MIT 3.071
Amorphous Materials

13: 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

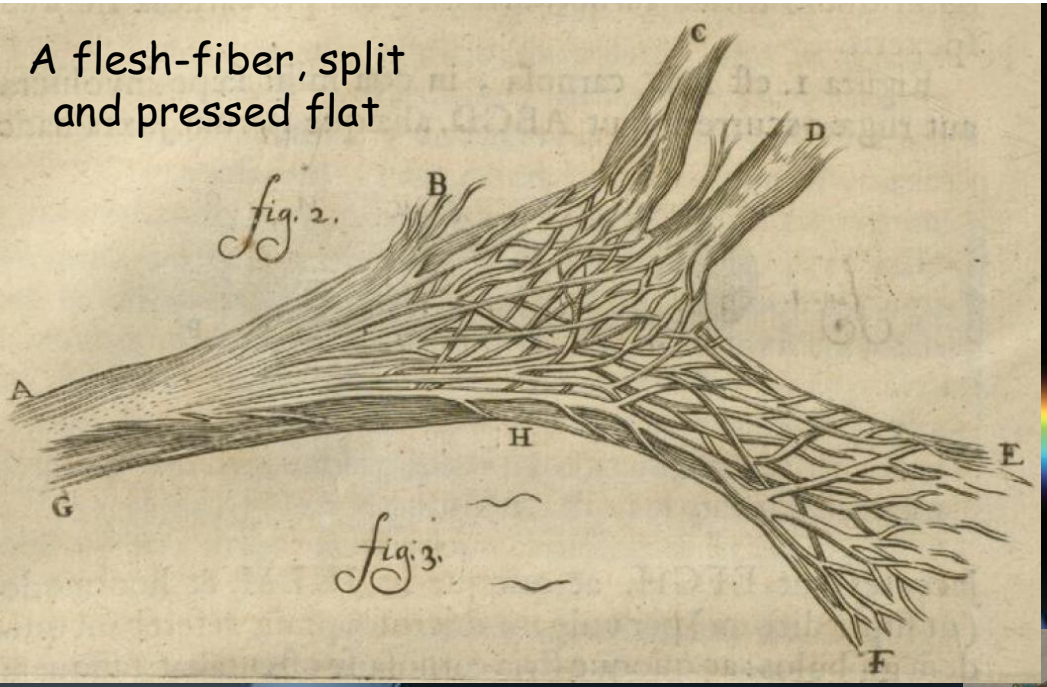
What's so special about  ?

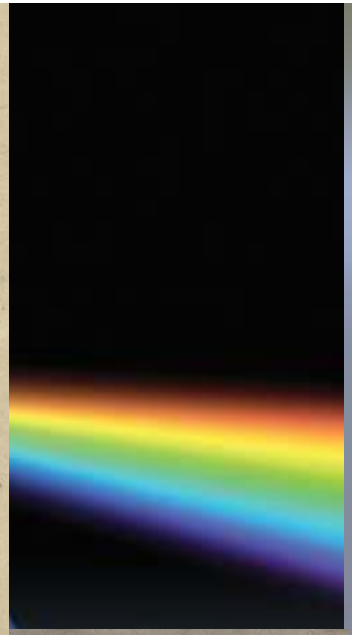
Refraction

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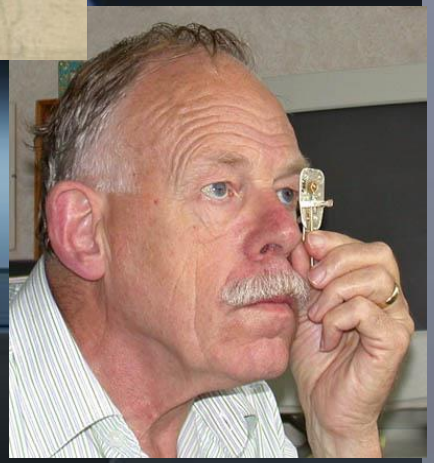
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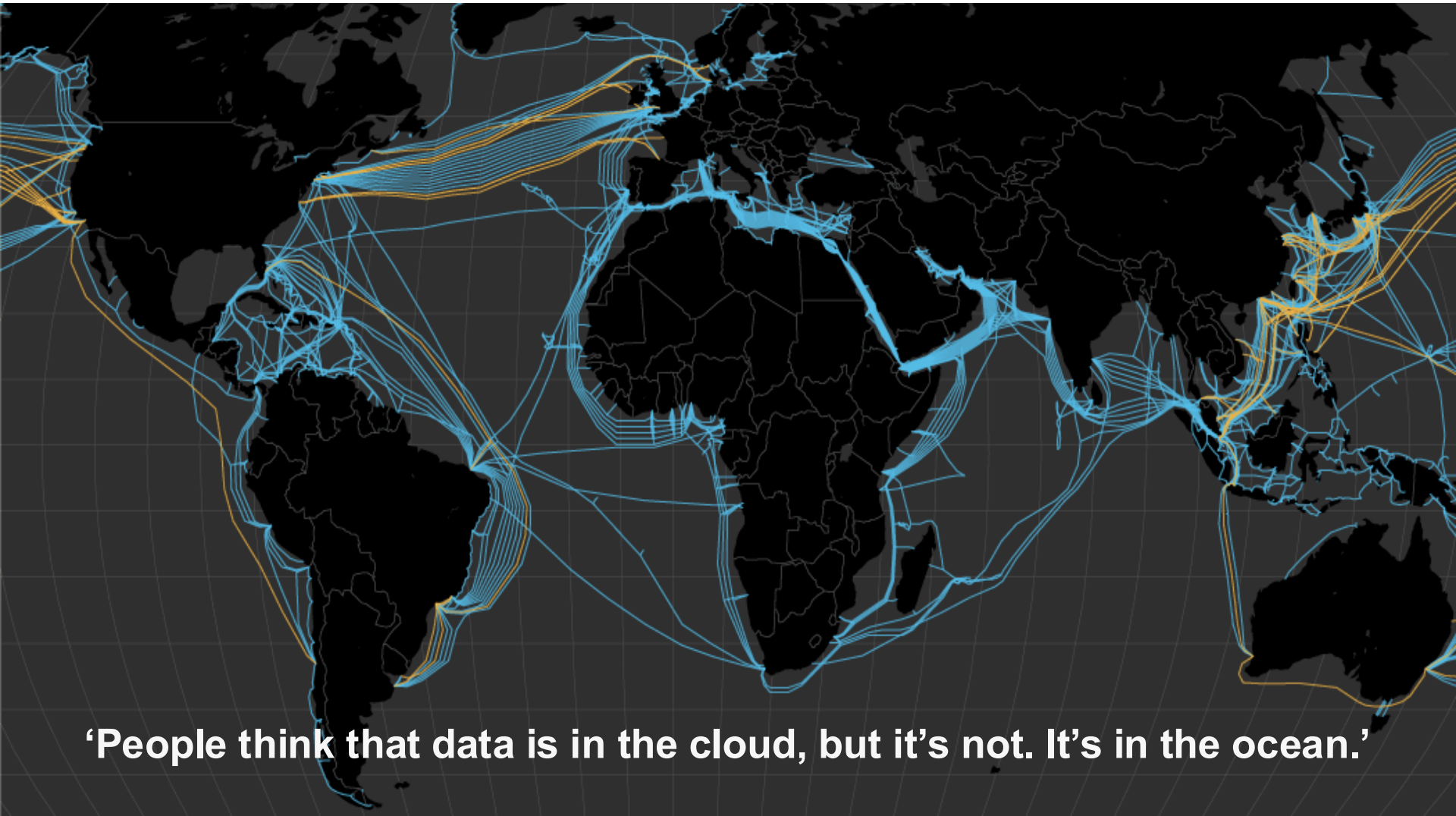






Transparency

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‘People think that data is in the cloud, but it’s not. It’s in the ocean.’

Color

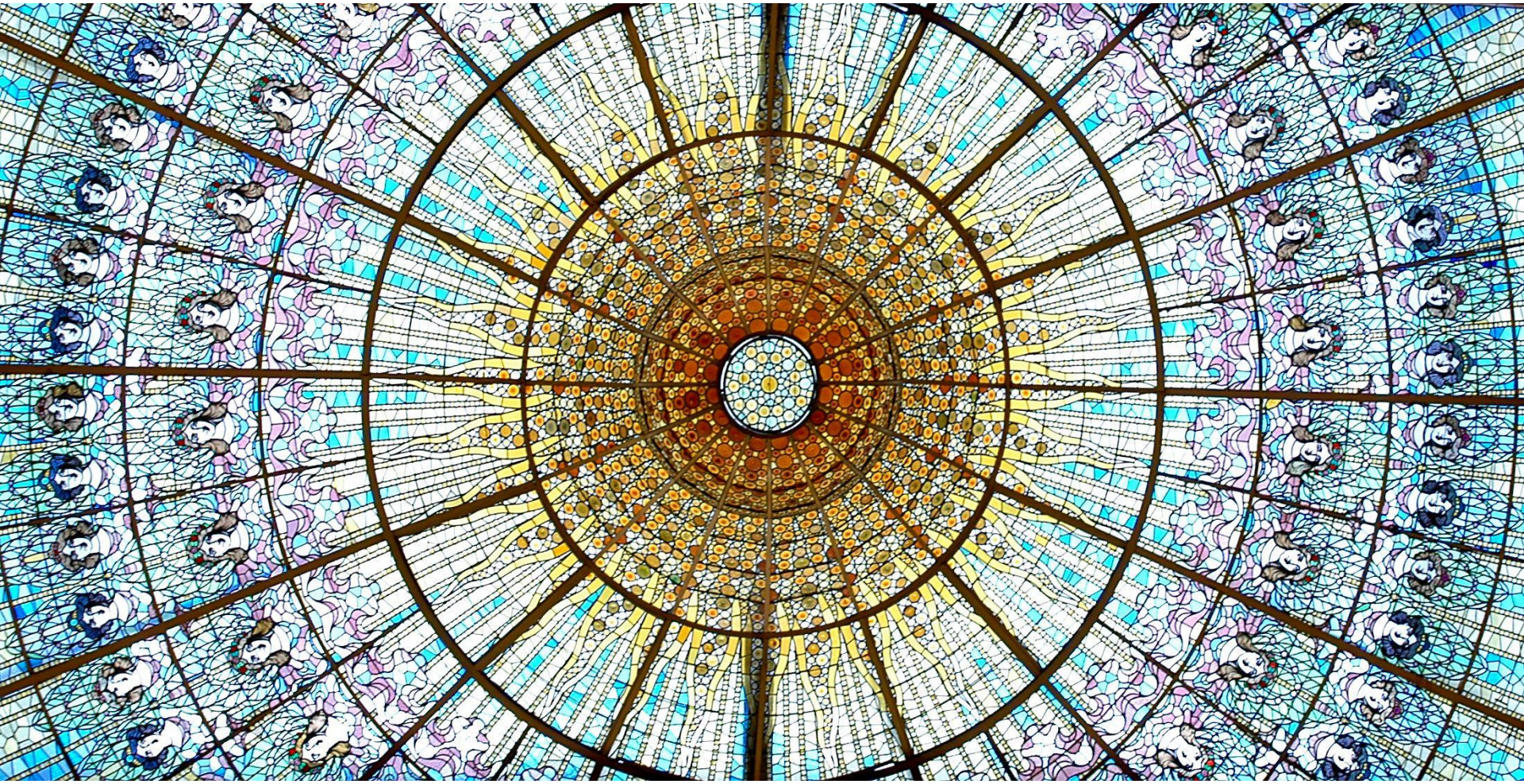


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Palau de la Musica Catalana, Barcelona

