film thickness, pressure etc.). $T_K$ is called the Kauzmann temperature (Kauzmann brought up the paradox that at some temperature, below $T_m$, the supercooled liquid would have an entropy which is lower than that of the corresponding crystal. This raises the debate whether the glass transition should be treated within the thermodynamic or kinetic framework.

# *Exponential rise of viscosity and relaxation time at Tg*




Viscosity-temperature relationship of some commercial glasses.
1: Silicate glass; 2: High (96%) silica glass; 3:Aluminosilicate glass; 4: Soda-lime silicate glass (sheet glass); 5: Borosilicate glass; 6: Soda-lime silicate glass (electric bulb); 7: Lead-alkali silicate glass (electric use); 8: Lead-alkali silicate glass (high lead content).
[Reprinted from E. B. Shand, Glass Engineering Handbook, (McGraw-Hill Book Company, Inc., 1958)



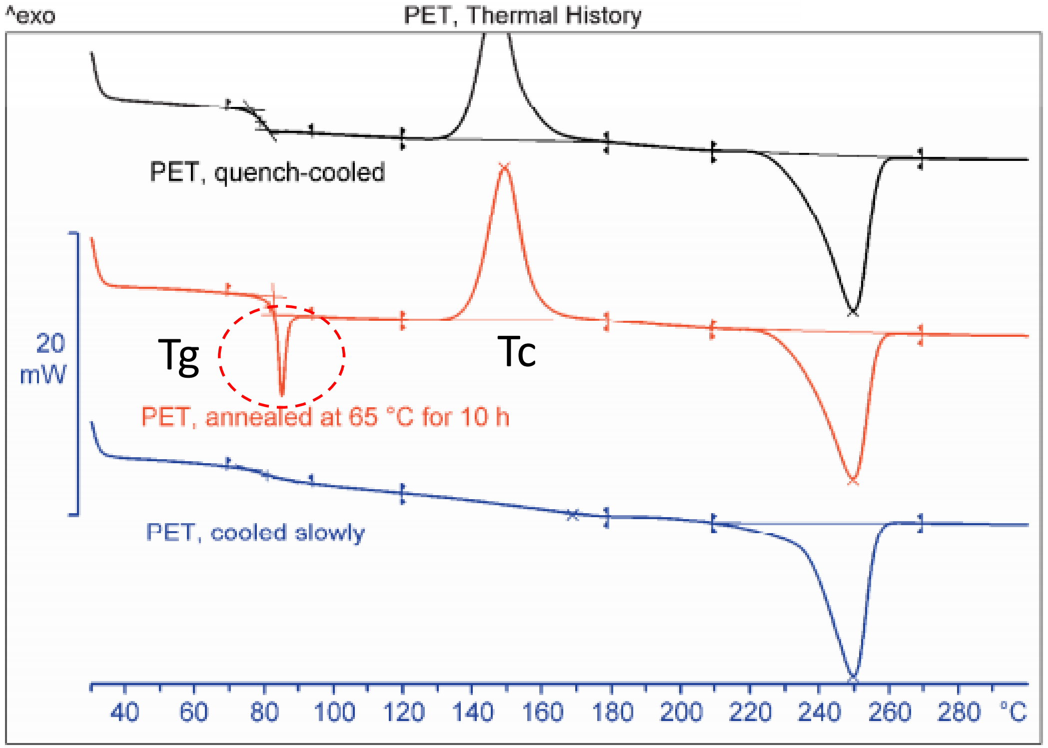

Vogel-Fulcher-Tammann (VFT) empirical equation

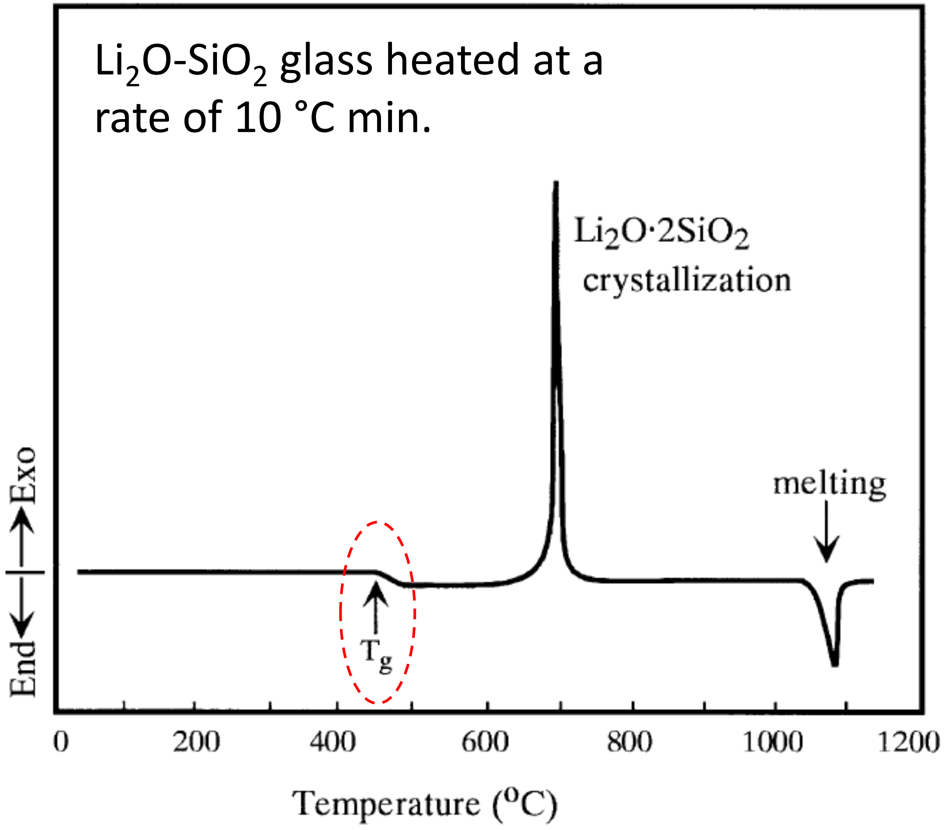
$\tau$ is proportional to the viscosity $\eta$

