MIT 3.071
Amorphous Materials

12: Optical Properties

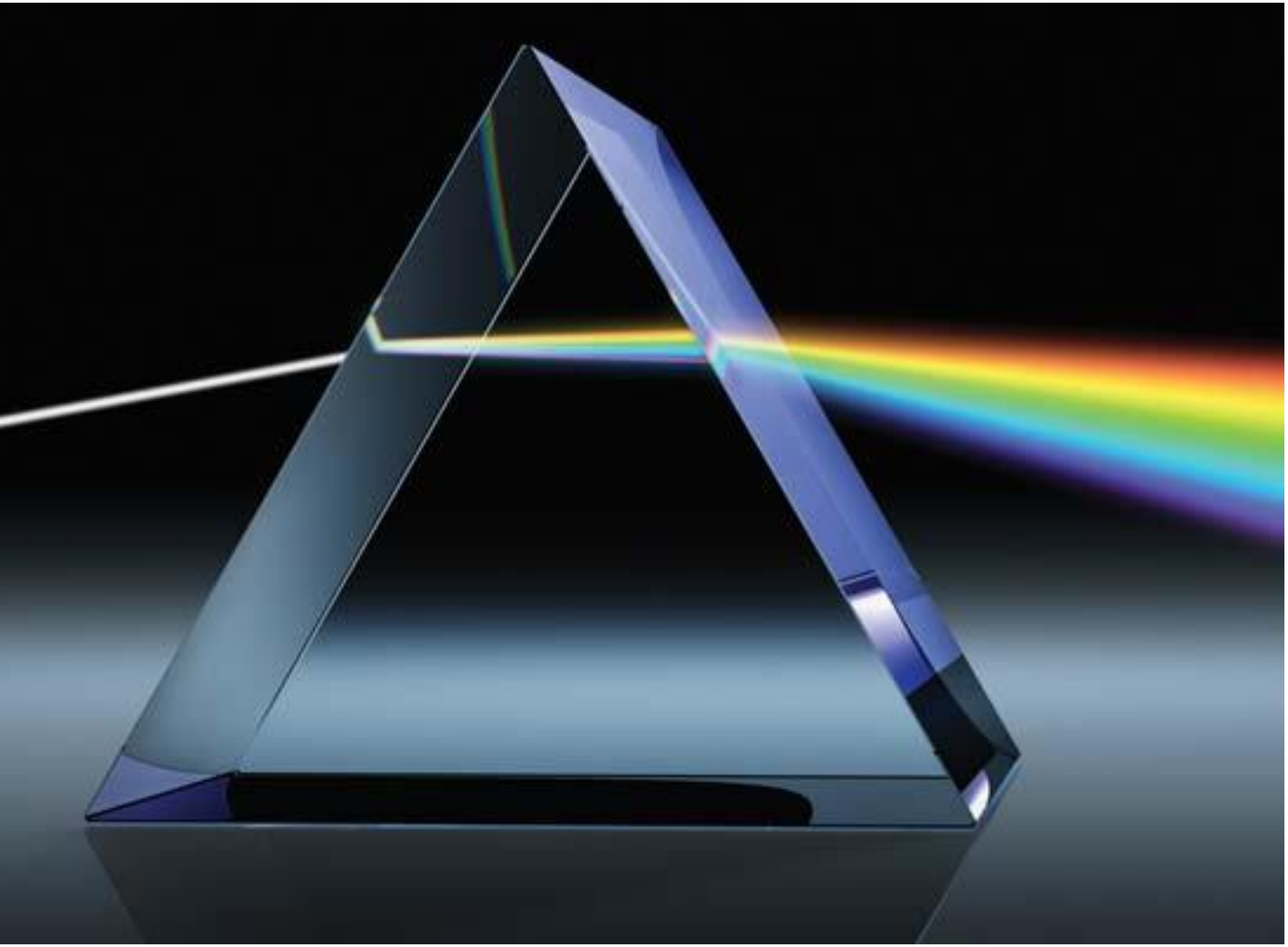
Juejun (JJ) Hu

After-class reading list

- Fundamentals of Inorganic Glasses
  - Ch. 19
- Introduction to Glass Science and Technology
  - Ch. 10
- 3.024 wave optics

What's so special about glass ?

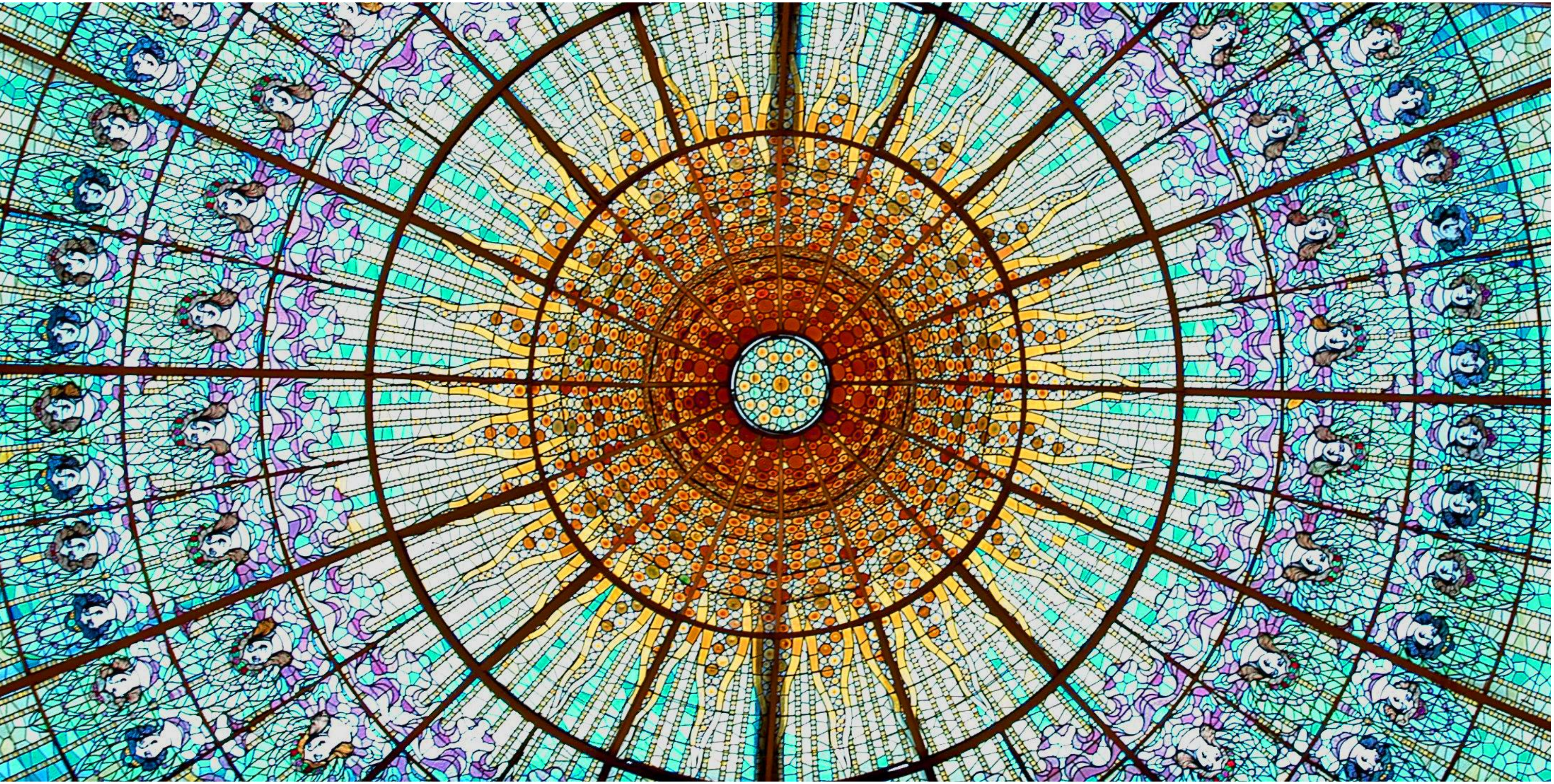
Refraction



Transparency

Image of underwater optical fiber network removed due to copyright restrictions. See The Fiber Optic Association, Inc. website.