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: $\nabla \times E = -\frac{\partial B}{\partial t}$
- Ampere's Law: $\nabla \times H = J_f + \frac{\partial D}{\partial t}$



James C. Maxwell
(1831-1879)

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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 ($\mu = \mu_0$)

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

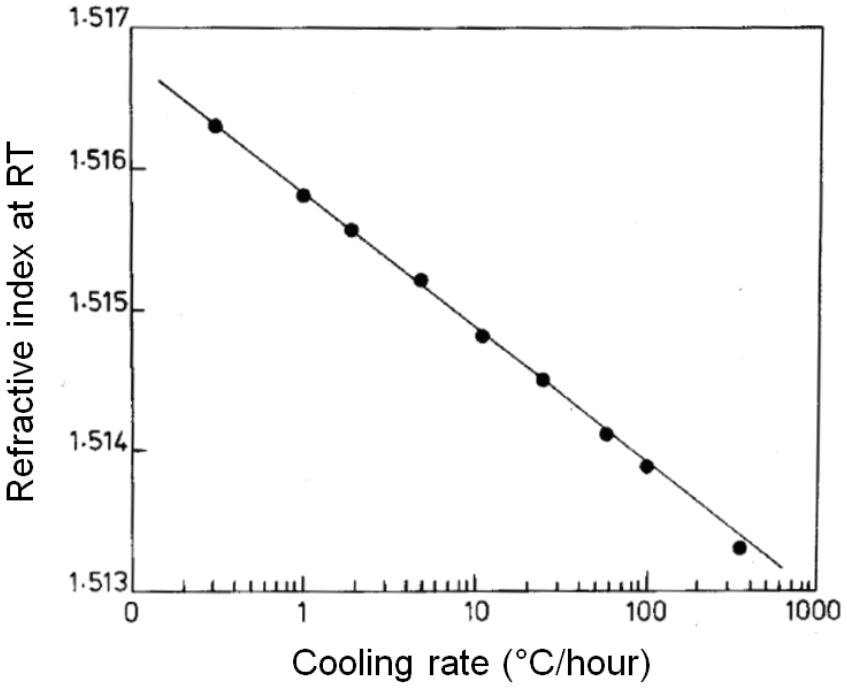
$$D = \varepsilon_0 (1+\chi) E = \varepsilon_0 \varepsilon_r E = \varepsilon E$$

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

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

Refractive index of glass: general trends

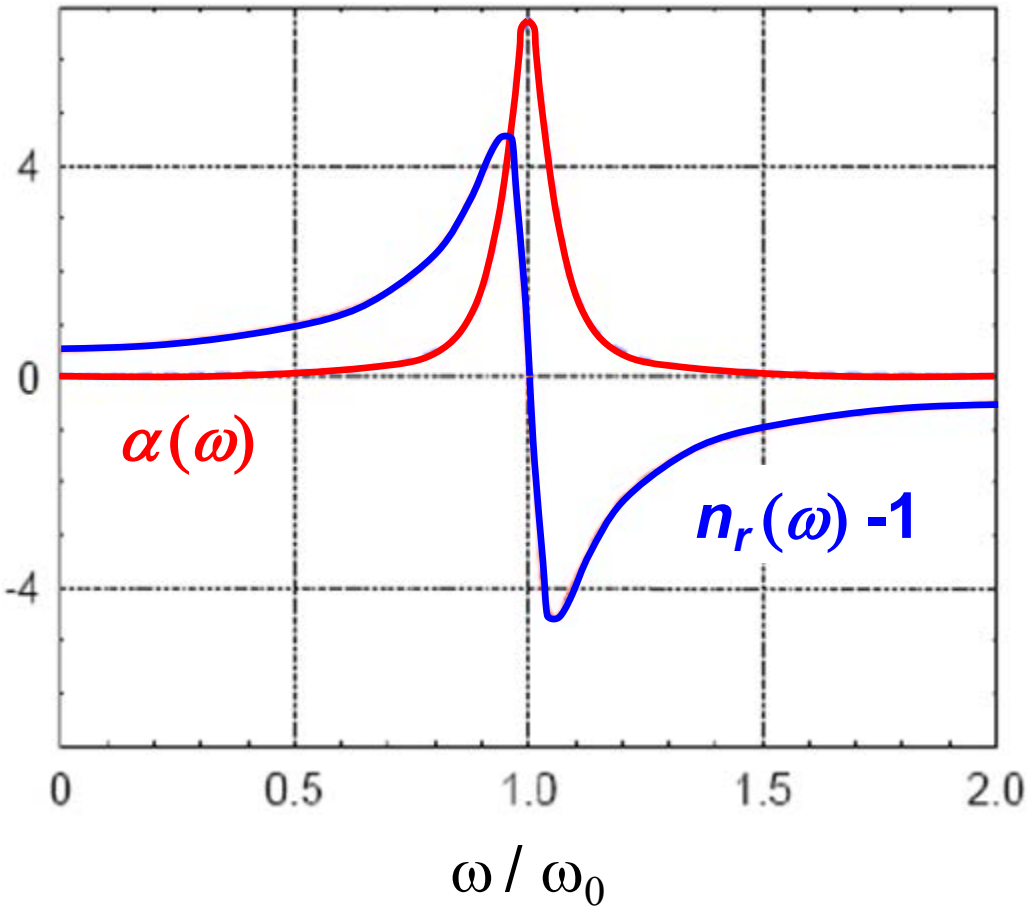
- Addition of heavy elements increases index
  - Lead-containing glasses
- Addition of alkali oxides increases index
  - NBOs have larger polarizability than BOs
- Fictive temperature (density) dependence



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

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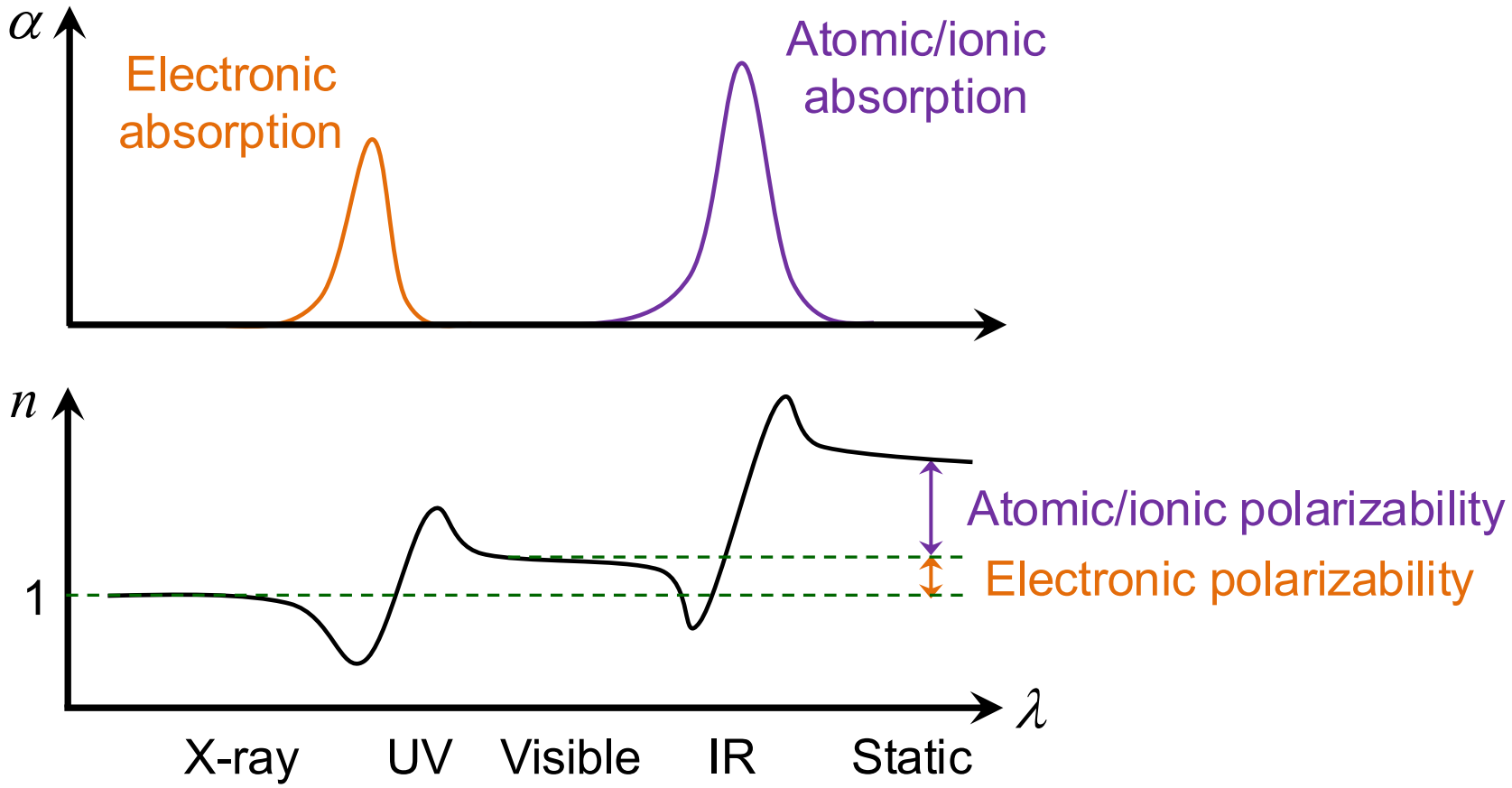
Kramers-Kronig (K-K) relation



Refractive index ***n*** and optical absorption α are not independent quantities!