H. Yin, A. Schönhals, *Broadband dielectr. spectr. of polymer blends*, Springer 2014, pp. 1299-1356

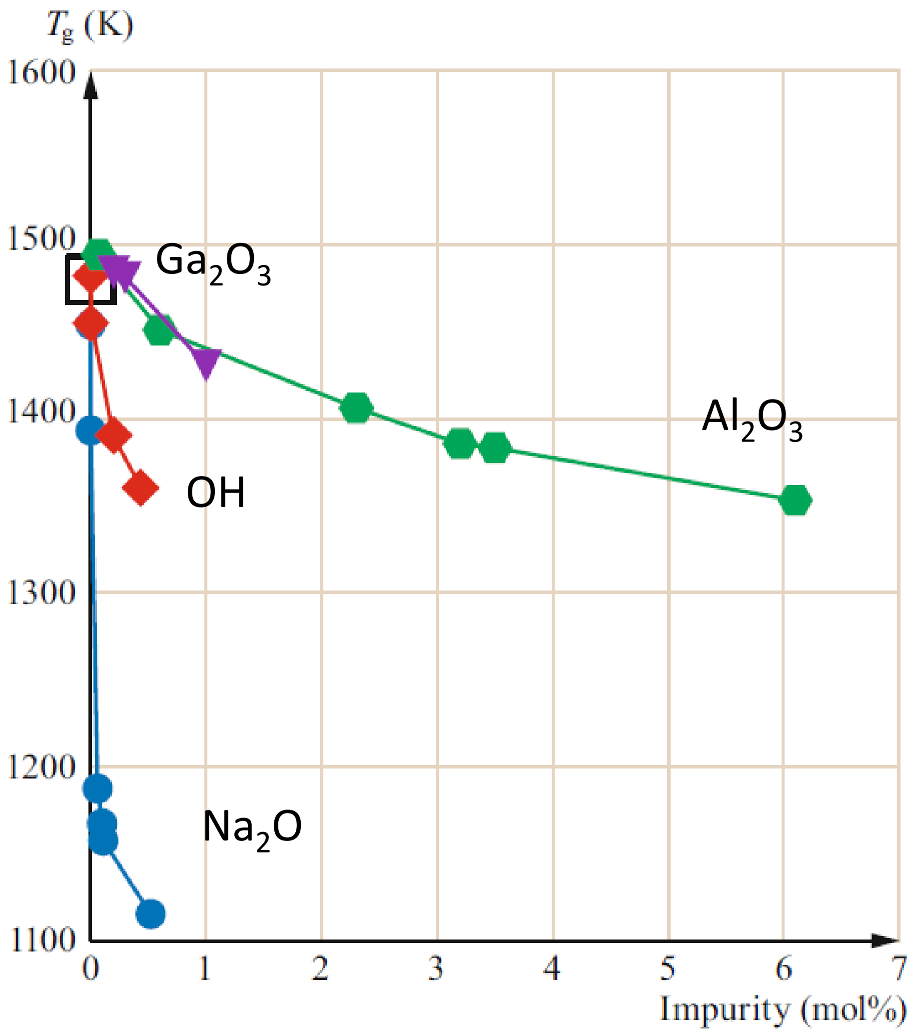
# *Differential scanning calorimetry analysis of the glass transition temperature $T_g$*

amorphous PET (heating rate of 20 °C min.)



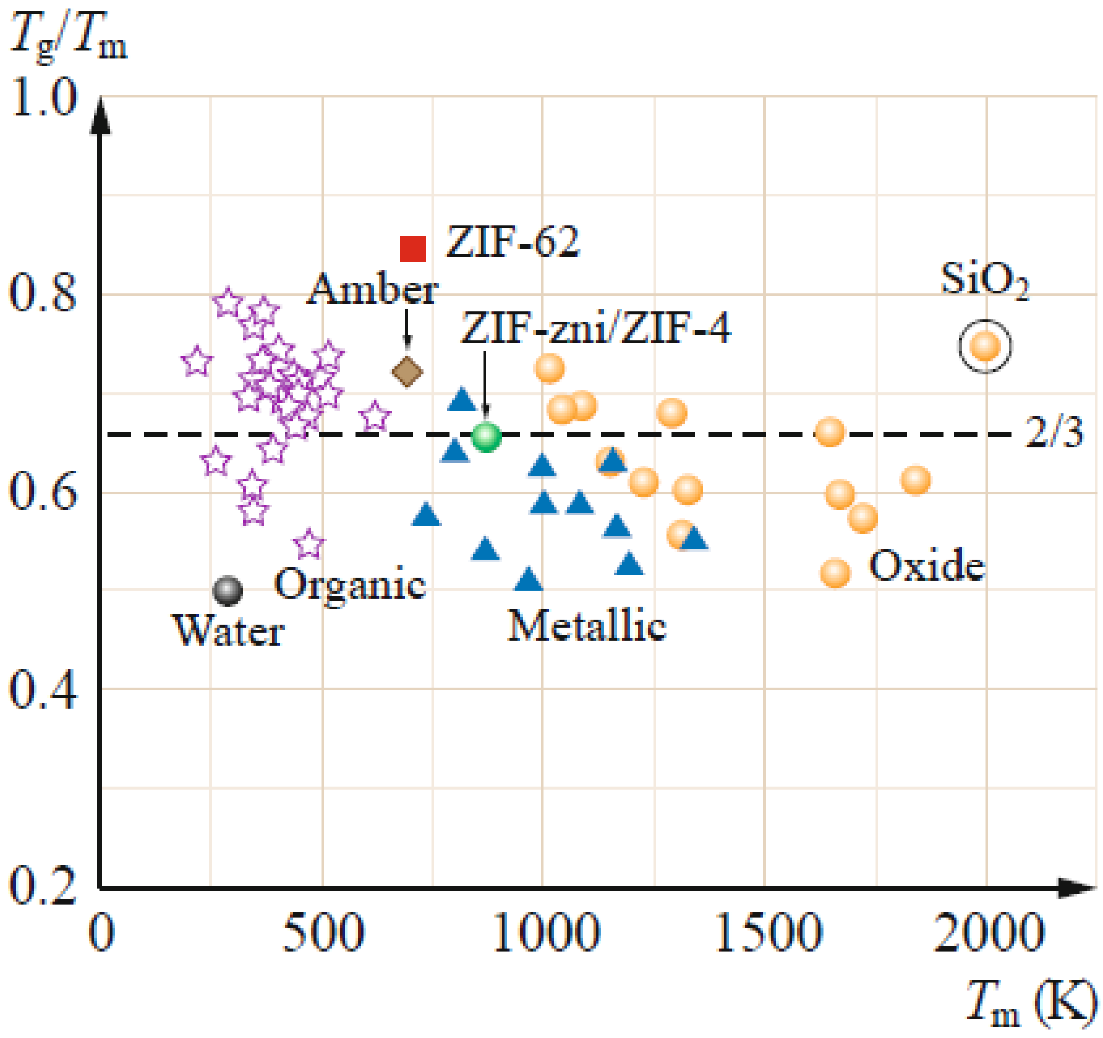
*Doped $SiO_2$ glasses*




Glass transition temperature Tg of silica glass as a function of the molar concentrations of $Na_2O$ (blue circles), OH (red diamonds), $Al_2O_3$ (green hexagons), or $Ga_2O_3$ impurities (purple triangles), predicted from the viscosity data assuming that log (viscosity) =12 Pa s at Tg.