Color



Palau de la Musica Catalana, Barcelona

Maxwell Equations (‘macroscopic’ differential form)

- Gauss’s Law: $\nabla \cdot D = \rho_f$
- Gauss’s Law for magnetism: $\nabla \cdot B = 0$
- Faraday’s Law: $\nabla \times E = -\dfrac{\partial B}{\partial t}$
- Ampere’s Law: $\nabla \times H = J_f + \dfrac{\partial D}{\partial t}$

James C. Maxwell
(1831-1879)

H	Magnetic field	B	Magnetic induction
E	Electric field	D	Electric displacement
J_f	Free current density	ρ_f	Free charge density

Constitutive relations in amorphous materials

- General form for non-bianisotropic media:

$$D = \varepsilon_0 E + P \qquad B = \mu_0 H + \mu_0 M$$

- Most amorphous materials are isotropic
  - *E* and *D* (or *B* and *H*) always align in the same direction
  - In most non-magnetic glasses, μ_r is close to 1 ($\mu = \mu_0$)

$$P = \varepsilon_0 \chi E \qquad M = \chi_m H$$ Linear media

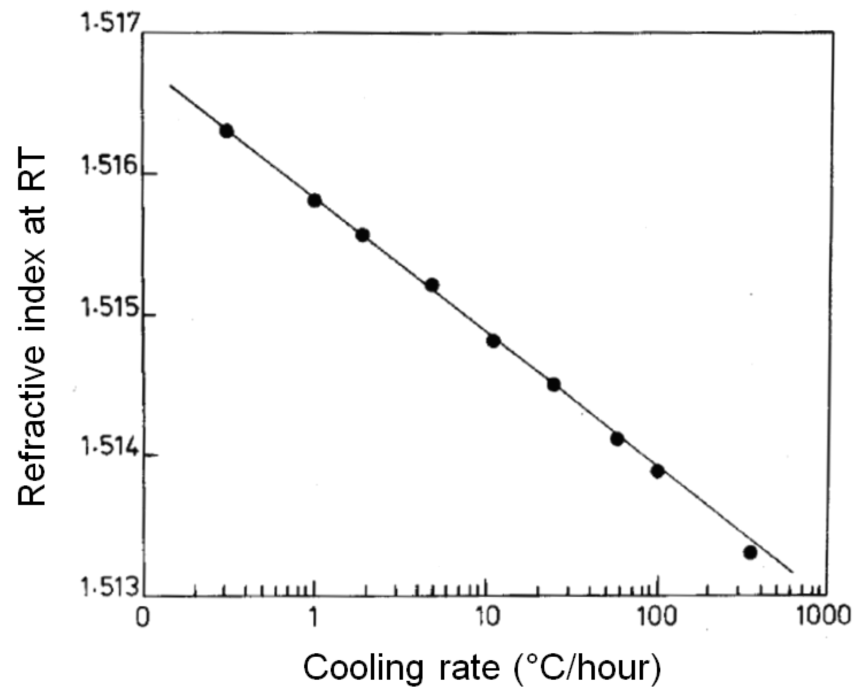
$$D = \varepsilon_0 (1+\chi) E = \varepsilon_0 \varepsilon_r E = \varepsilon E$$

$$B = \mu_0 (1+\chi_m) H = \mu_0 \mu_r H = \mu H \sim \mu_0 H$$ Non-magnetic media

$$n = \sqrt{\mu_r \varepsilon_r} \sim \sqrt{\varepsilon_r} = \sqrt{1+\chi}$$ Non-magnetic media

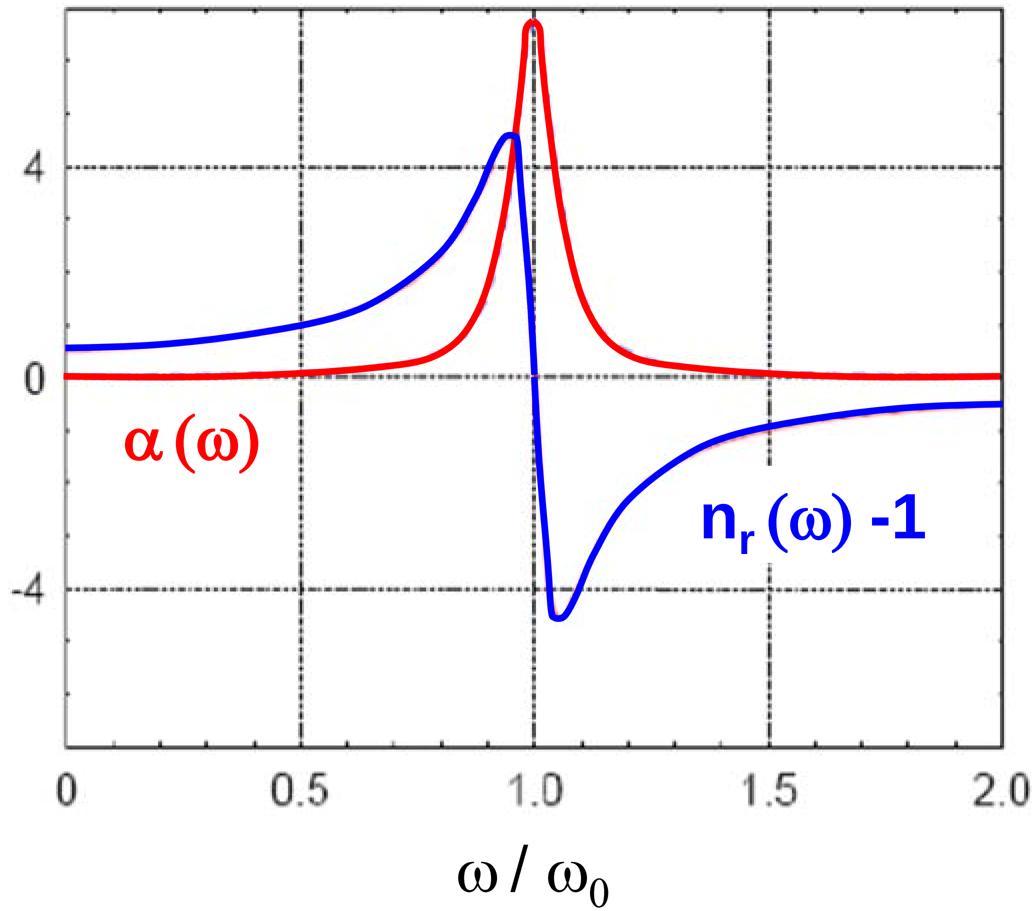
Refractive index of glass: general trends

- Addition of heavy elements increases index
  - Lead-containing glasses
- Addition of alkali oxides increases index
  - NBOs have larger polarizability than BOs
- Fictive temperature (density) dependence



Rawson, *Properties and Applications of Glasses* (1980)