Refractive index of glasses

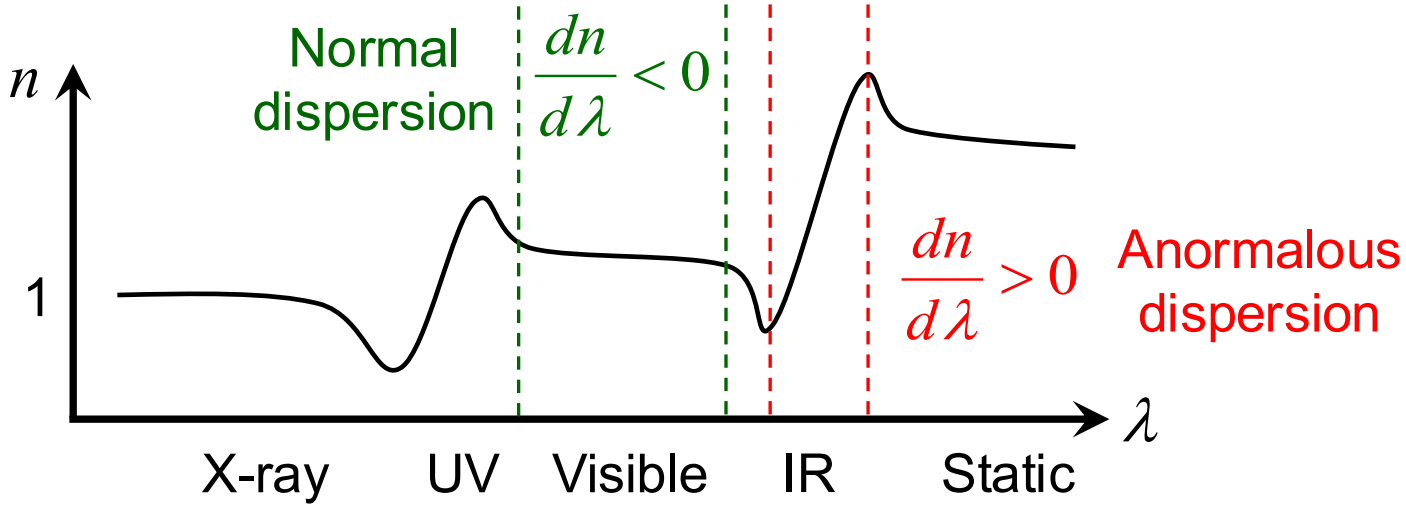
- Wavelength/frequency dependent (Lorentz oscillators)



Chromatic dispersion of glasses

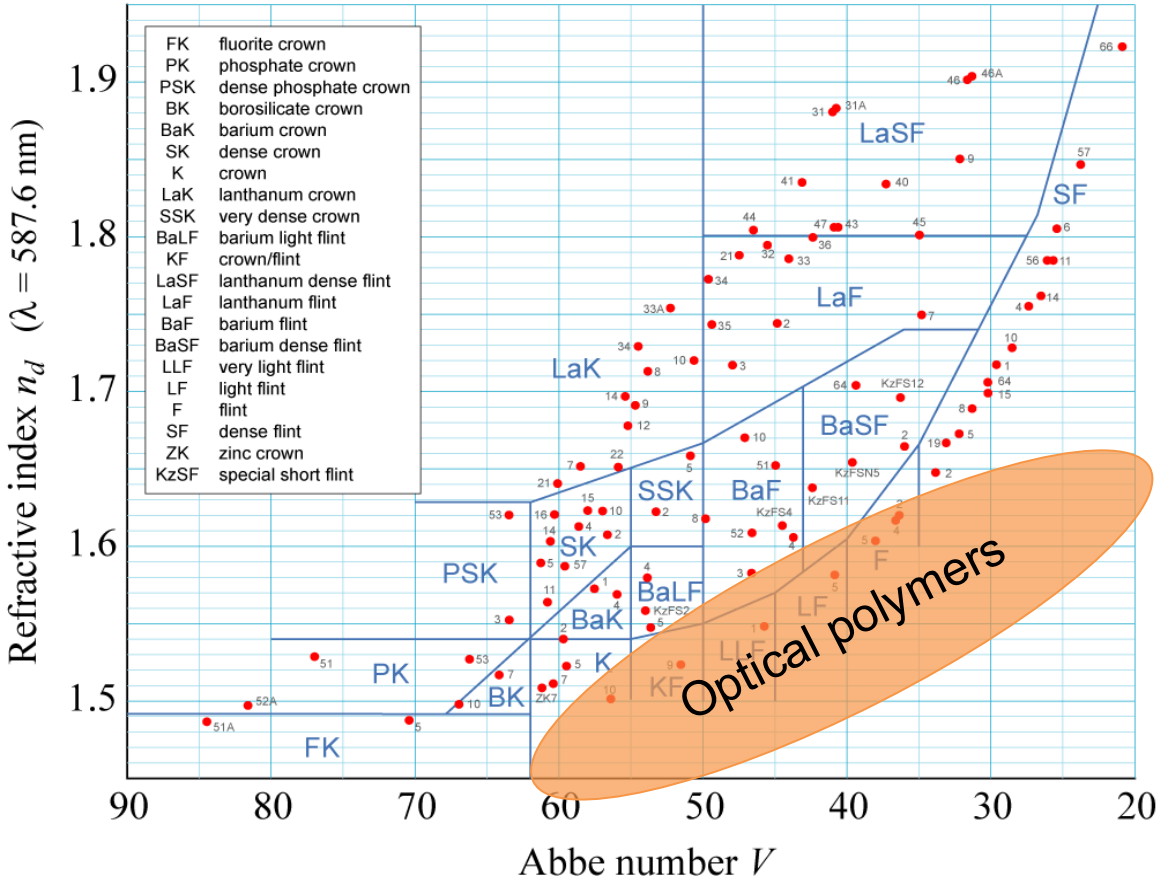
- Abbe number (V-number): $V_D = (n_D - 1)/(n_F - n_C)$
  - D, F and C spectral lines: 589.3 nm, 486.1 nm and 656.3 nm





Chromatic dispersion of glasses

- Abbe number (V-number): $V_D = (n_D - 1)/(n_F - n_C)$



Crown glass ("K")

- Soda-lime silicates
- Low index
- Low dispersion

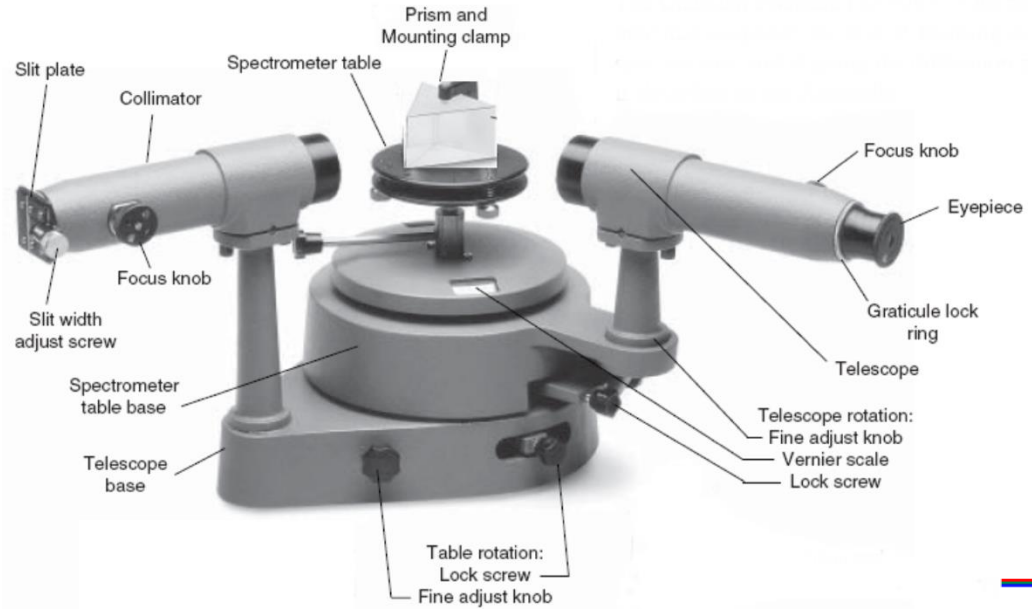
Flint glass ("F")

- Lead glasses
- High index
- High dispersion

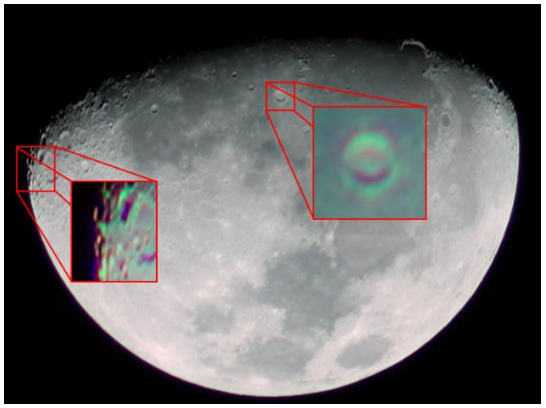
SCHOTT
glass made of ideas

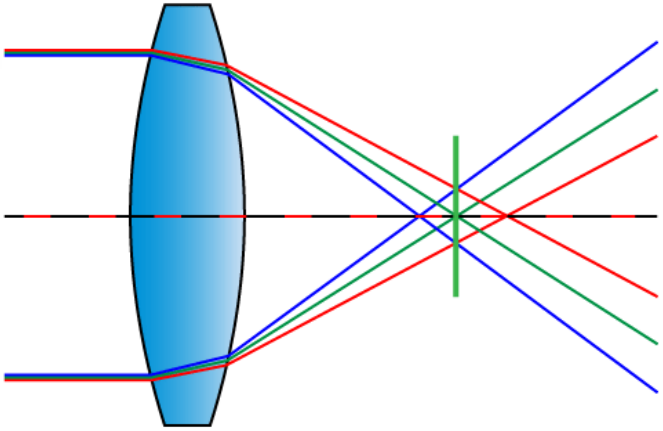
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Chromatic dispersion of glasses