For comparison, the calorimetric Tg of Richet and Bottinga is also reported as an empty square. Lines are guides for the eyes.

## «Universal» $T_g/T_m$ ratio



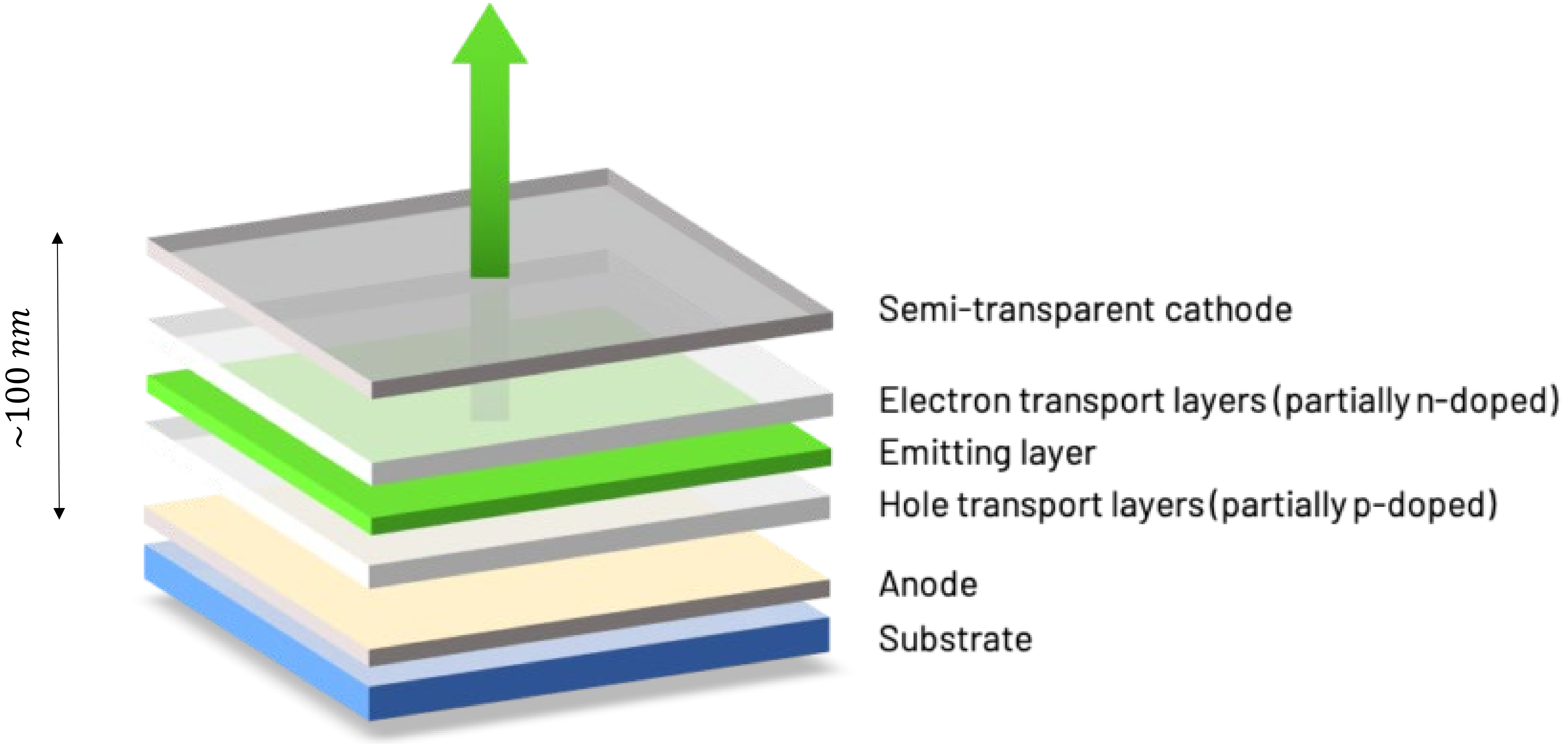

Comparison in Tg/Tm ratio between ZIF-62* (0,84) and other types of glass-forming systems, including water, oxide, metallic, and organic liquids

Good glass forming ability (i.e. GFA > 0:67) typified by coordination polymers, PMMA, $B_2O_3$, and $SiO_2$ and amber.

The poorest Tg/Tm recorded so far for elemental bcc metals like Ta is 0:5.

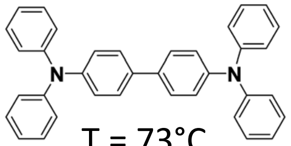
* $Zn(C_3H_3N_3)_{1,75}(C_7H_5N_2)_{0,2}$ or ZIF-62 is a melt quenched glass.