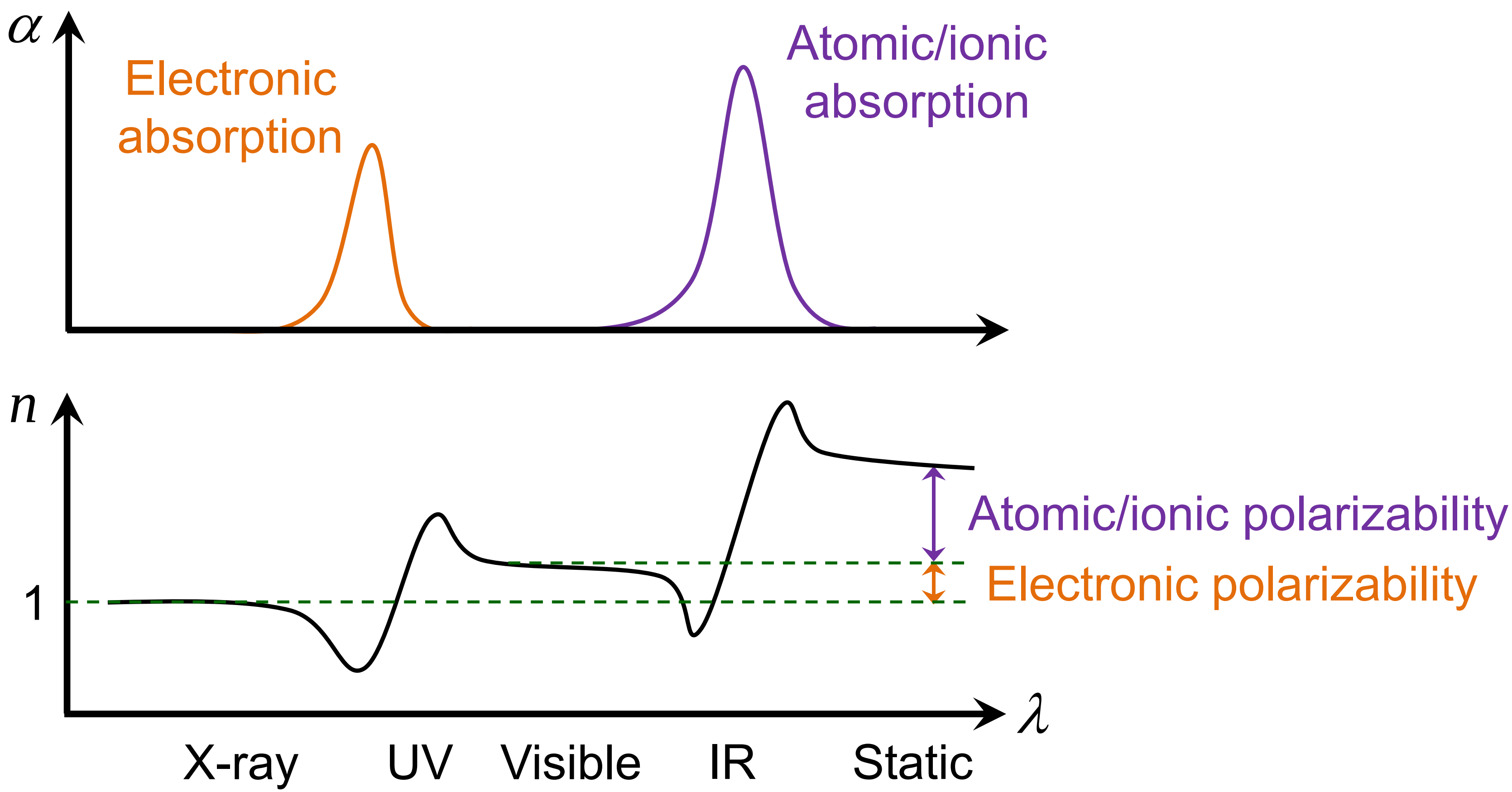
Kramers-Kronig (K-K) relation



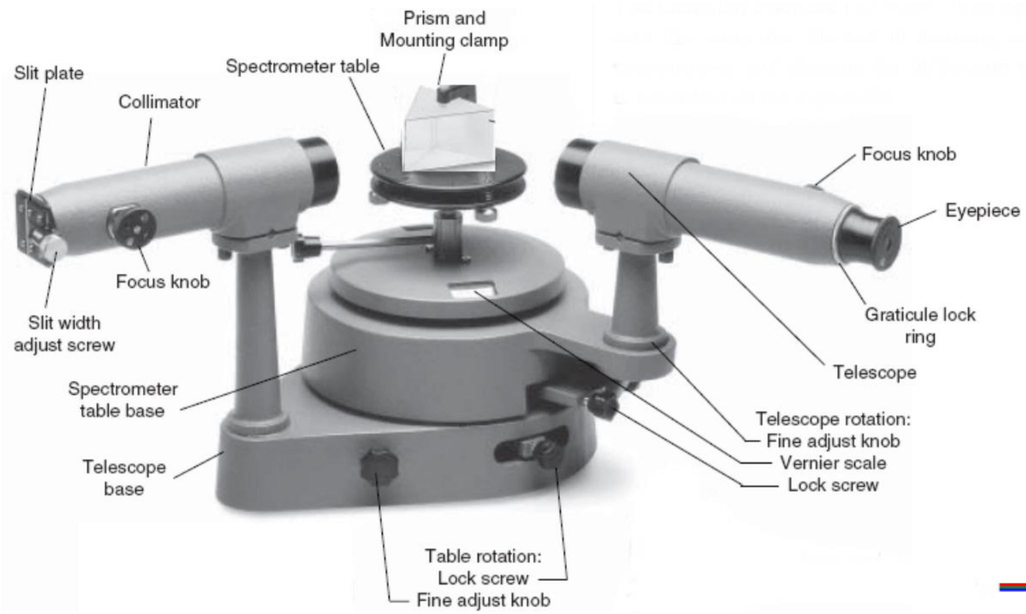
Refractive index and optical absorption are not independent quantities!

Refractive index of glasses

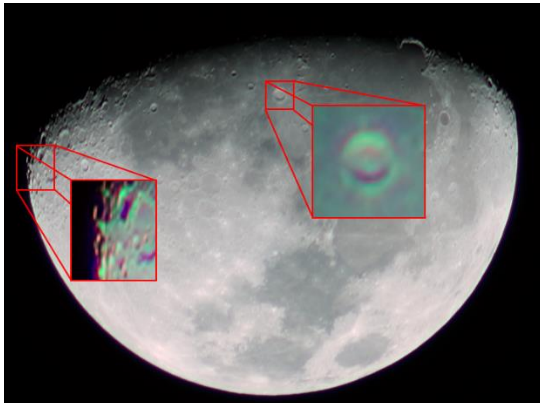
- Wavelength/frequency dependent (Lorentz oscillators)

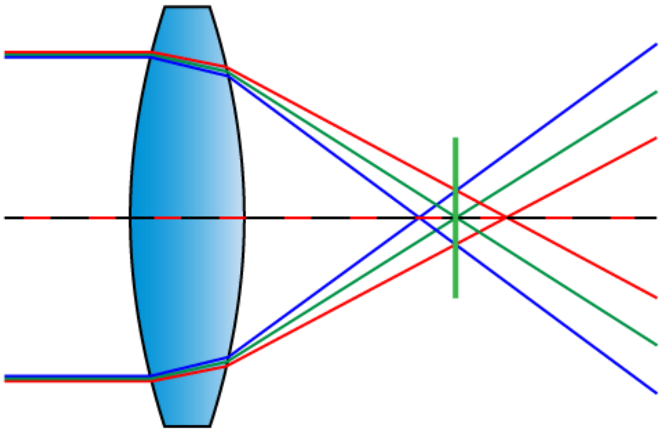


Chromatic dispersion of glasses



Prism dispersive spectrometer

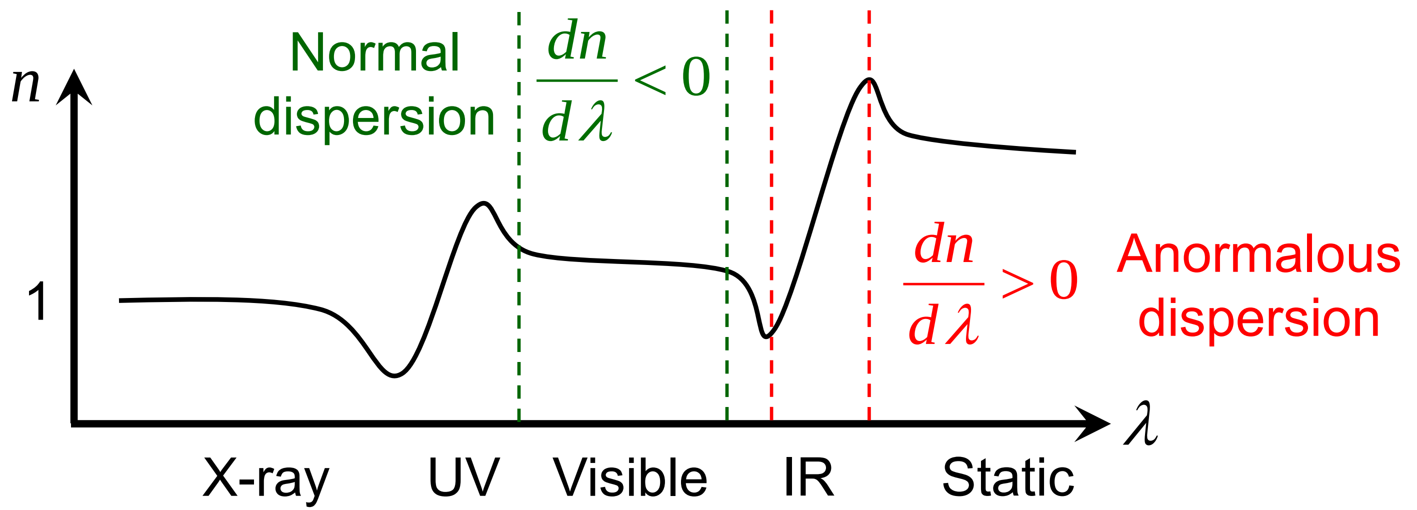




Chromatic aberration

Chromatic dispersion of glasses

- Abbe number (V-number): $V_D = (n_D - 1)/(n_F - n_C)$
  - D, F and C spectral lines: 589.3 nm, 486.1 nm and 656.3 nm



Chromatic dispersion of glasses

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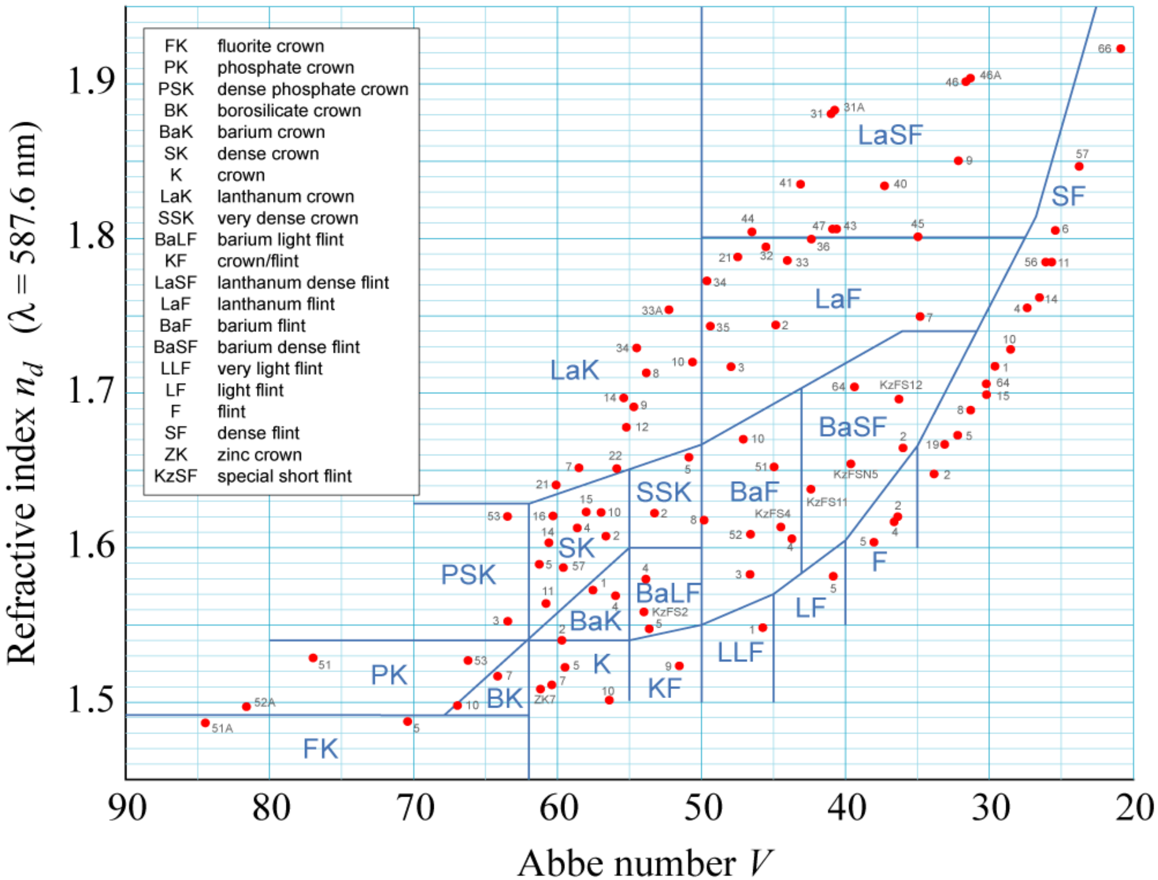