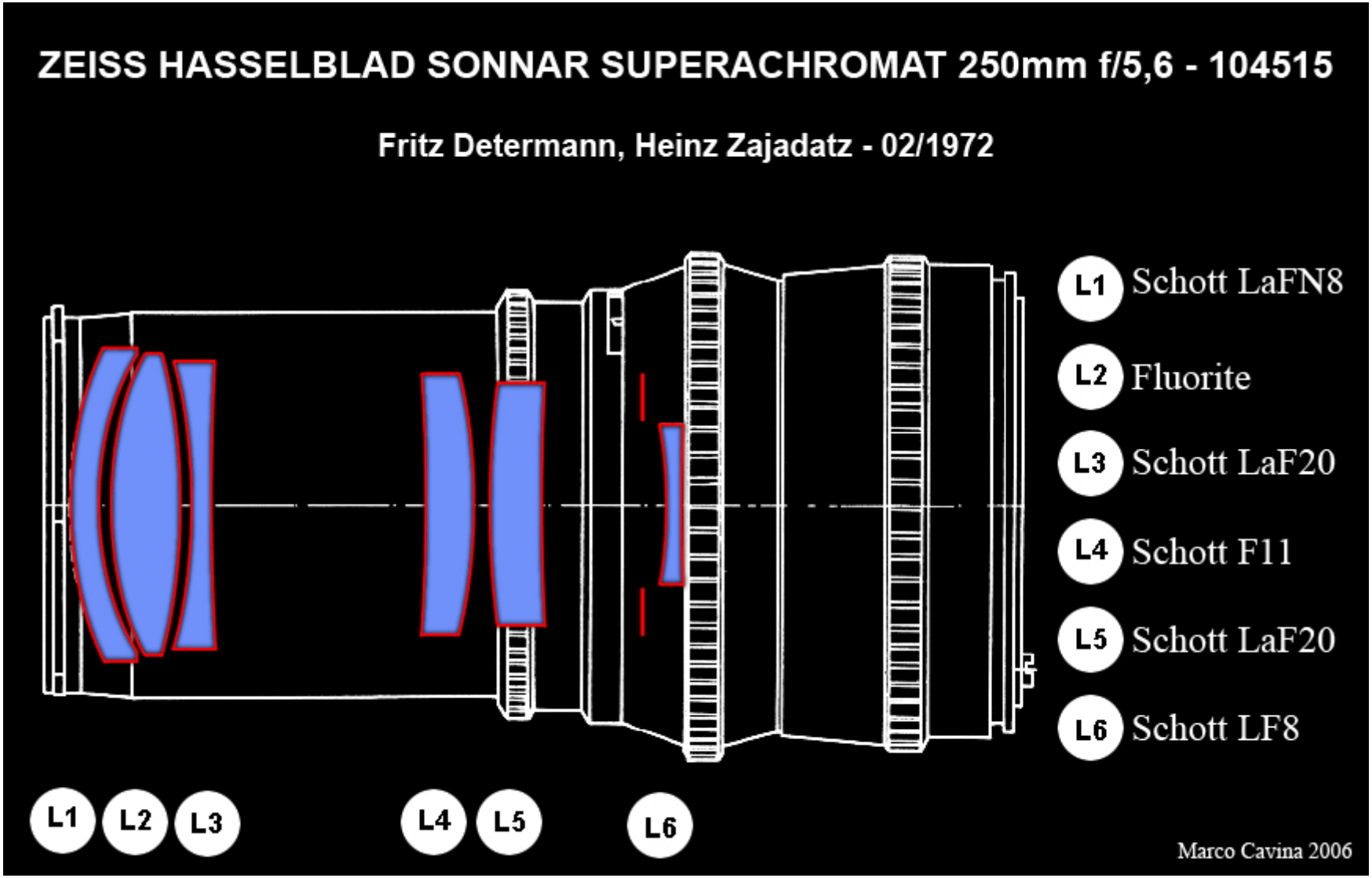
Prism dispersive spectrometer





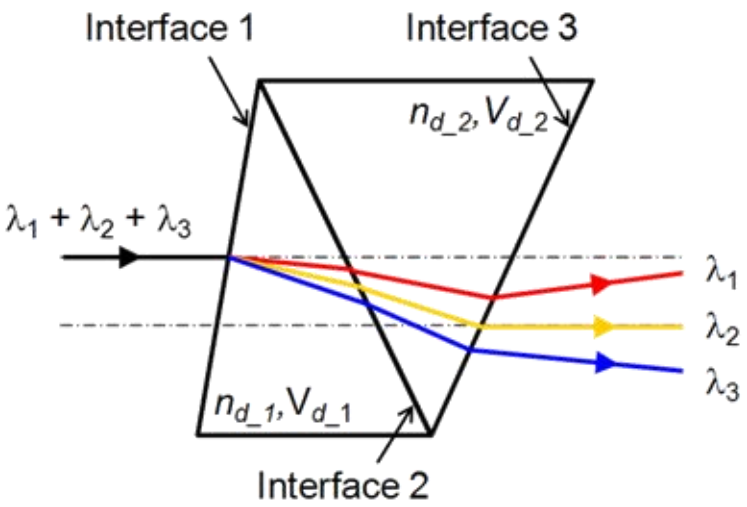
Chromatic aberration

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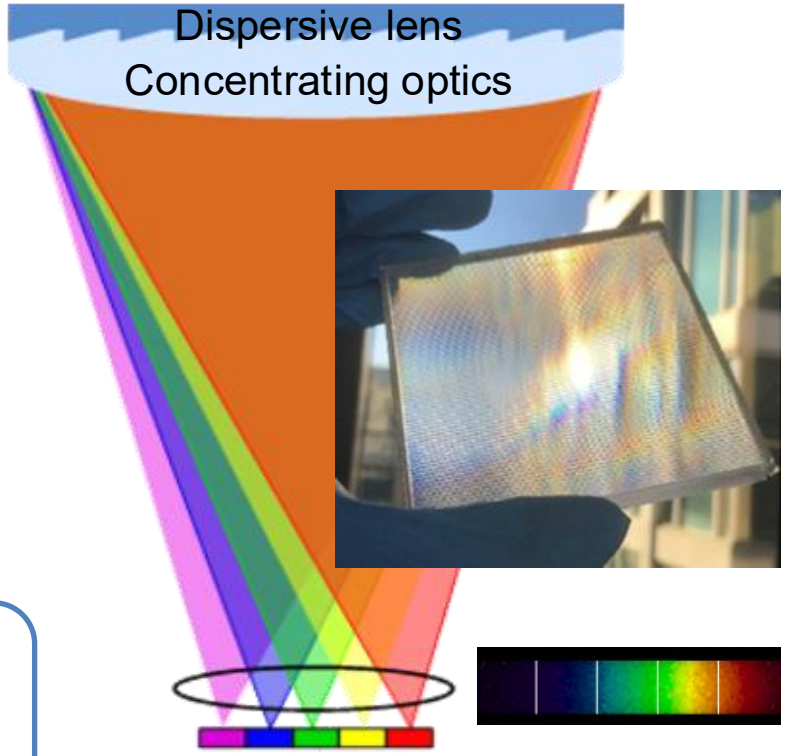


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Dispersive concentrators for lateral solar spectrum splitting



Combining two materials (glass & polymer) with identical refractive index and different dispersion to split sunlight without bending optical axis

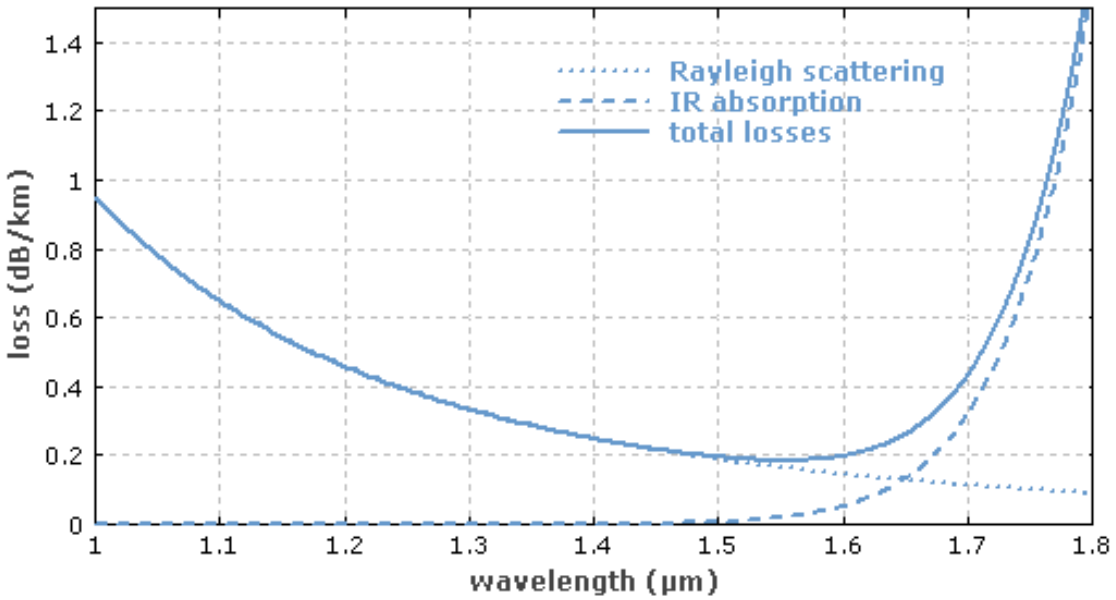


Lateral cell arrays

Opt. Lett. **44**, 3274 (2019)

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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*"

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Optical loss / attenuation mechanisms

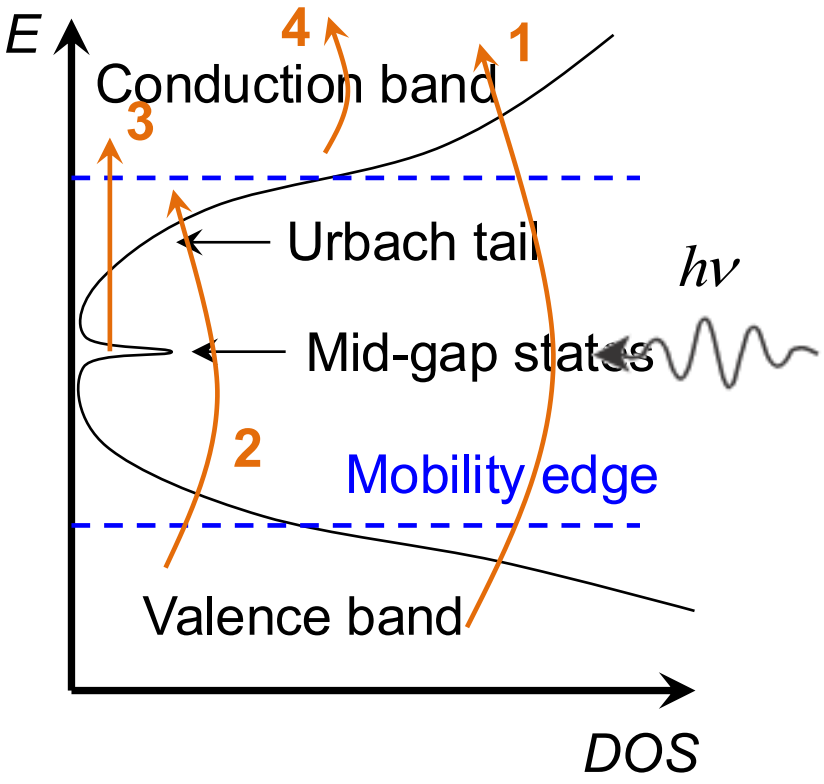
Semiconductor optoelectronics	*Soda-lime glass in the infrared*	*Transparent ceramics*	*Fiber-optic glasses*
Electronic absorption	Phonon absorption	Defect scattering	Rayleigh scattering
Absorption induced by electronic transitions	Absorption resulting from atomic / ionic vibrations	Scattering by crystalline 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