# *Typical structure of an organic light-emitting diode (OLED)*

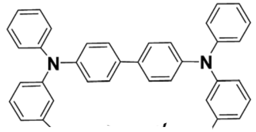


# *Tuning the glass transition temperature of hole transporting materials used in OLEDs*

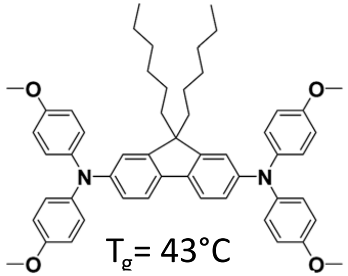
## TAD derivatives



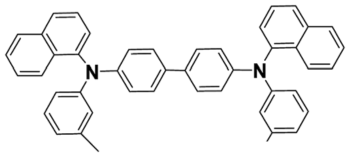
$T_g$= 73°C



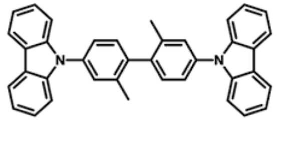
$T_g$= 60°C



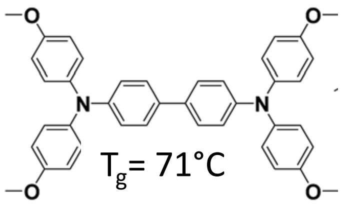
$T_g$= 43°C



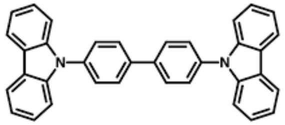
$T_g$= 95°C



$T_g$= 94°C

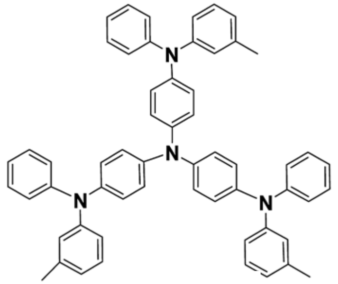


$T_g$= 71°C

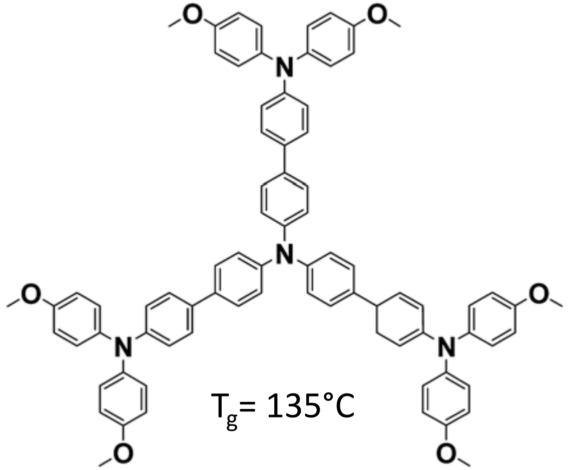


crystallizes

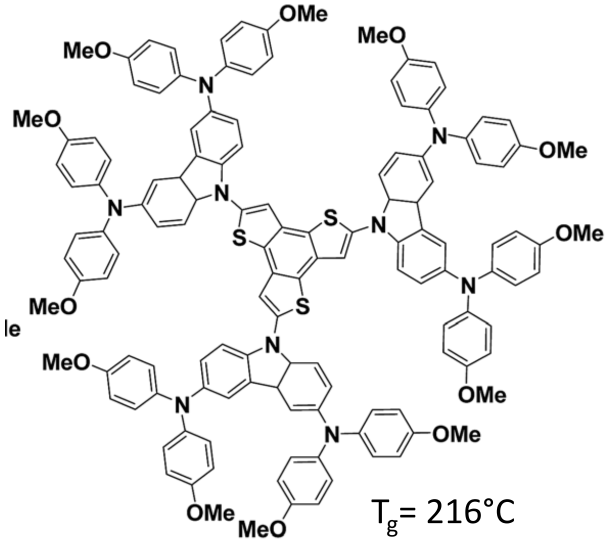
## Starburst compounds



$T_g$= 75°C

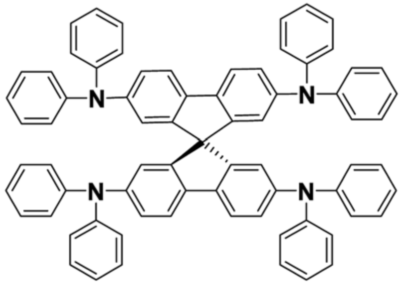


$T_g$= 135°C

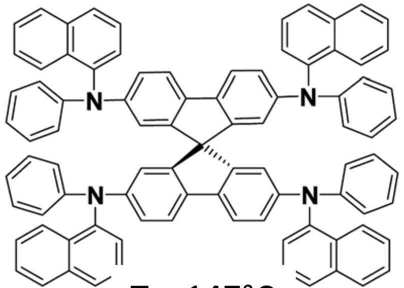


$T_g$= 216°C

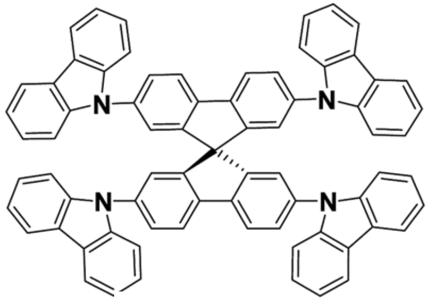
## Spiro compounds



$T_g$= 135°C



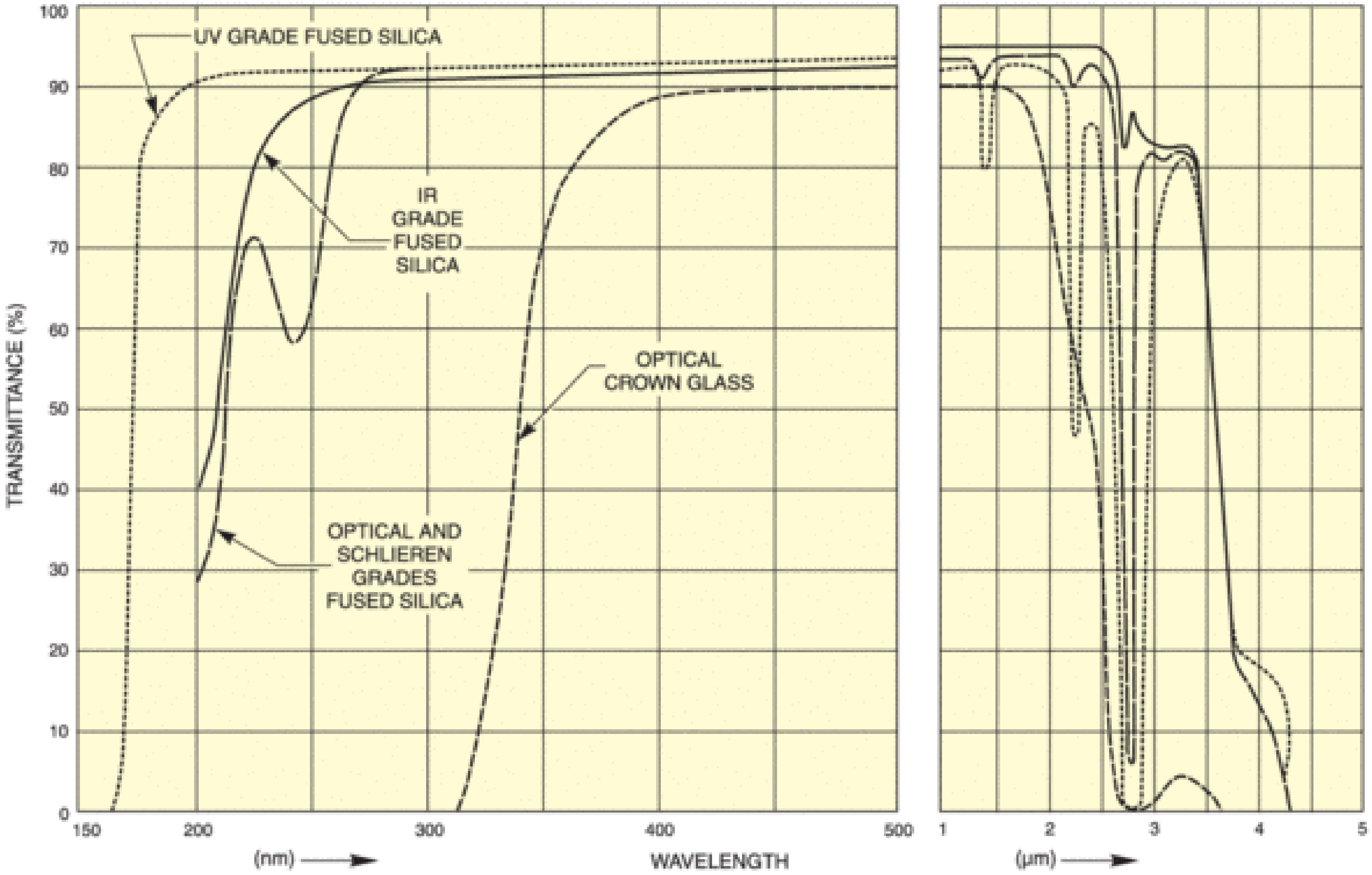
$T_g$= 147°C



$T_g$= 240°C