Crown glass ("K")

- Soda-lime silicates
- Low index
- Low dispersion

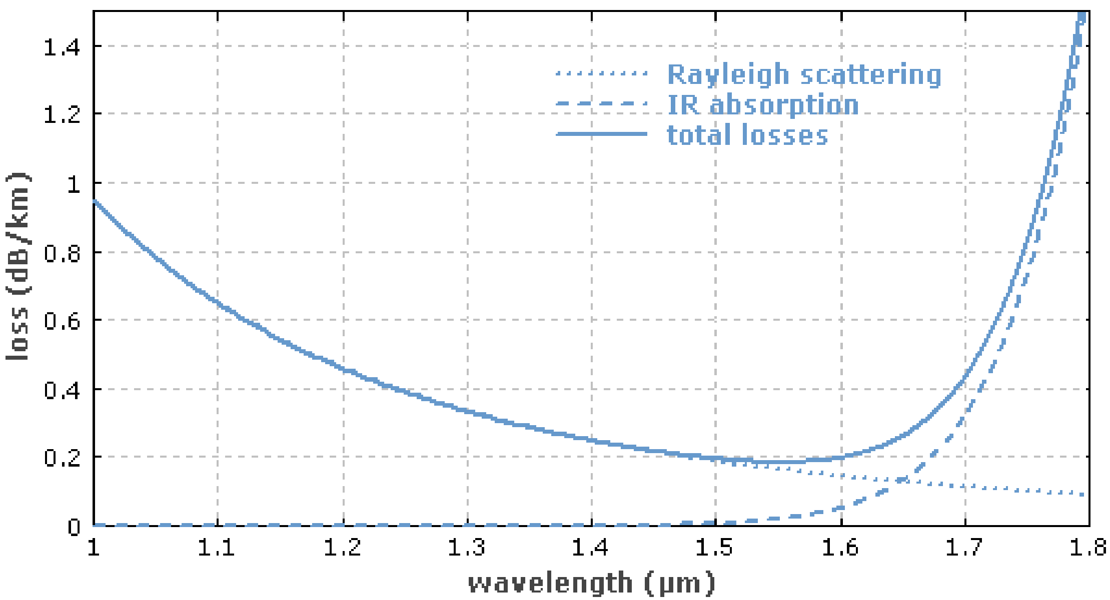
Flint glass ("F")

- Lead glasses
- High index
- High dispersion

SCHOTT
glass made of ideas

Diagram of Zeiss Hasselblad Sonnar Superachromat lens removed due to copyright restrictions.

Optical loss in silica glass



$$P\ (\mathrm{dB}) = 10 \cdot \log_{10}\left(\frac{I}{I_0}\right) \qquad \frac{I}{I_0} = \exp(-\alpha d) \ \Rightarrow$$

$$10 \cdot \log_{10}(0.5) \sim 3.0\ \mathrm{dB} \qquad 1\ \mathrm{dB/cm} = 0.23\ \mathrm{cm}^{-1}$$

The Nobel Prize in Physics 2009

Charles Kuen Kao

Prize motivation:

"*for groundbreaking achievements concerning the transmission of light in fibers for optical communication*"

Optical loss / attenuation mechanisms

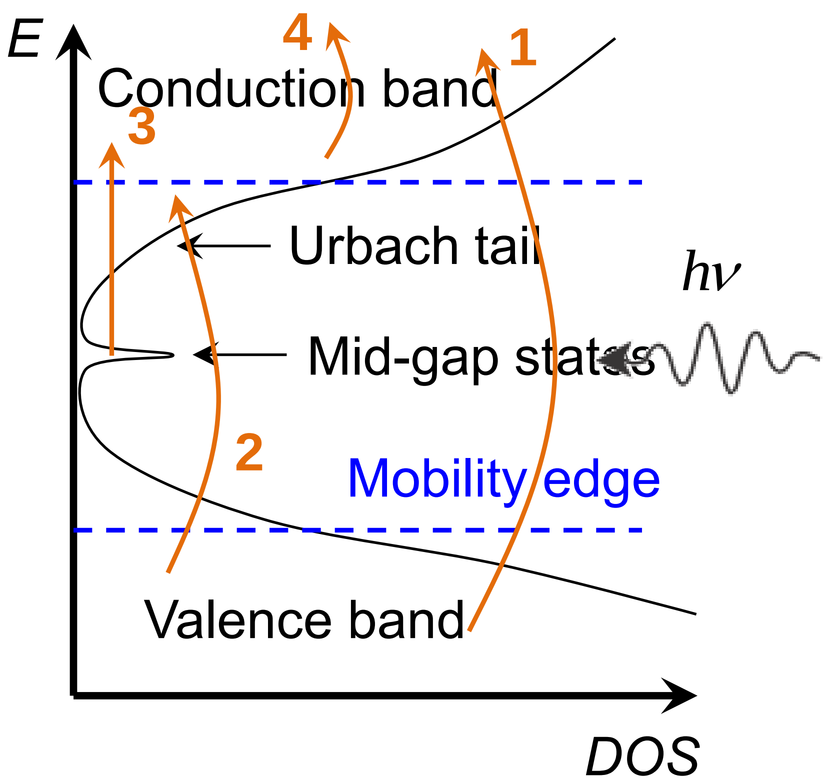
Semiconductor optoelectronics	*Soda-lime glass in the infrared*	*Transparent ceramics*	*Fiber-optic glasses*
Electronic absorption	Phonon absorption	Defect scattering	Rayleigh scattering
Absorption induced by electronic transitions	Absorption resulting from atomic / ionic vibrations	Scattering by crystalline grains, grain boundaries, micro-voids, etc.	Scattering due to density, structure or composition fluctuations

Optical loss mechanisms in glasses

- Extrinsic absorption (impurities or dopants)
  - Transition metal or rare earth ions
  - Vibrational absorption
- Intrinsic attenuation
  - Band-to-band transitions
  - Urbach tail absorption
  - Mid-gap defect state absorption
  - Free carrier absorption (FCA)
  - Phonon (vibrational) absorption
  - Rayleigh scattering
    - Density fluctuation
    - Structural moieties

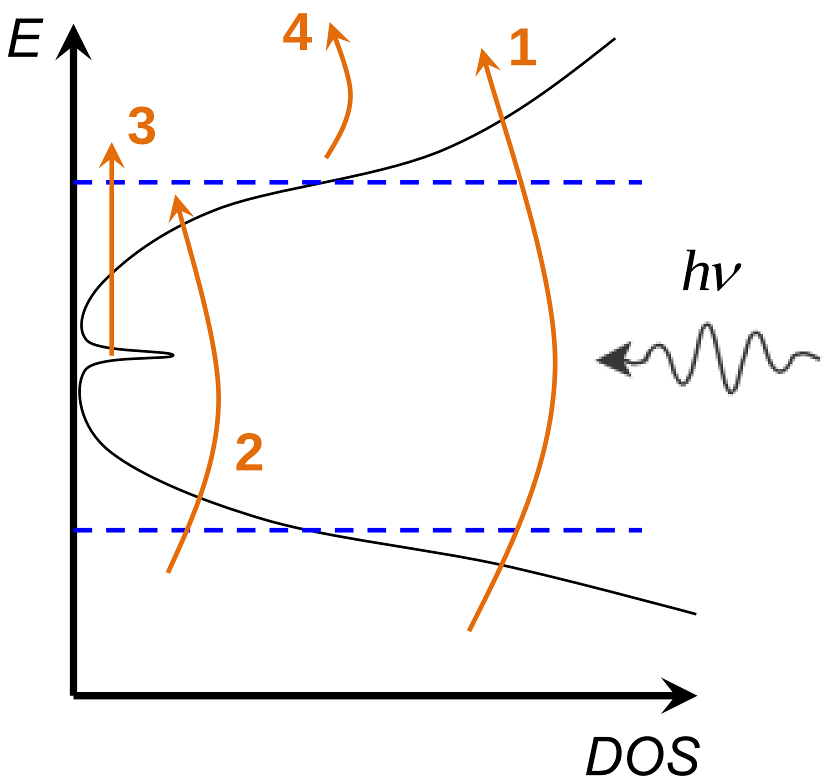
Color codes:
Atomic/ionic absorption
Electronic absorption
Scattering