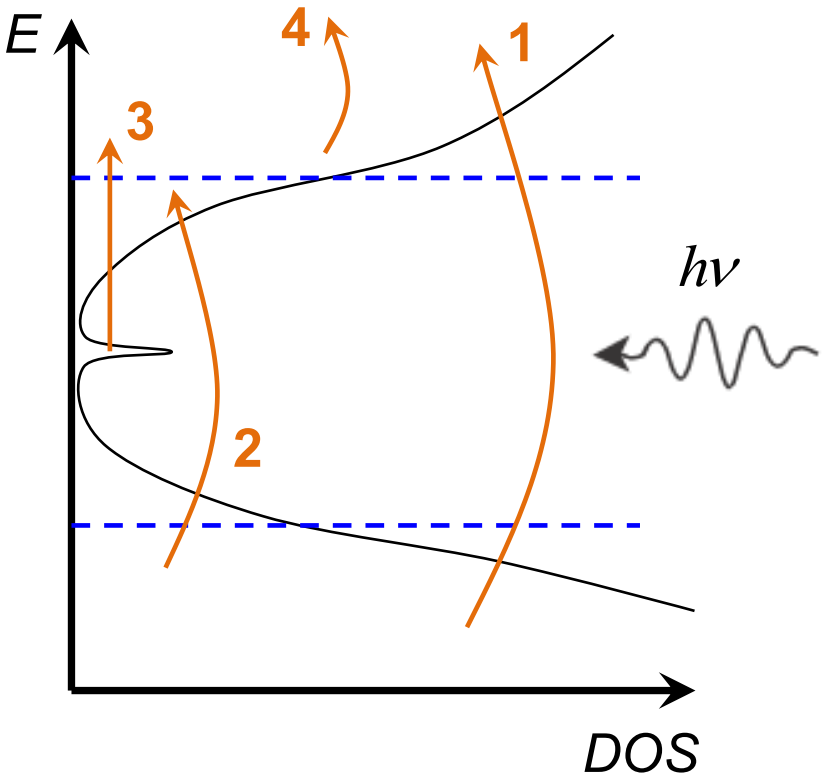
Color codes:
Atomic/ionic absorption
Electronic absorption
Scattering

Electronic absorption in amorphous solids



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

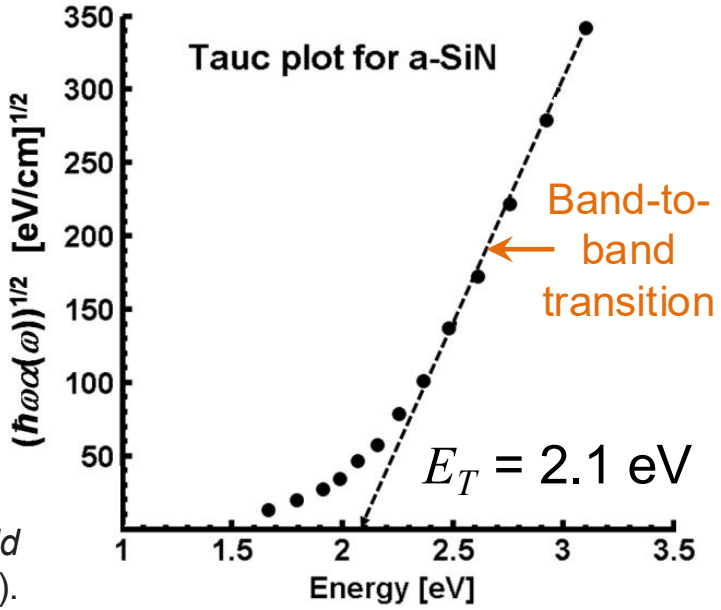
Electronic absorption in amorphous solids



1. Band-to-band transition

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

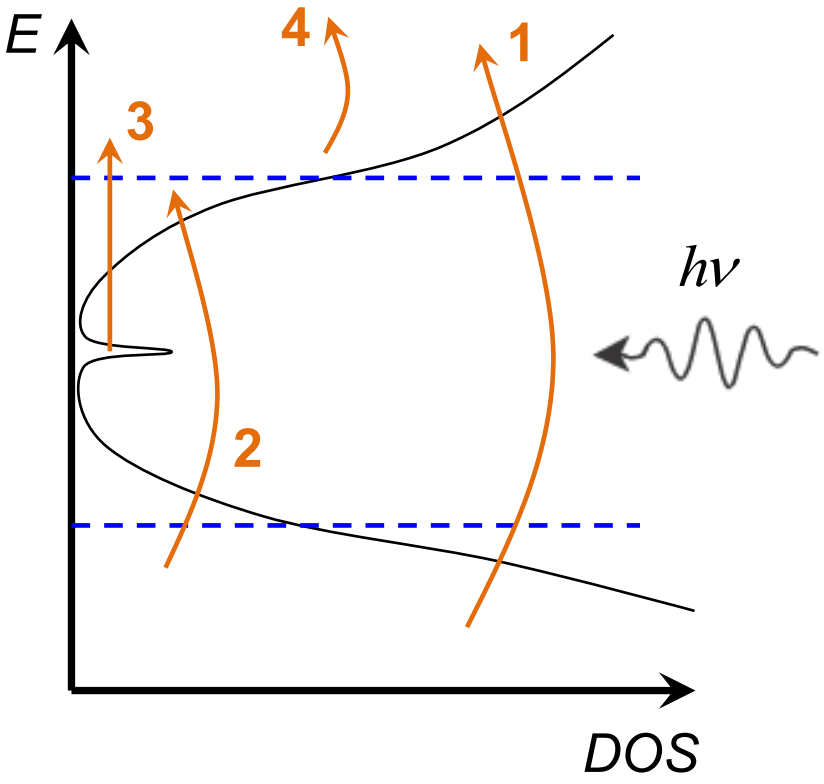
E_T : Tauc gap



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

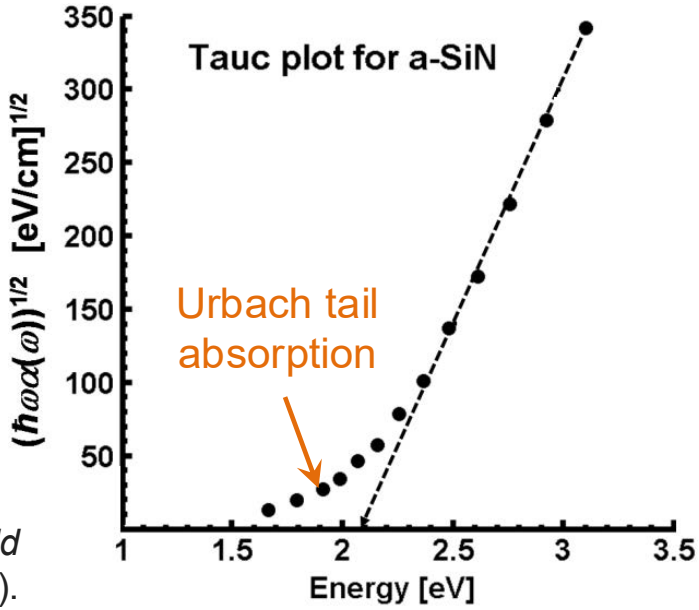
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Electronic absorption in amorphous solids



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

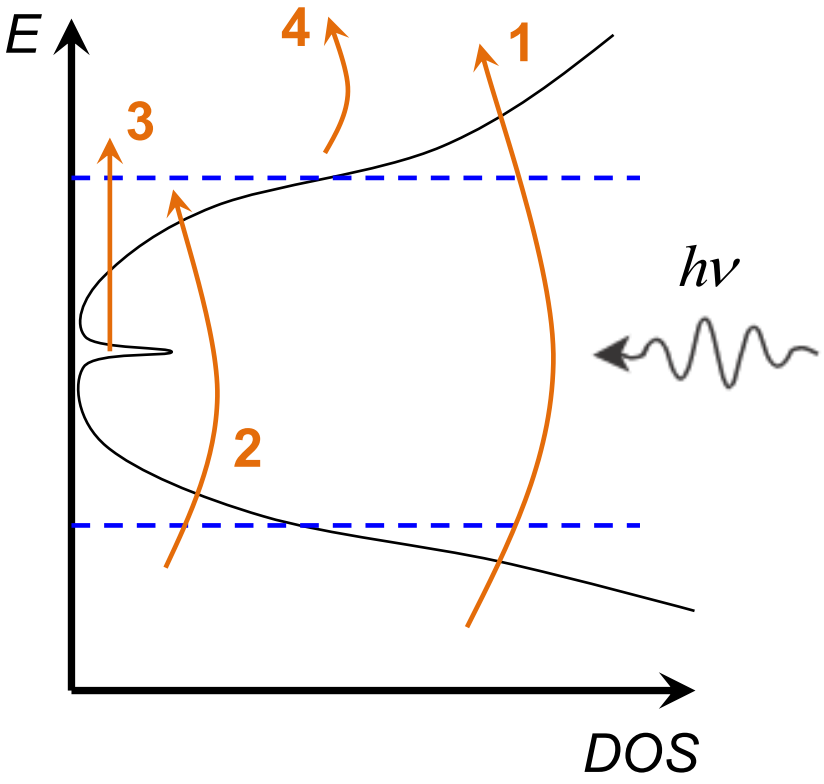
$$\alpha = \alpha_U \exp\left[\left(\mathrm{h}\omega - E_g\right)/E_U\right]$$



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

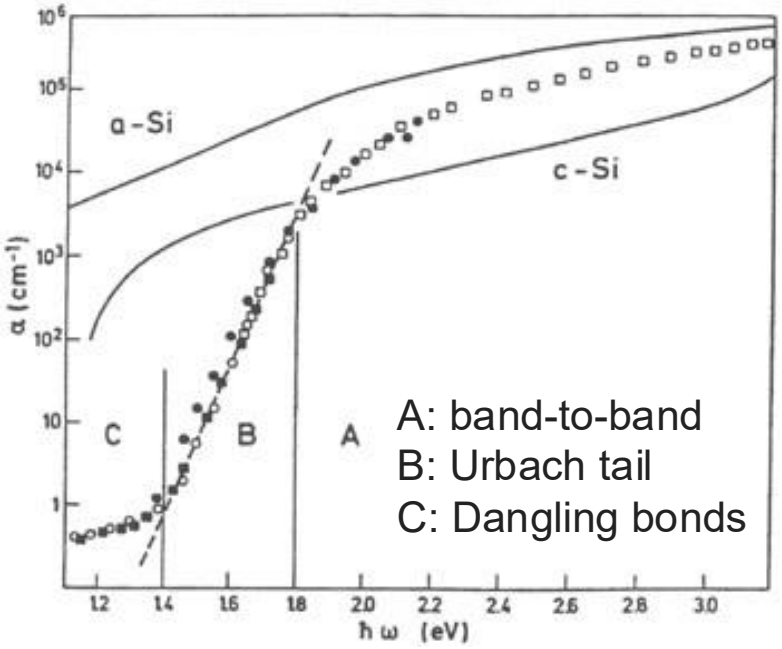
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Electronic absorption in amorphous solids