# 2.3 Optical properties of glasses

## *Silica ($SiO_2$) based glasses*

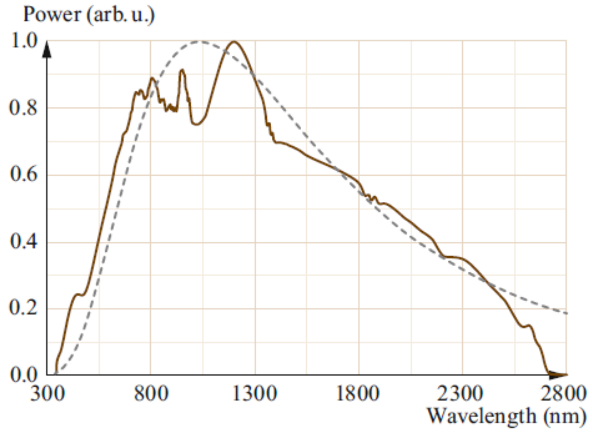


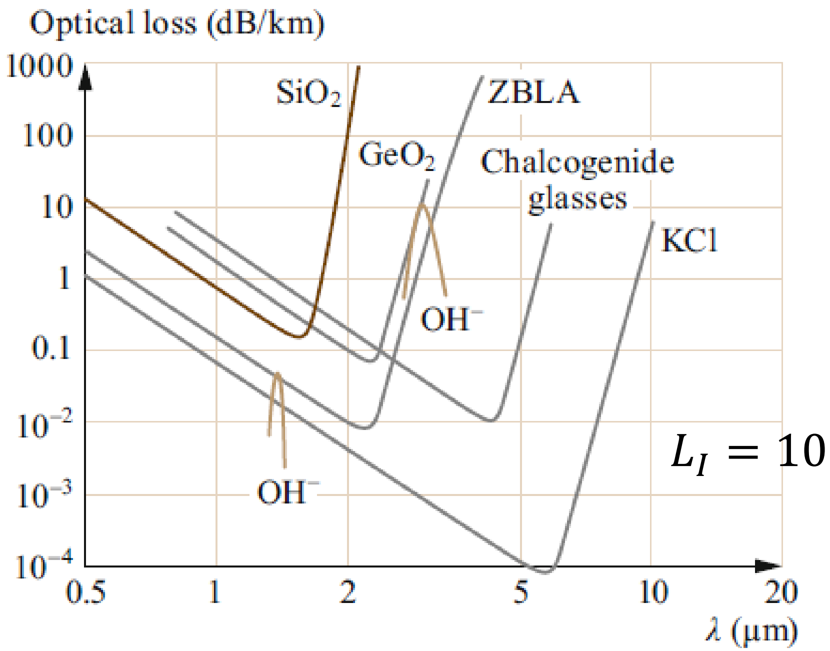

Springer Handboox of glass, J. David Musgraves, Juejun Hu, Laurent Calvez (Eds.), Springer, Nature, Switzerland, 2019

# *Fluoride glasses*

The most common multicomponent fluoride is ZBLAN, $ZrF_4$-$BaF_2$-$LaF_3$-$AlF_3$-NaF, and is commercially available from multiple sources including Fiber- Labs, Inc., IR-Photonics, Le Verre Fluoré, and Thor- Labs. Unfortunately, halides are very susceptible to processing conditions. They are sensitive to oxidation, moisture, and temperature due to preferential volatilization of the different species.

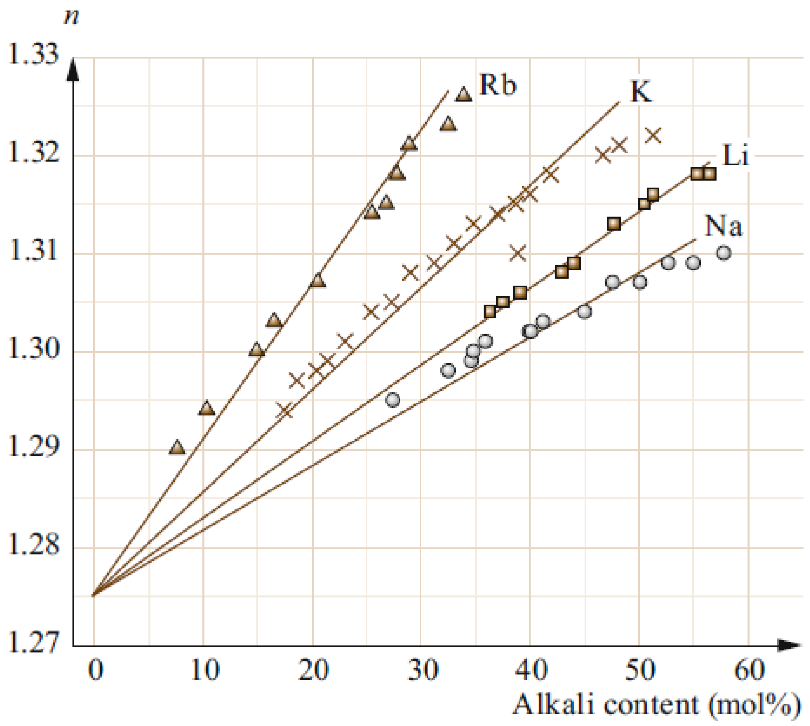
ZBLAN's transmission window from the deep ultraviolet through the infrared, combined with its excellent rare earth solubility and hot formability, makes this material almost uniquely suited for broadband supercontinuum generation