Electronic absorption in amorphous solids



1. Band-to-band transition
2. Urbach bandtail absorption
3. Defect state absorption
4. Free carrier absorption

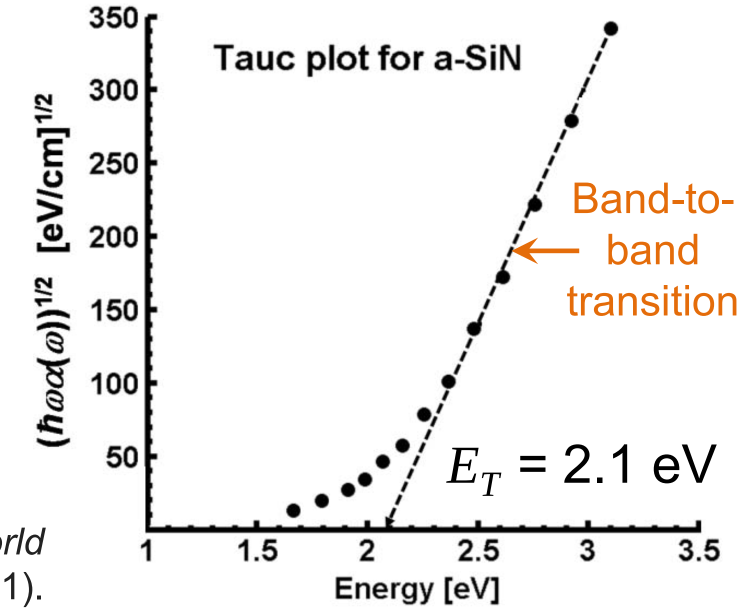
Electronic absorption in amorphous solids



1. Band-to-band transition

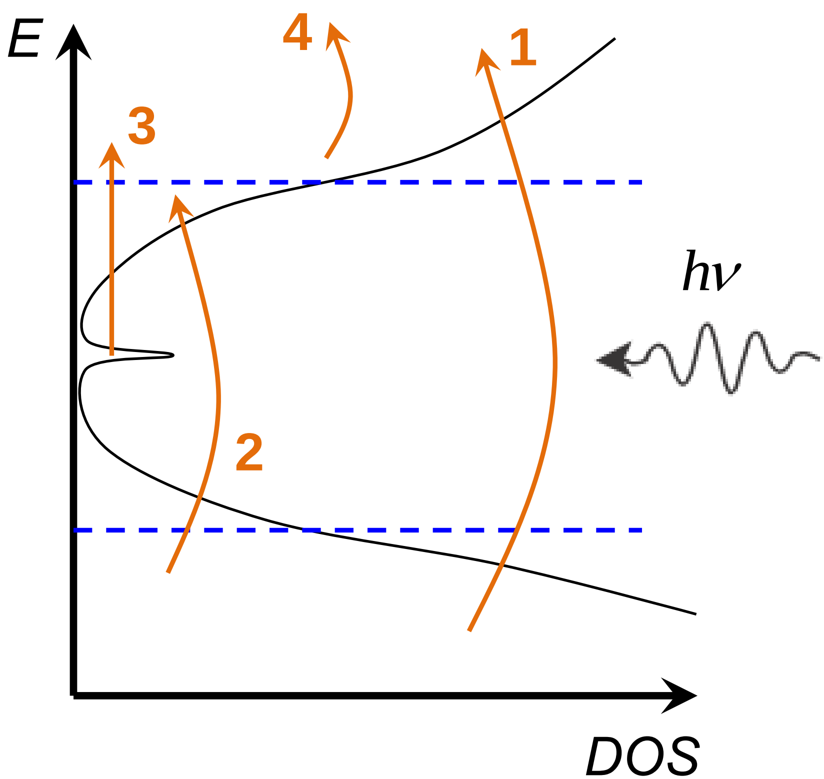
$$(\alpha \hbar \omega)^{1/2} \propto \hbar \omega - E_T$$

E_T : Tauc gap



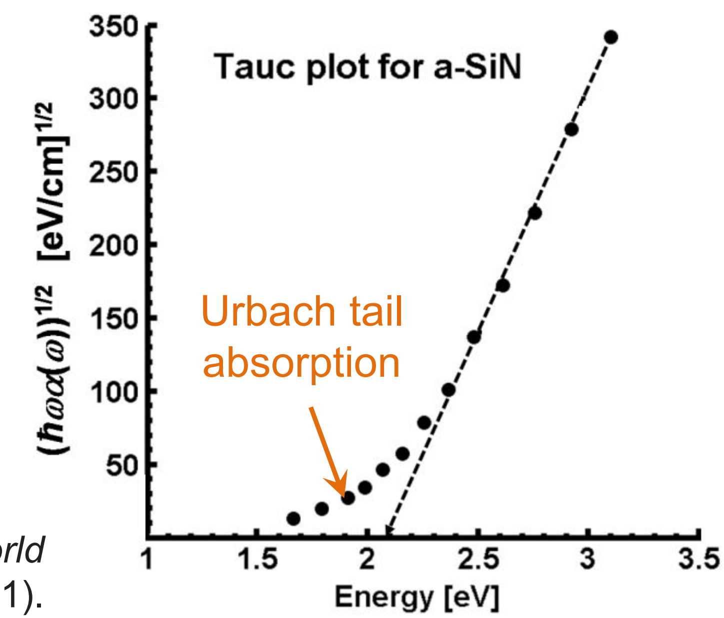
A. Stern, *Photodiodes – World Activities in*, 267 (2011).

Electronic absorption in amorphous solids



1. Band-to-band transition
2. Urbach bandtail absorption

$$\alpha = \alpha_U \exp\left[\left(\hbar\omega - E_g\right)/E_U\right]$$



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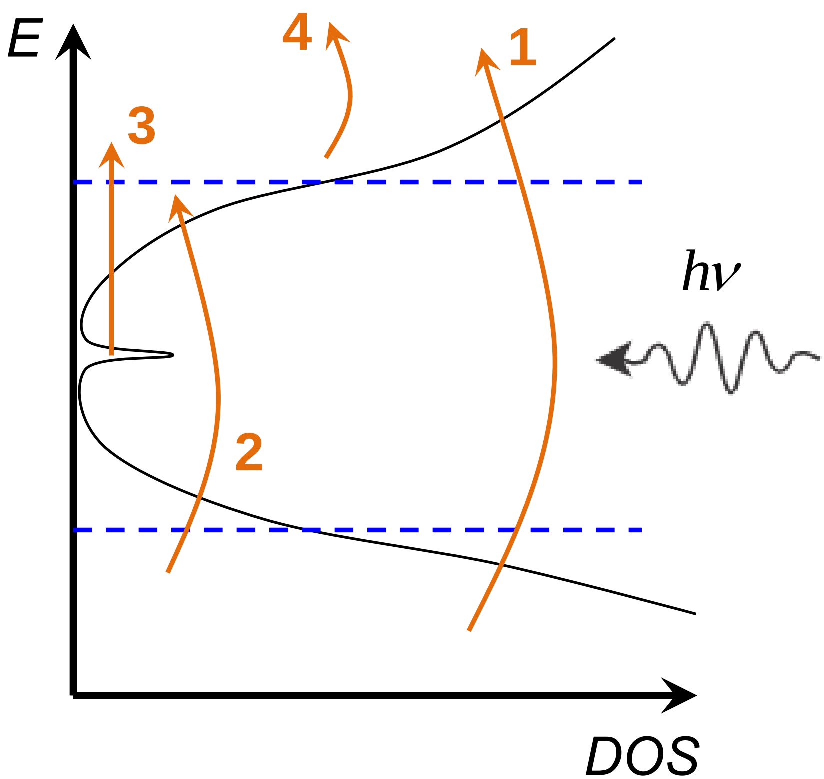
Electronic absorption in amorphous solids