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

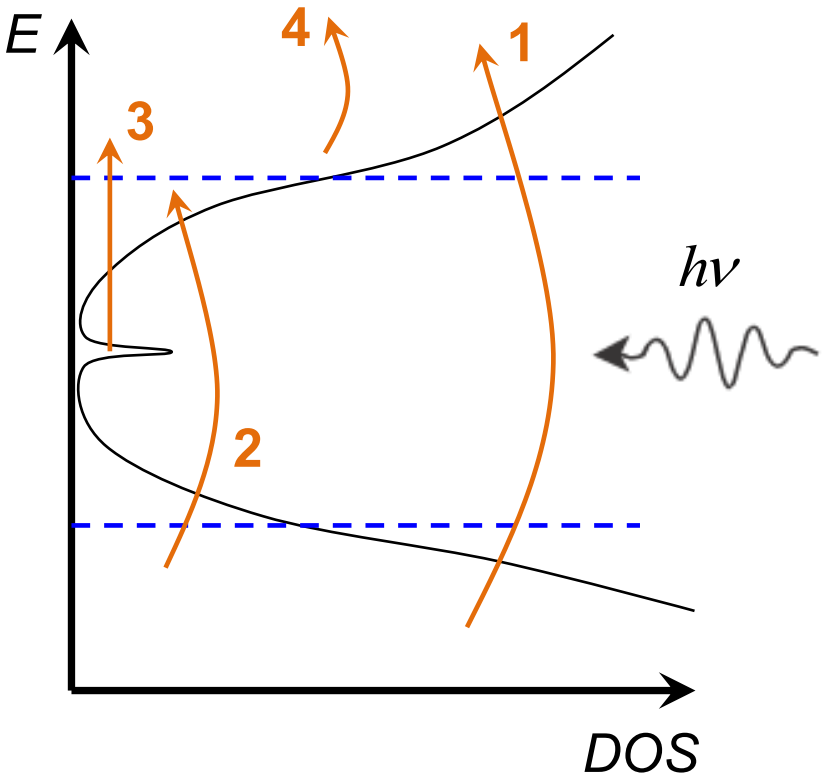
$$\alpha = \alpha_U \exp\left[\left(\hbar\omega - E_g\right)/E_U\right]$$



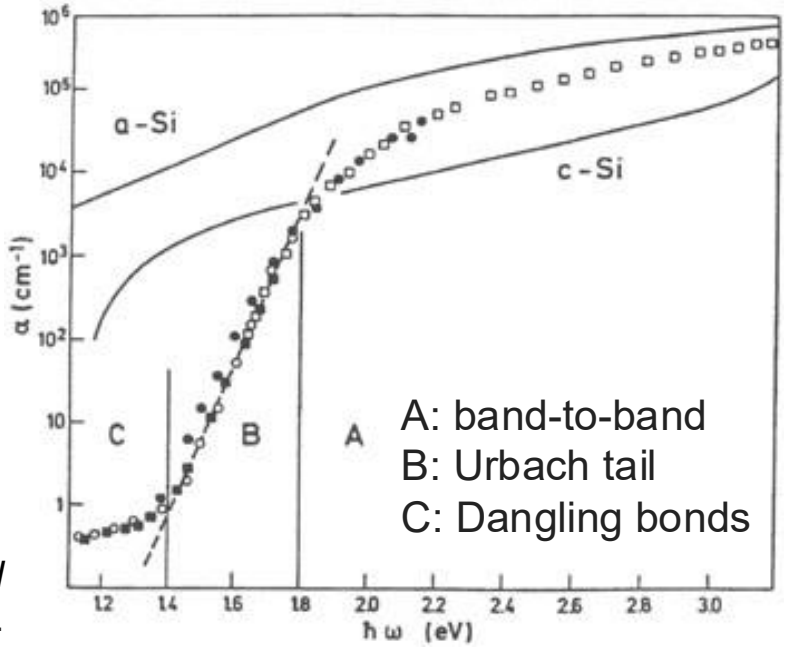
L. Ley, *The Physics of Hydrogenated Amorphous Silicon*, 141 (1984).

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Electronic absorption in amorphous solids



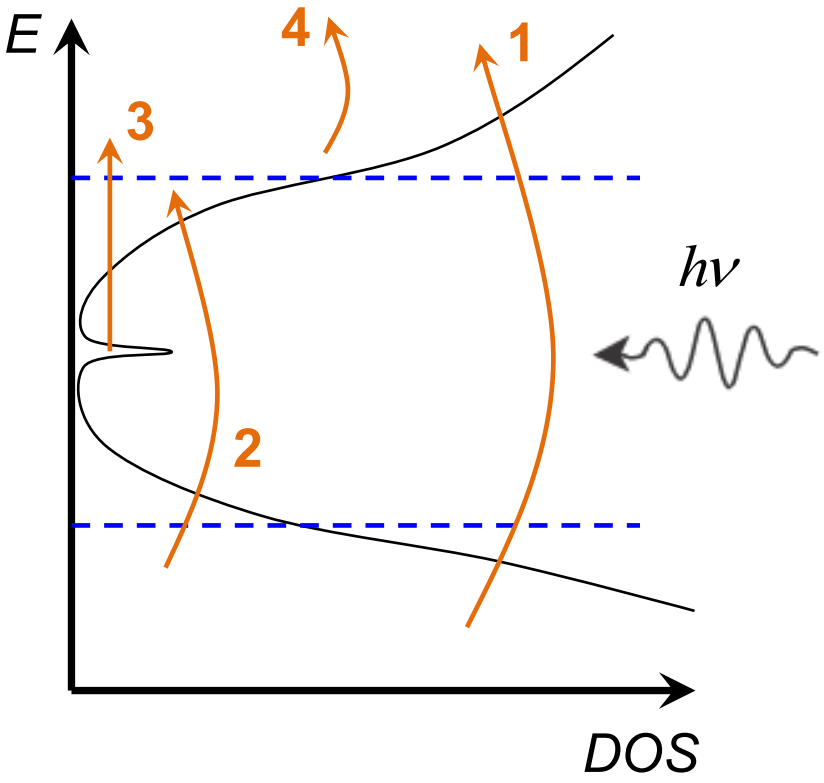
1. Band-to-band transition
2. Urbach bandtail absorption
3. Defect state absorption



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

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Electronic absorption in amorphous solids



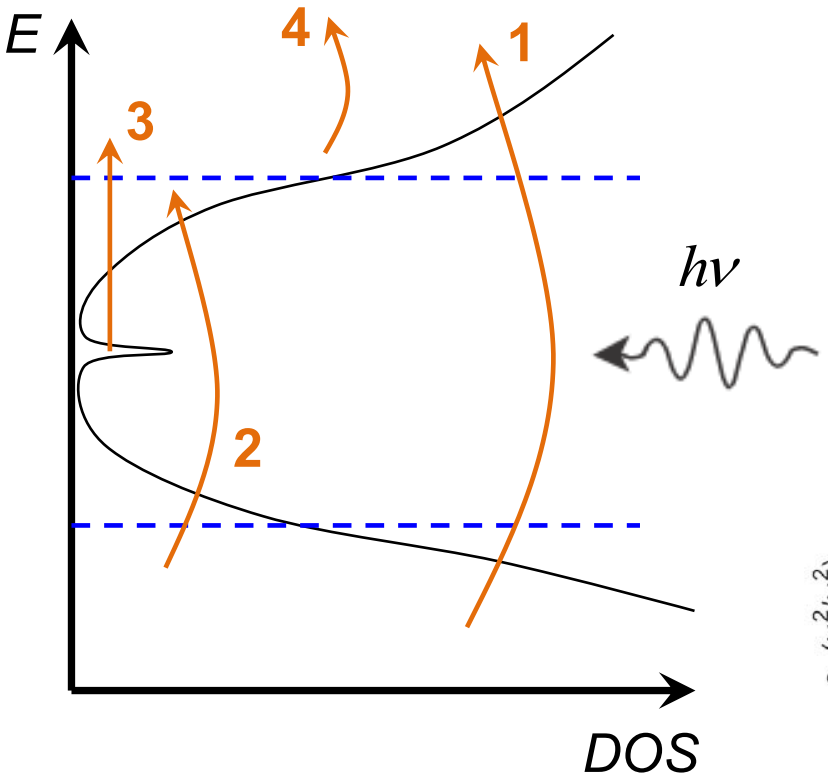
1. Band-to-band transition
2. Urbach bandtail absorption
3. Defect state absorption
4. Free carrier absorption

Drude model:

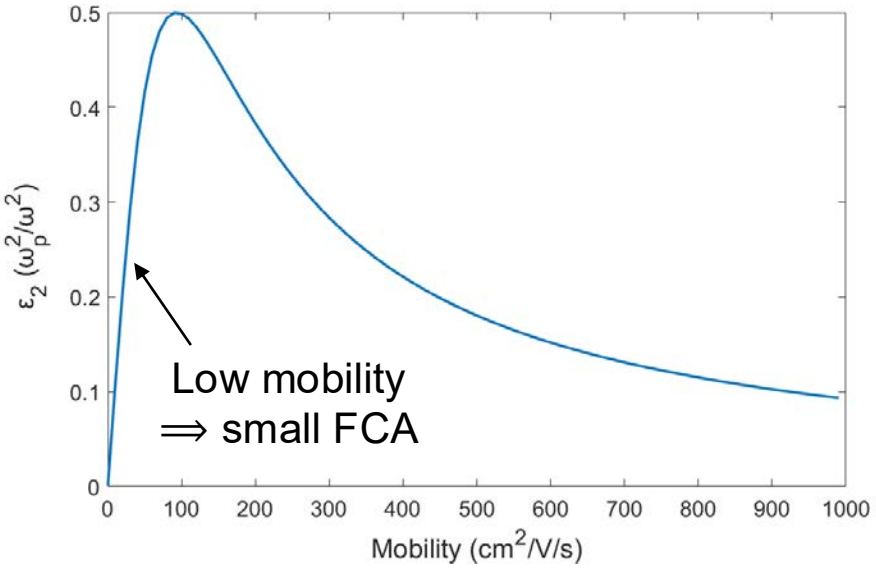
$$n + ik = \sqrt{\frac{\varepsilon_m - \frac{e^2}{\omega}\left(\frac{n}{m_e^*\omega + ie/\mu_e} + \frac{p}{m_h^*\omega + ie/\mu_h}\right)}{\varepsilon_0}}$$