comparison of attenuation between oxides, halides, and chalcogenides

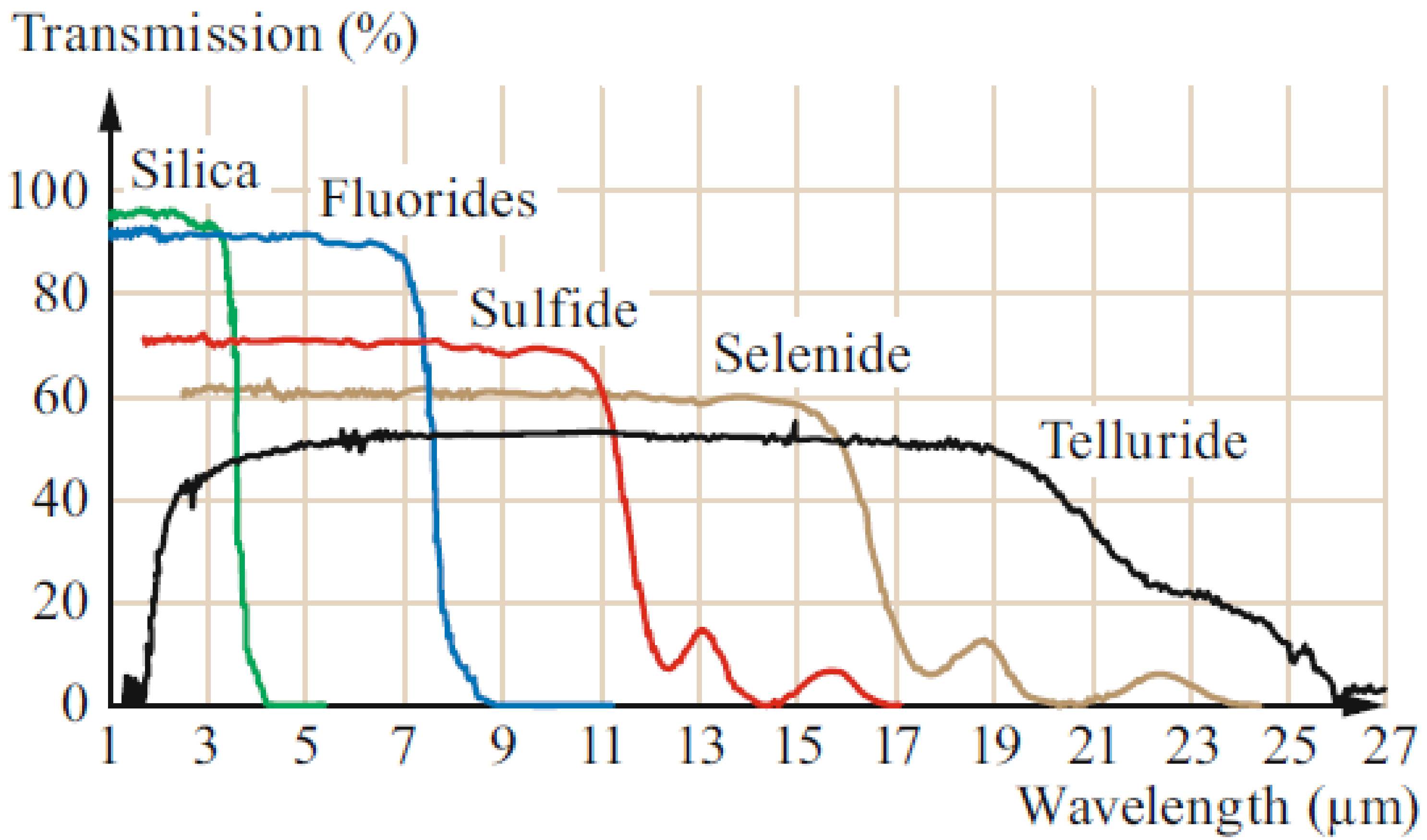
$$L_I = 10 \cdot log_{10}\left(\frac{I_0}{I}\right) \text{ dB}$$