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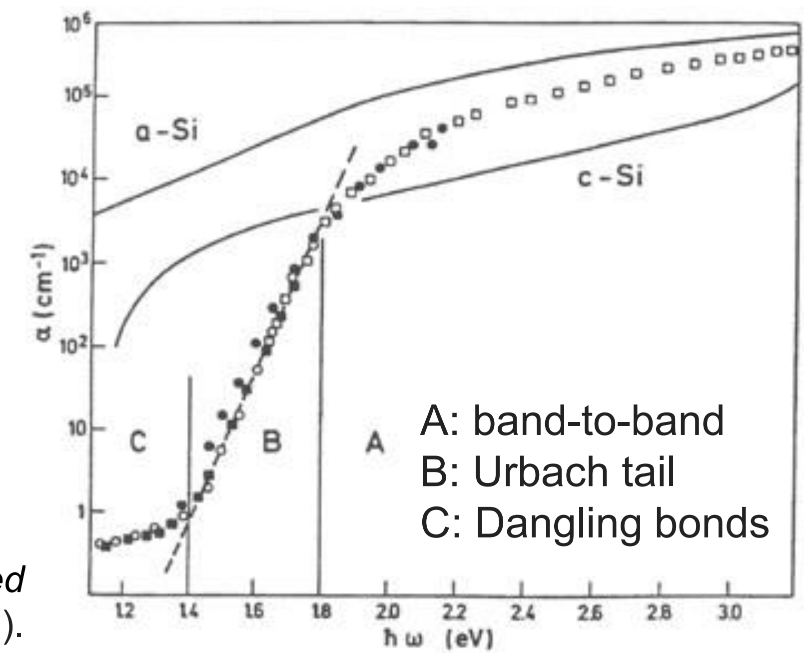
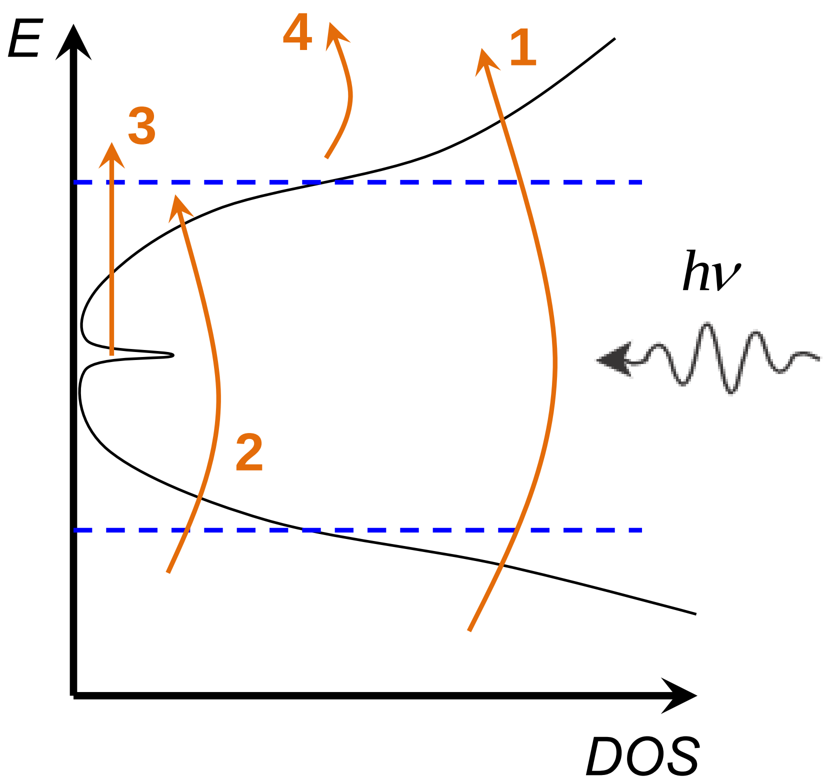
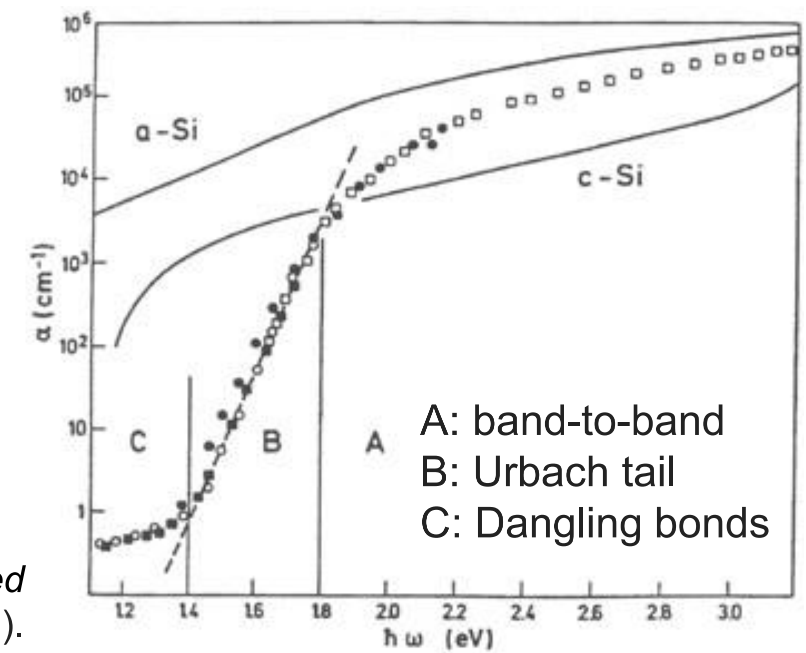


L. Ley, *The Physics of Hydrogenated Amorphous Silicon*, 141 (1984).

Electronic absorption in amorphous solids



1. Band-to-band transition
2. Urbach bandtail absorption
3. Defect state absorption



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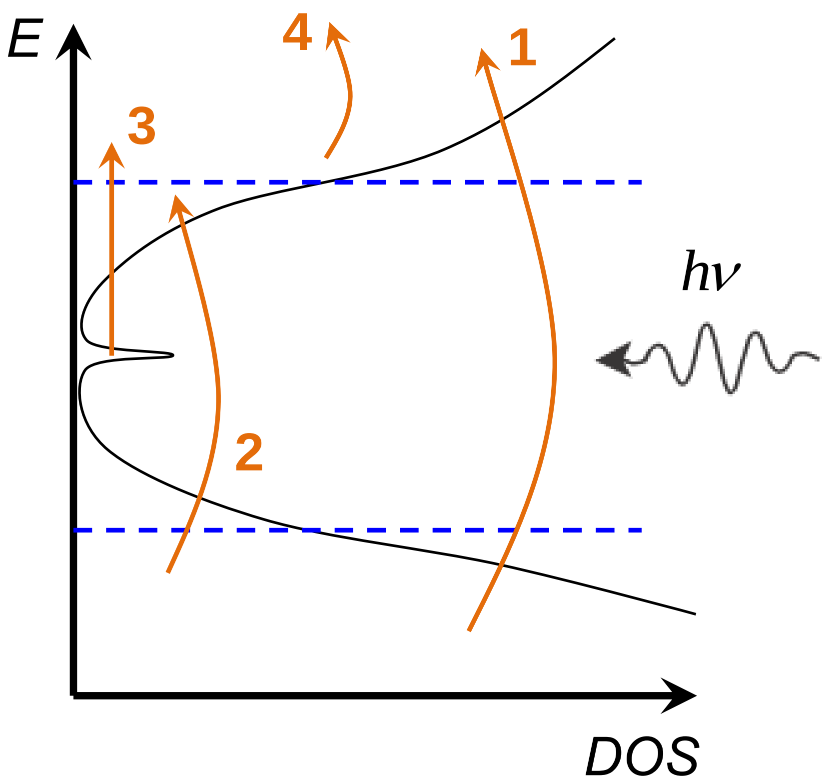
Electronic absorption in amorphous solids

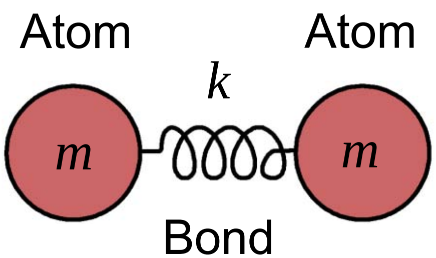


1. Band-to-band transition
2. Urbach bandtail absorption
3. Defect state absorption
4. Free carrier absorption

Absorption coefficient (cm^{-1})

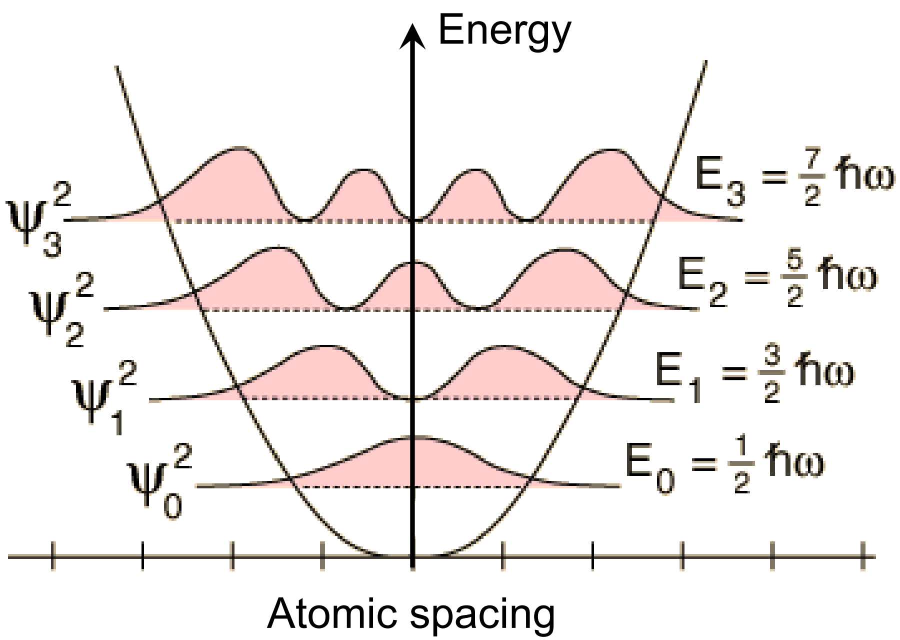
- Band-to-band: > 10^3
- Bandtail and defect states: 1 – 10^3
- FCA: generally weak in amorphous solids

Vibrational absorption



Harmonic oscillator

$$\omega \propto \sqrt{k/m}$$



Compound or functional group	Primary absorption bands (μm)
O-H	2.92
S-H	4.01, 3.65, 3.11, 2.05
Ge-H	4.95
P-H	4.35
As-H	5.02
Si-O	9.1 – 9.6
Ge-O	12.8
H_2O	6.3, 2.8