Theory behind the generalized Drude (Plasma) model

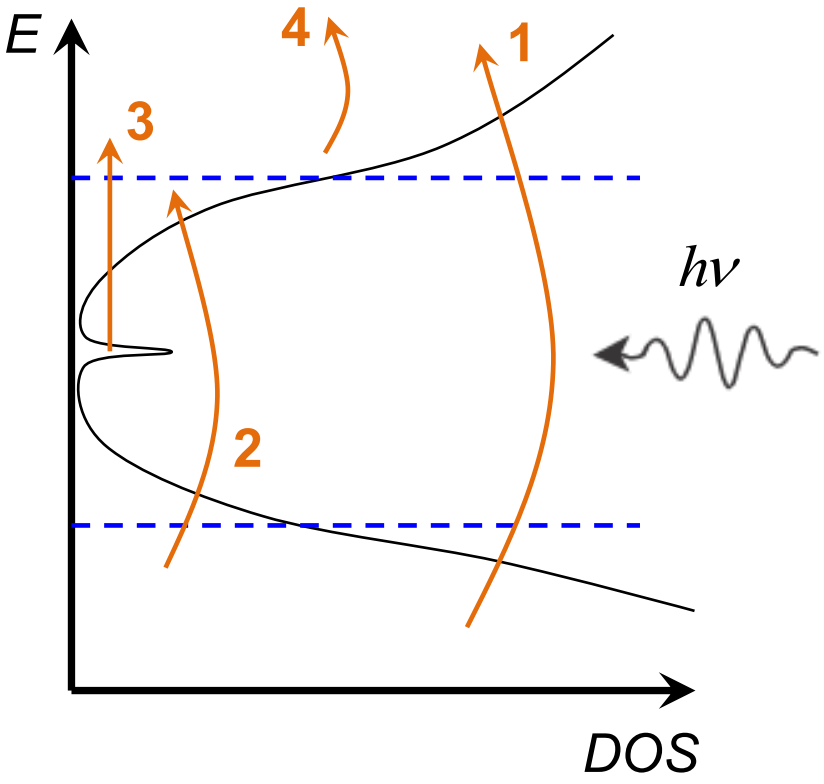
Electronic absorption in amorphous solids



1. Band-to-band transition
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Electronic absorption in amorphous solids

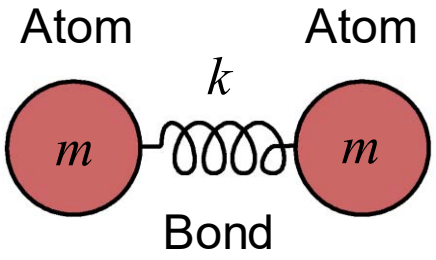


1. Band-to-band transition
2. Urbach bandtail absorption
3. Defect state absorption
4. Free carrier absorption

Absorption coefficient (cm^{-1})

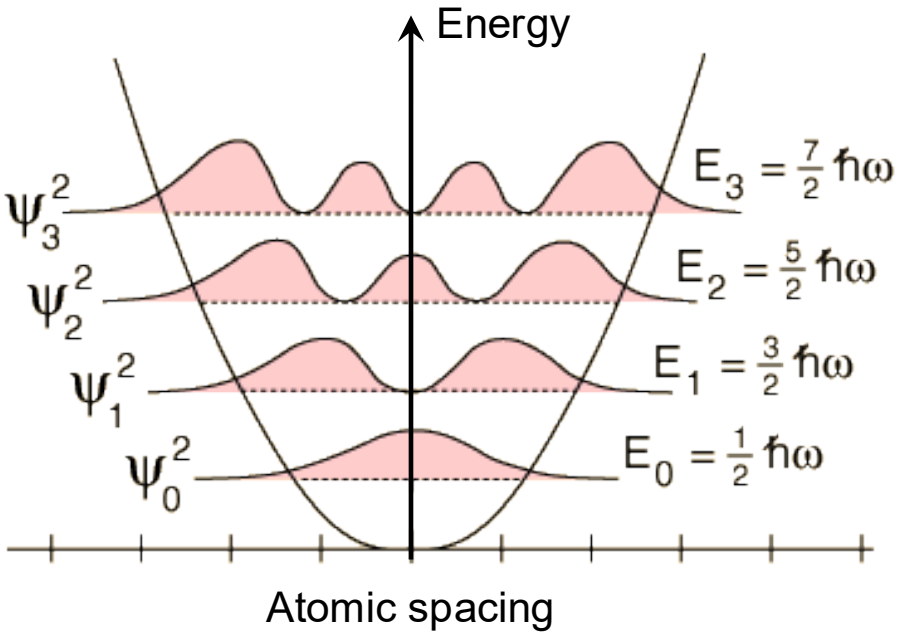
- Band-to-band: > 10^3
- Bandtail and defect states: 1 – 10^3
- FCA: generally weak in amorphous solids

Vibrational absorption



Harmonic oscillator

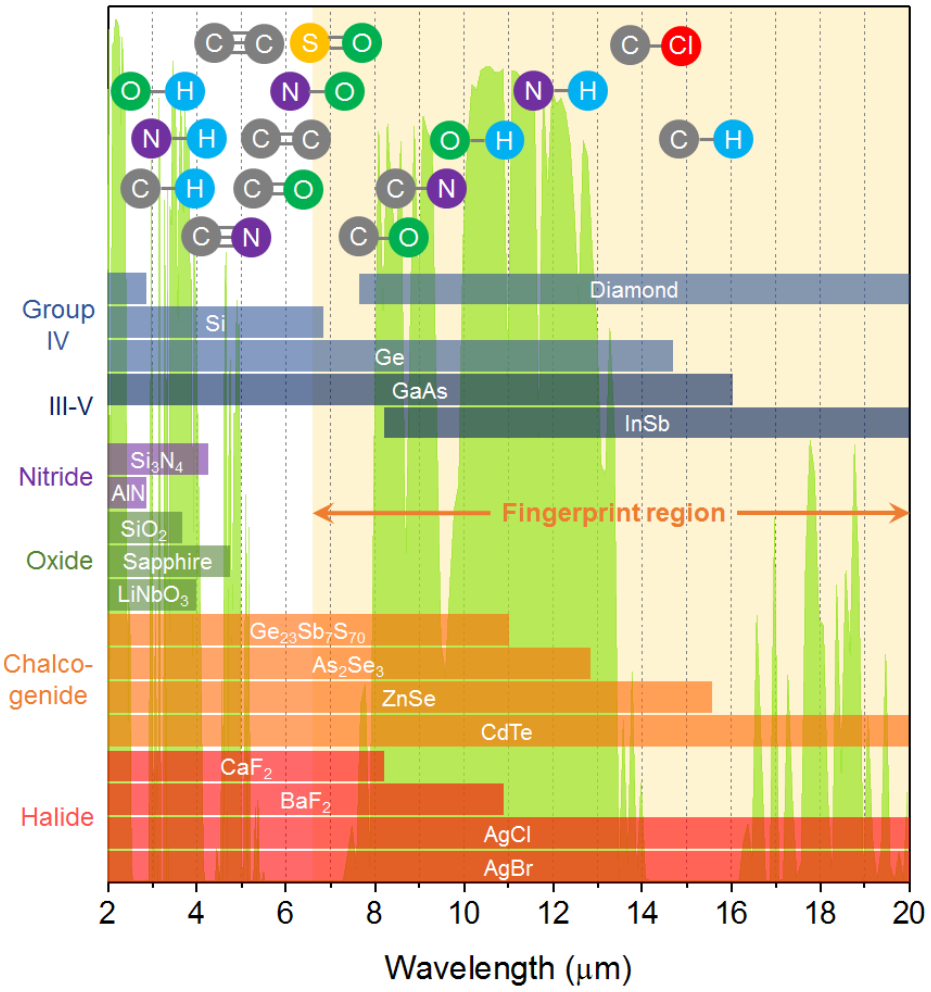
$$\omega \propto \sqrt{k/m}$$



Compound or functional group	Primary absorption bands (μm)
O-H	2.92
S-H	4.01, 3.65, 3.11, 2.05
P-H	4.35
Ge-H	4.95
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)

Infrared windows of common optical materials



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Single-crystal germanium lens

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Black diamond (BD-2): $Ge_{28}Sb_{12}Se_{60}$

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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

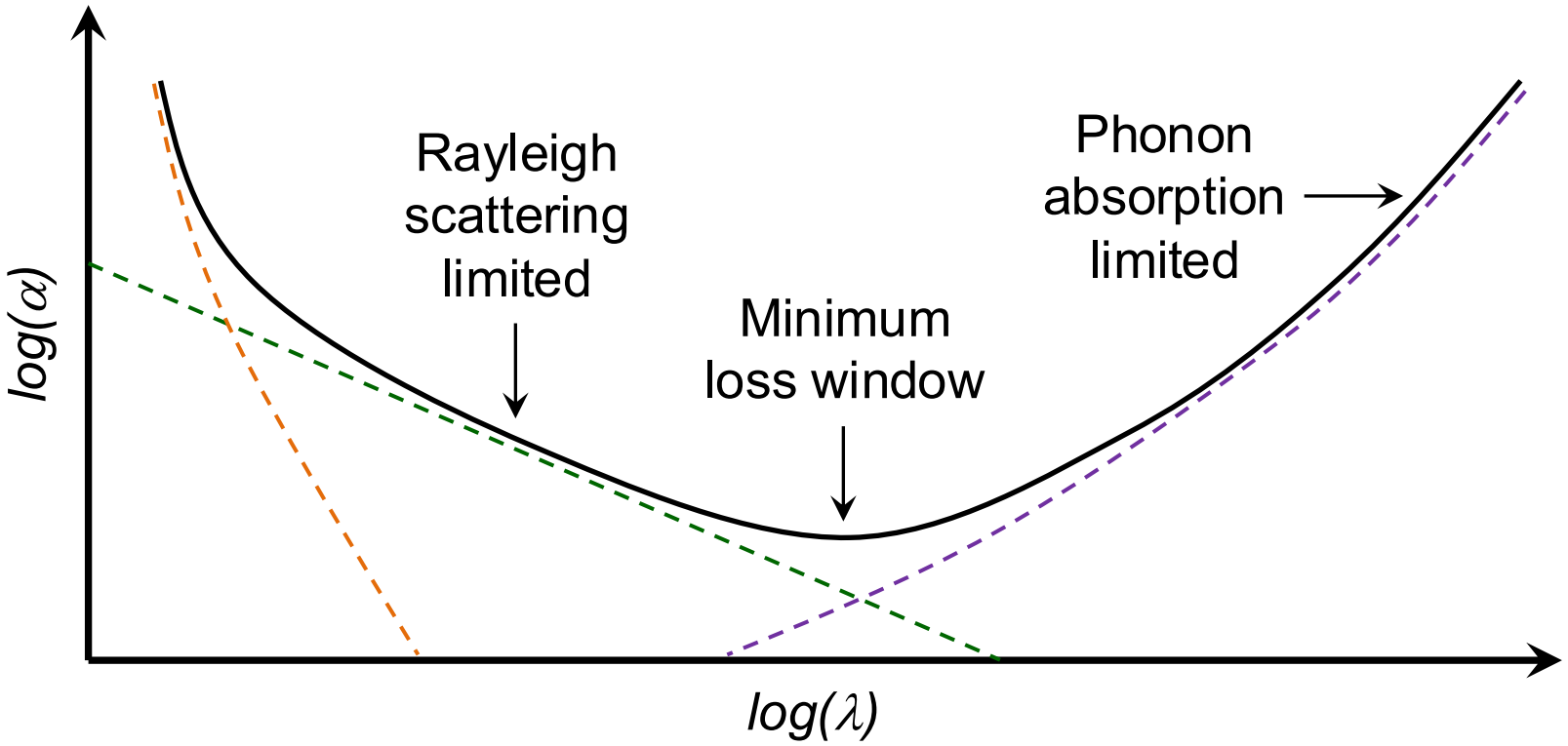
Ann. Physik **33**, 1275 (1910);
Ann. Physik **25**, 205 (1908);
J. Appl. Phys. **55**, 4052 (1984).