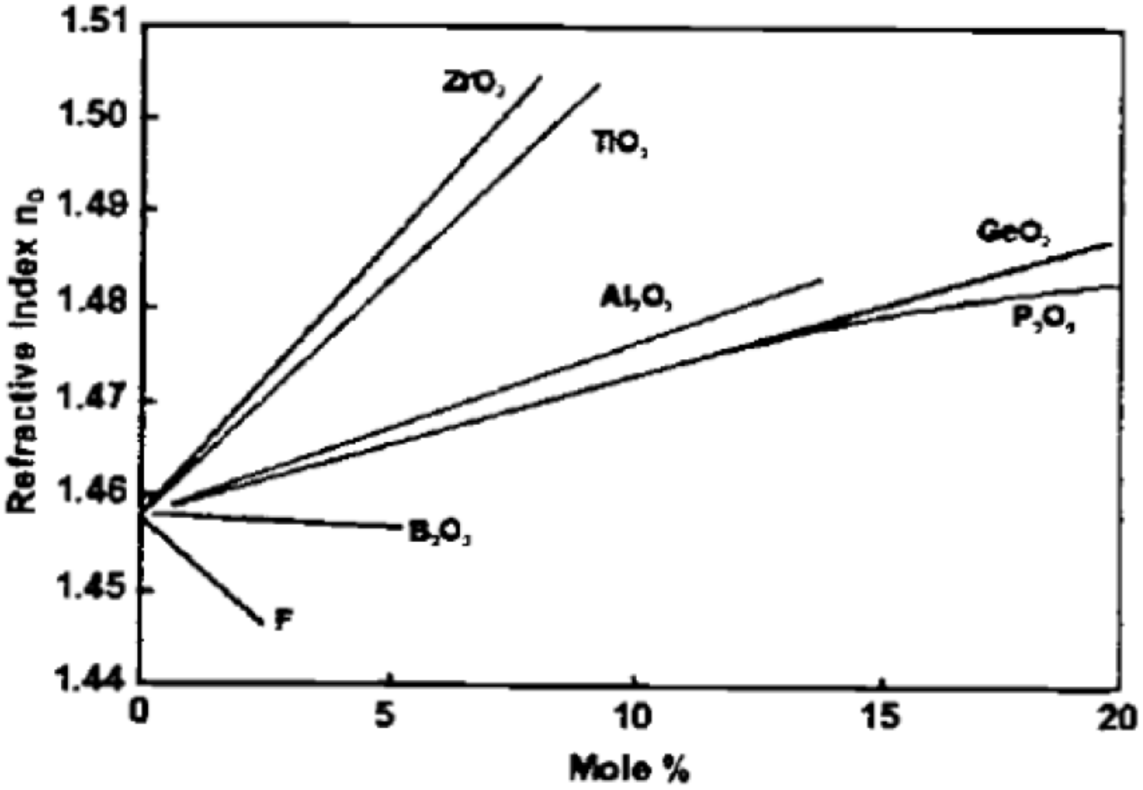

Trends in $BeF_2$ glasses as a function refractive index n.

# *Chalcogenide glasses*

Chalcogenide glasses are vitreous materials based on sulfur, selenium or tellurium. They exhibit unique optical properties such as broad infrared transparency, high quantum efficiency of rare-earth ions emission, and high nonlinear refractive indices. The most important application of bulk chalcogenide glasses is optical lenses for thermal imaging. This market is still dominated by single crystalline germanium lenses, which are produced, one by one, with complex single point diamond turning. In addition to some superior optical properties of bulk chalcogenide glasses, associated with the about ten times lower thermal coefficient of refractive index, facilitating the conception of a thermal optical systems, the glasses can be more easily shaped into complex optical components.



# *Tuning the refractive index*




Influence of different oxides and fluorine on the refractive index of fused silica (λ~500 nm)

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N. Neuroth, 1996, Proc. of SPIE Vol. 10286 102860B-18

## Flint glasses (e.g. SF1)

$SiO_2$: about 62 %
$Na_2O$: about 6 %
$K_2O$: about 8 %
PbO: about 24 %

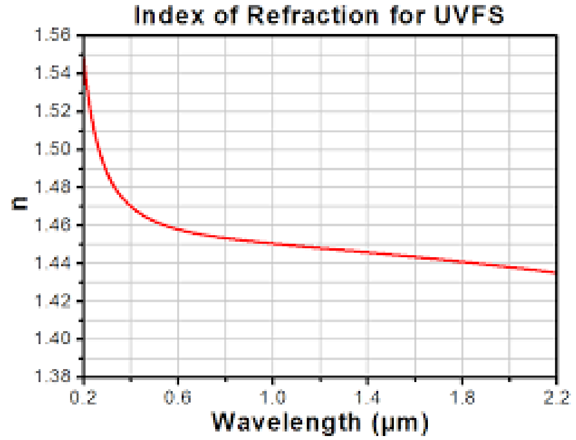
typically n=1.7, 1.8, 1.9

Traditionally, flint glasses were lead glasses containing around 4–60% lead(II) oxide; however, the manufacture and disposal of these glasses were sources of pollution. In many modern flint glasses, lead oxides are replaced with other metal oxides such as titanium dioxide and zirconium dioxide without significantly altering the optical properties of the glass.

## Crown glass (e.g. BK7)

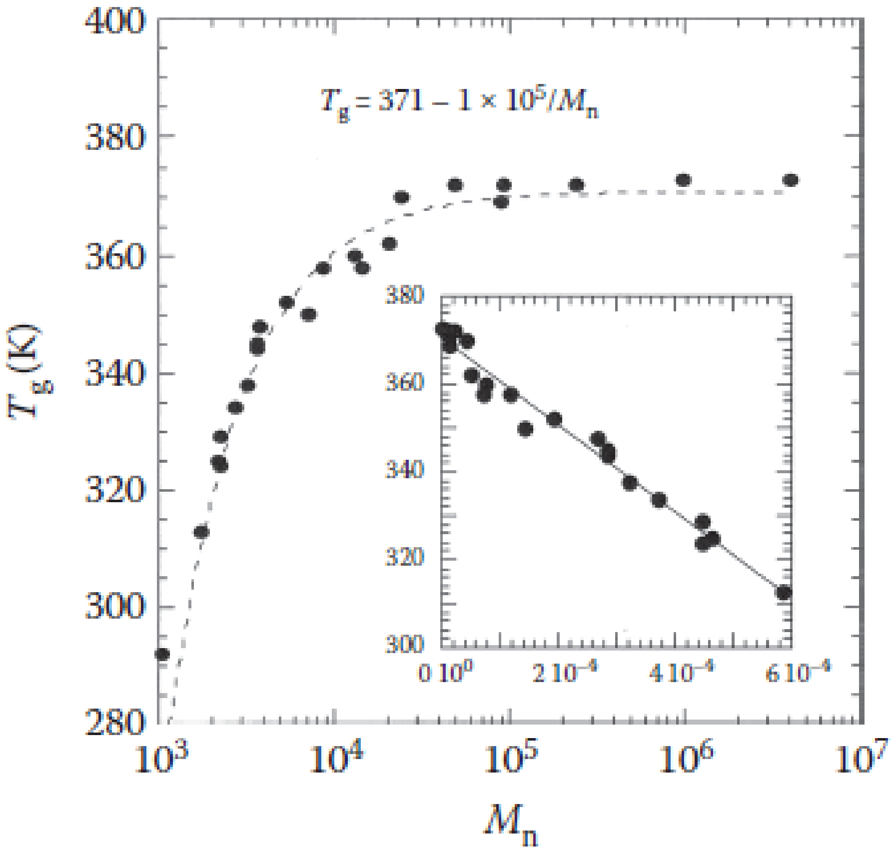
$SiO_2$: 70–80 wt%
$B_2O_3$: 7–13 wt%
$Na_2O$: 4–8 wt% or $K_2O$
$Al_2O_3$: 2–8 wt%

n = 1.517 (λ=587.6 nm)



# *Polymers*

Polymers are important materials in everyday life. They have unparalleled mechanical and optical properties. Their fabrication possibilities are extremely advantageous (blow extrusion, extrusion, molding, casting etc.). Polymers are showcases for glass forming materials. It is possible to have high crystallinity too, but we are talking about microcrystalline regions surrounded by amorphous regions.