J. Optoelectron. Adv. Mater. **3**, 341 (2001)

Sources of Rayleigh scattering in glass

- Local density fluctuation

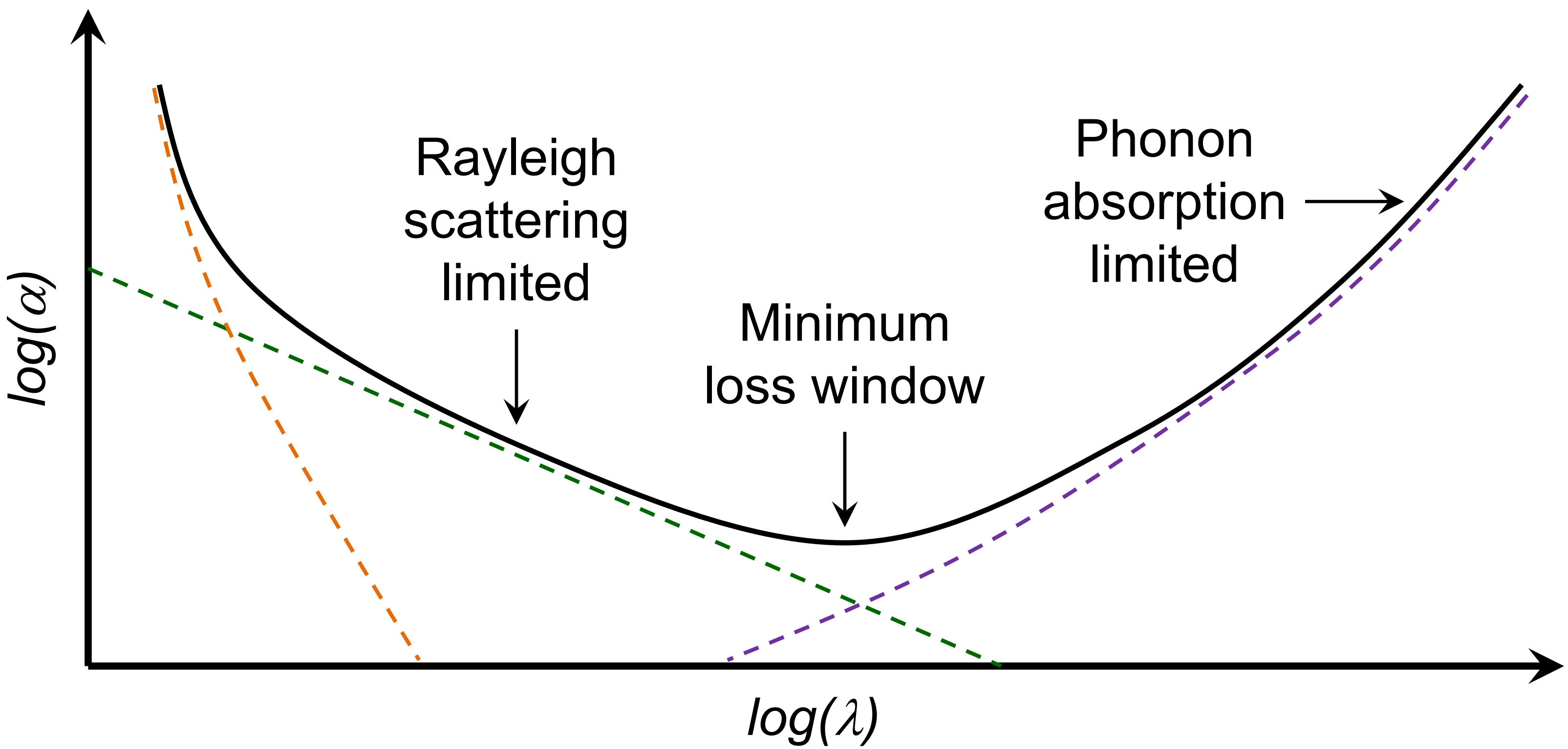
$$\alpha = A_1/\lambda^4 \qquad A_1 = \frac{8}{3}\pi^3 n^8 p^2 \beta k_B T_f$$

  - p : photoelastic constant
  - β : isothermal compressibility
- Concentration scattering
  - Local composition fluctuation in multi-component glasses

Ann. Physik **33**, 1275 (1910);
Ann. Physik **25**, 205 (1908);
J. Appl. Phys. **55**, 4052 (1984).

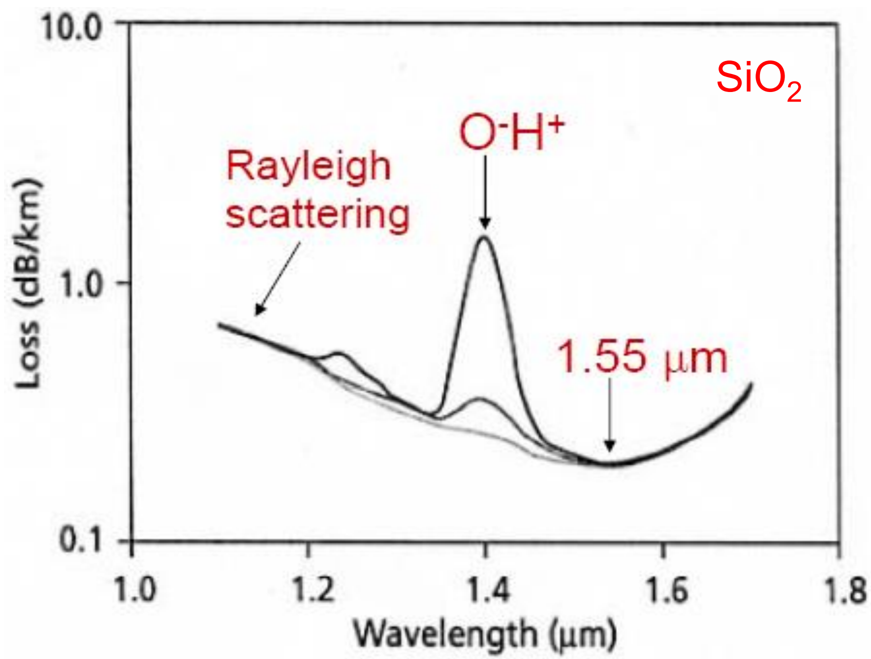
Einstein-Smoluchowski scattering: density fluctuation of atmosphere

Intrinsic optical loss spectrum in glass

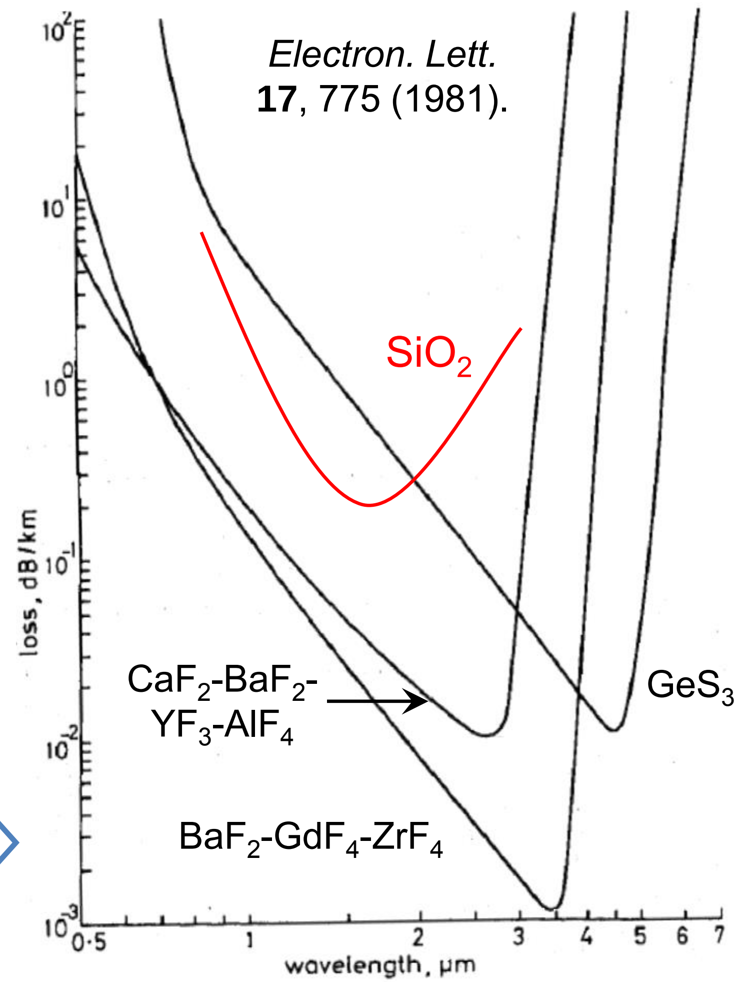


Total loss: $\alpha_t = (A_1 + A_2)/\lambda^4 + B_1 \exp(B_2/\lambda) + C_1 \exp(-C_2/\lambda)$

Total optical loss in glasses



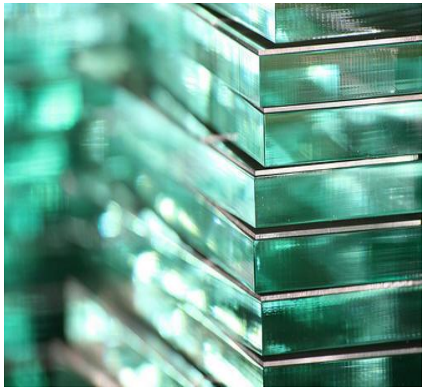
Concentration scattering is not taken into account, resulting in unrealistically low loss values