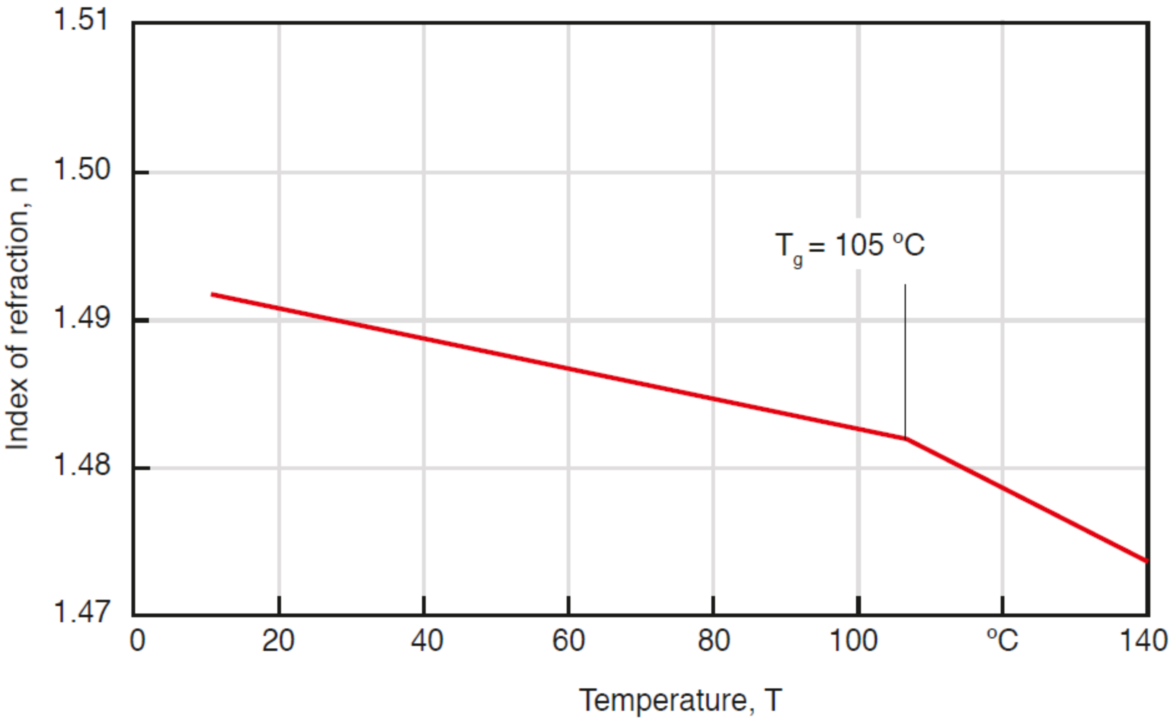

Optical properties of polymers:

- With few exceptions, polymers are transparent
- They can be colored easily by addition of dyes or pigments
- There are also intrinsically colored conjugated polymers (for example polyaniline)
- The refractive index of transparent polymers varies from 1.35 (PTFE) to 1.67 (polyaryl sulfone)
- Under stress, polymers become birefringent (colors appear under crossed polarizers)
- Monoaxial orientation induces birefringence
- If polymers contain crystalline domains of a certain size, they become opaque (can be induced by straining)
- The possibilities of creating composites opens a wide range of materials properties.

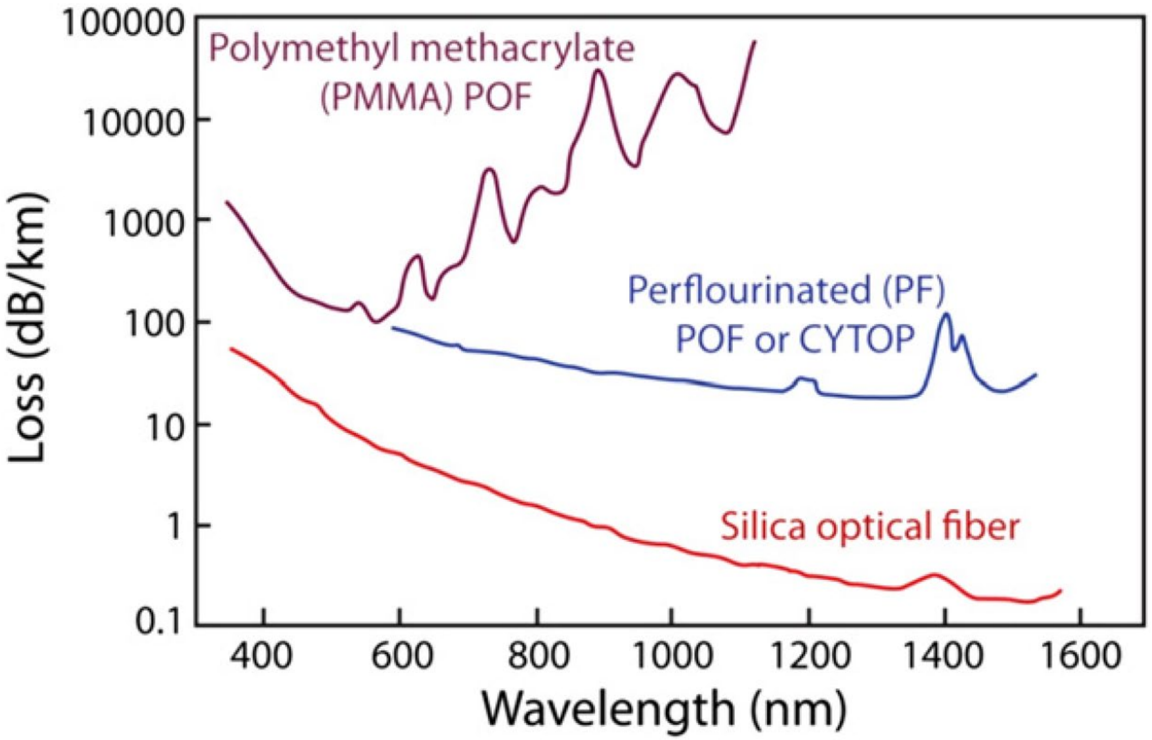
Molecular weight dependence of the glass transition temperature *Tg* for polystyrene, showing that *Tg* saturates at a limiting value of ~100°C beyond *M*n ≈ 20 kg/mol (~200 monomers). This has to do with the proportion of chain ends with larger mobility

Polymer glasses, Taylor and Francis Connie B. Roth ed. Boca Raton, 2017

# *Some optical properties of polymers*




Index of refraction as a function of temperature for PMMA ($\lambda$= 589.3 nm)




Attenuation behavior of silica and polymer fibers