Transparent glass coloring: absorption

- Transition metal or rare earth ion additives

Transition metal ions			Rare earth ions		
Configuration	Ion	Color	Configuration	Ion	Color
d^0	Ti^{4+}	Colorless	$4f^0$	La^{3+}	None
	V^{5+}	Faint yellow		Ce^{4+}	Weak yellow
		to colorless	$4f^1$	Ce^{3+}	Weak yellow
	Cr^{6+}	Faint yellow	$4f^2$	Pr^{3+}	Green
		to colorless	$4f^4$	Nd^{3+}	Violet-pink
d^1	Ti^{3+}	Violet-purple	$4f^4$	Pm^{3+}	None
	V^{4+}	Blue	$4f^5$	Sm^{3+}	None
	Mn^{6+}	Colorless	$4f^6$	Sm^{2+}	Green
d^2	V^{3+}	Yellow-green		Eu^{3+}	None
d^3	Cr^{3+}	Green	$4f^7$	Eu^{2+}	Brown
d^4	Cr^{2+}	Faint blue		Gd^{3+}	None
	Mn^{3+}	Purple	$4f^8$	Tb^{3+}	None
d^5	Mn^{2+}	Light yellow	$4f^9$	Dy^{3+}	None
	Fe^{3+}	Faint yellow	$4f^{10}$	Dy^{2+}	Brown
d^6	Fe^{2+}	Blue-green		Ho^{3+}	Yellow
	Co^{3+}	Faint yellow	$4f^{11}$	Er^{3+}	Weak pink
d^7	Co^{2+}	Blue-pink	f^{12}	Tm^{3+}	None
d^8	Ni^{2+}	Brown-purple	$4f^{13}$	Tm^{2+}	None
d^9	Cu^{2+}	Blue-green		Yb^{3+}	None
d^{10}	Cu^{+}	Colorless	$4f^{14}$	Lu^{3+}	None



Green tint due to Fe^{2+} ions

Glass decolorization:

$$Fe^{2+} \underset{\text{reduction}}{\overset{\text{oxidation}}{\rightleftharpoons}} Fe^{3+}$$

Examples of color glasses with ion additives

Cobalt blue

Chromium green

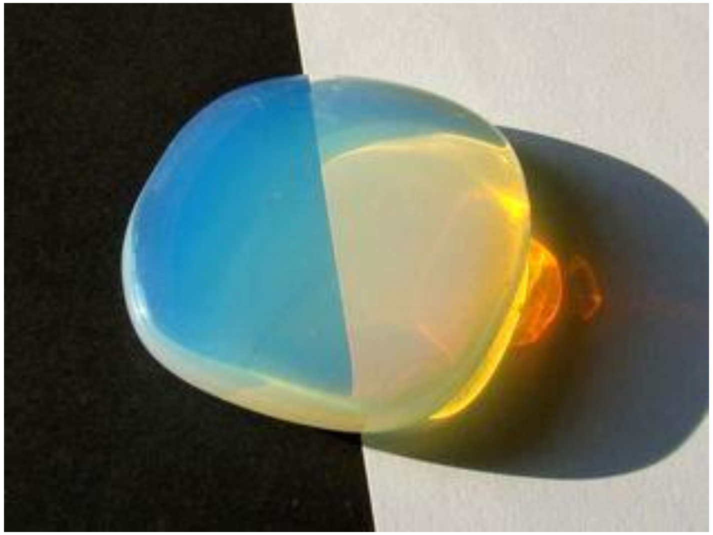
Room light UV illumination

Uranium glass (Vaseline glass)

Manganese amethyst

Transparent glass coloring: scattering

- Precipitation of small crystals or metal nanoparticles
  - Rayleigh scattering by nanocrystals
  - Plasmon resonance of metal nanoparticles



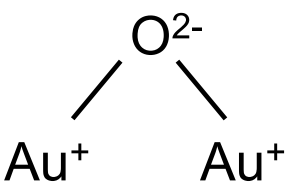
Opalescent glass: nanocrystals

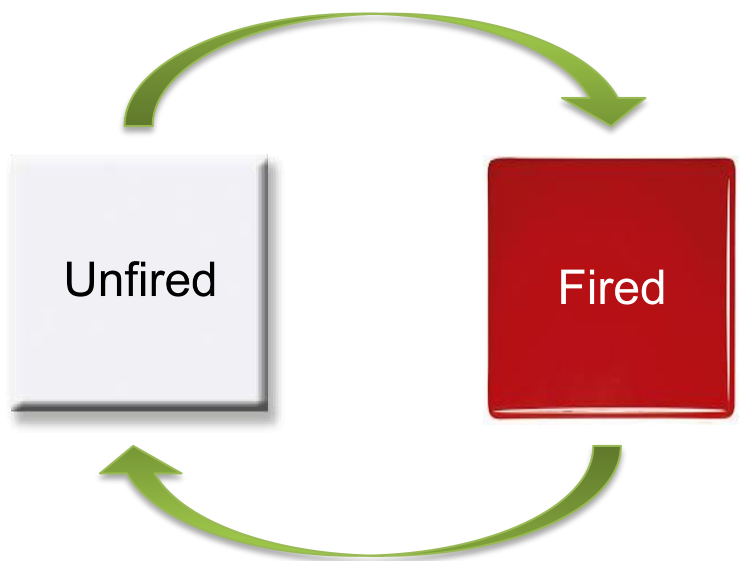
Lycurgus Cup: Au-Ag nanoparticles

Striking colors

- Coloring of glass via heat treatment
- Example: gold-ruby striking

Annealing at 500 – 700 °C





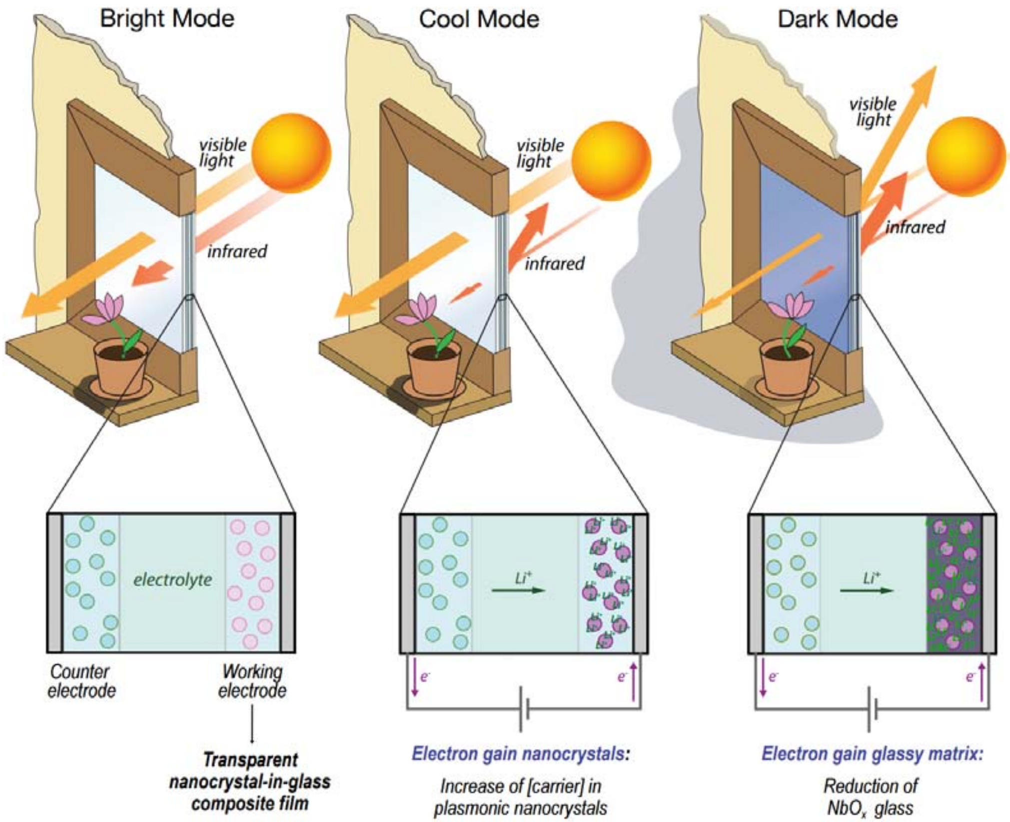
Au nanoparticles
(dia. 5 – 60 nm)

Melt at 1400 °C and quench

Nature **407**, 691 (2000)

Photochromic and electrochromic glasses

- Optical or electrical control of redox state of ions
- Carrier injection into transparent conductors to modulate FCA



Bleached
transparent

$$Nb_2O_5 + x\, Li^+ + x\, e^-$$

$$\updownarrow$$

$$Li_xNb_2O_5$$

Colored
brown-gray

Nature **500**, 323 (2013)

Photochromic and electrochromic glasses

- Optical or electrical control of redox state of ions
- Carrier injection into transparent conductors to modulate FCA

Nature **500**, 323 (2013)

Summary

- Refraction
  - Microscopic origin of refraction and chromatic dispersion
  - Composition dependence of refractive indices
  - Abbe number
- Attenuation
  - Optical loss mechanisms in general materials
  - Optical loss mechanisms in glasses
  - Electronic, vibrational, and scattering losses
- Coloring
  - Ion additives
  - Scattering by nanoparticles