Einstein-Smoluchowski scattering: density fluctuation of atmosphere

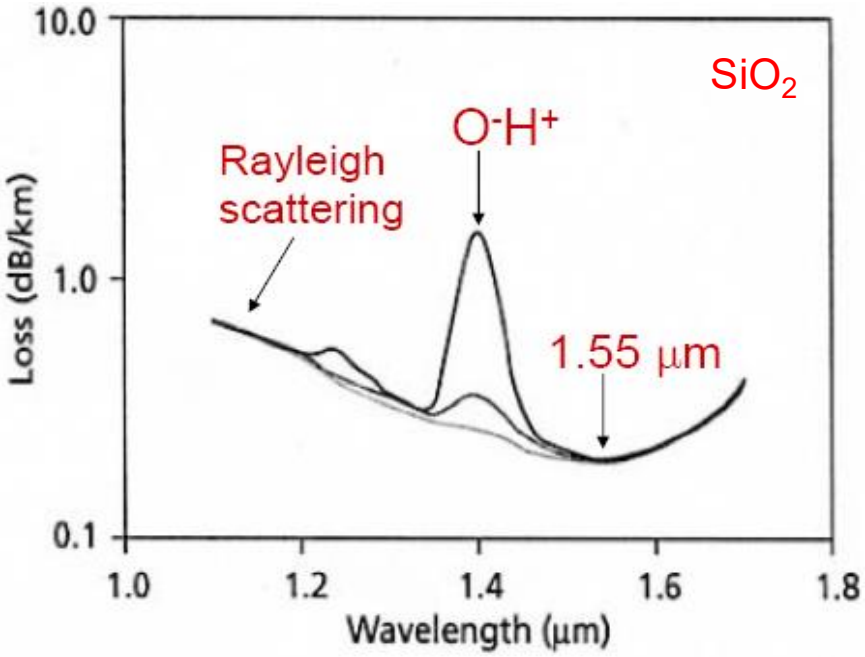
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Intrinsic optical loss spectrum in glass



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

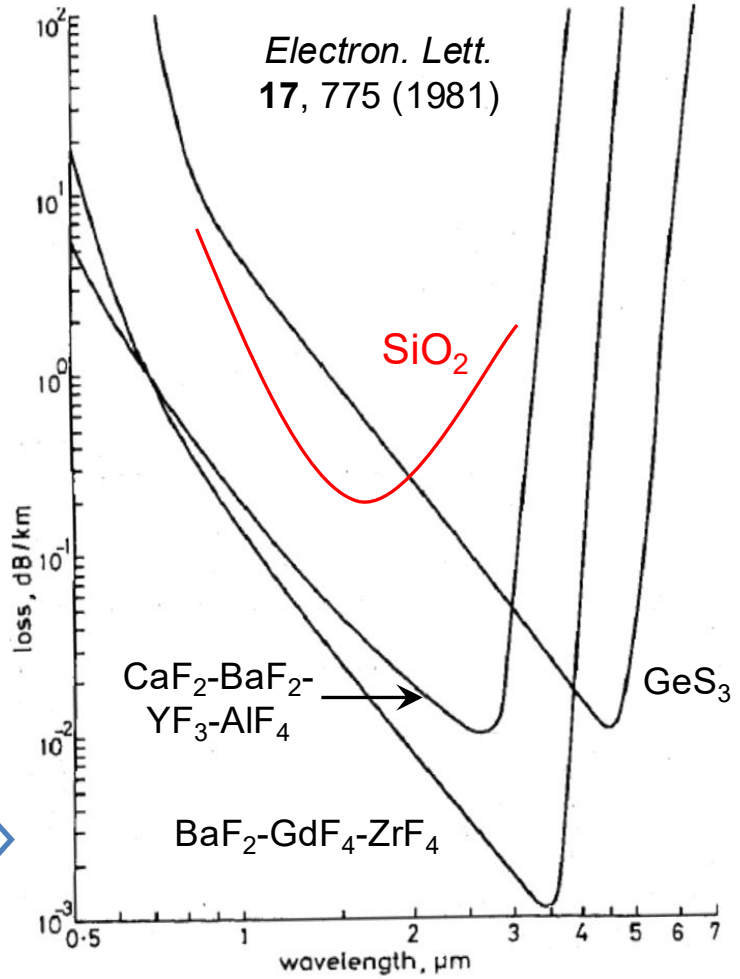




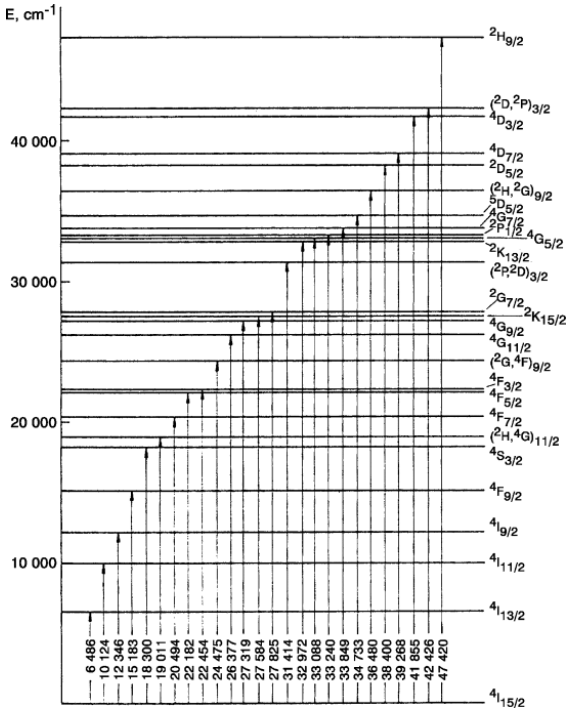
Photo taken at the [Corning Glass Science and Engineering Laboratory](), Rutgers University

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 to colorless		Ce^{4+}	Weak yellow
			$4f^1$	Ce^{3+}	Weak yellow
	Cr^{6+}	Faint yellow to colorless	$4f^2$	Pr^{3+}	Green
			$4f^4$	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

Er^{3+} energy levels

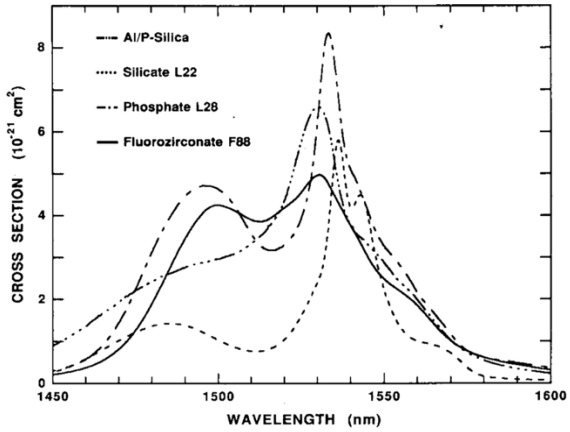


Modern Aspects of Rare Earths and Their Complexes (2003)

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 to colorless		Ce^{4+}	Weak yellow
			$4f^1$	Ce^{3+}	Weak yellow
	Cr^{6+}	Faint yellow to colorless	$4f^2$	Pr^{3+}	Green
			$4f^4$	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



Absorption spectra of Er^{3+} in different glasses

J. Lightwave Technol. **9**, 234 (1991)

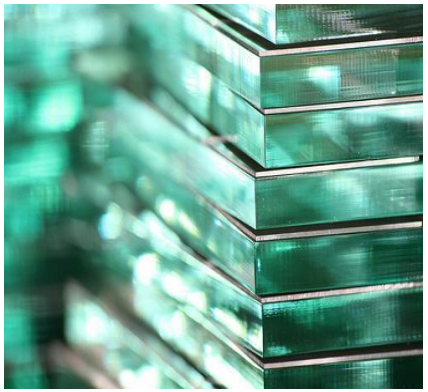
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Transparent glass coloring: absorption

- 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 to colorless		Ce^{4+}	Weak yellow
			$4f^1$	Ce^{3+}	Weak yellow
	Cr^{6+}	Faint yellow to colorless	$4f^2$	Pr^{3+}	Green
			$4f^4$	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

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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



Manganese amethyst



Room light



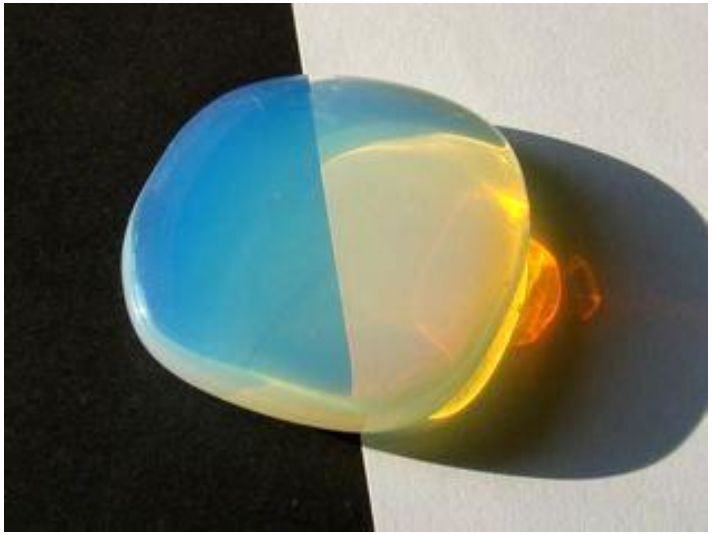
UV illumination

Uranium glass (Vaseline glass)

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Transparent glass coloring: scattering

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



Opalescent glass: nanocrystals



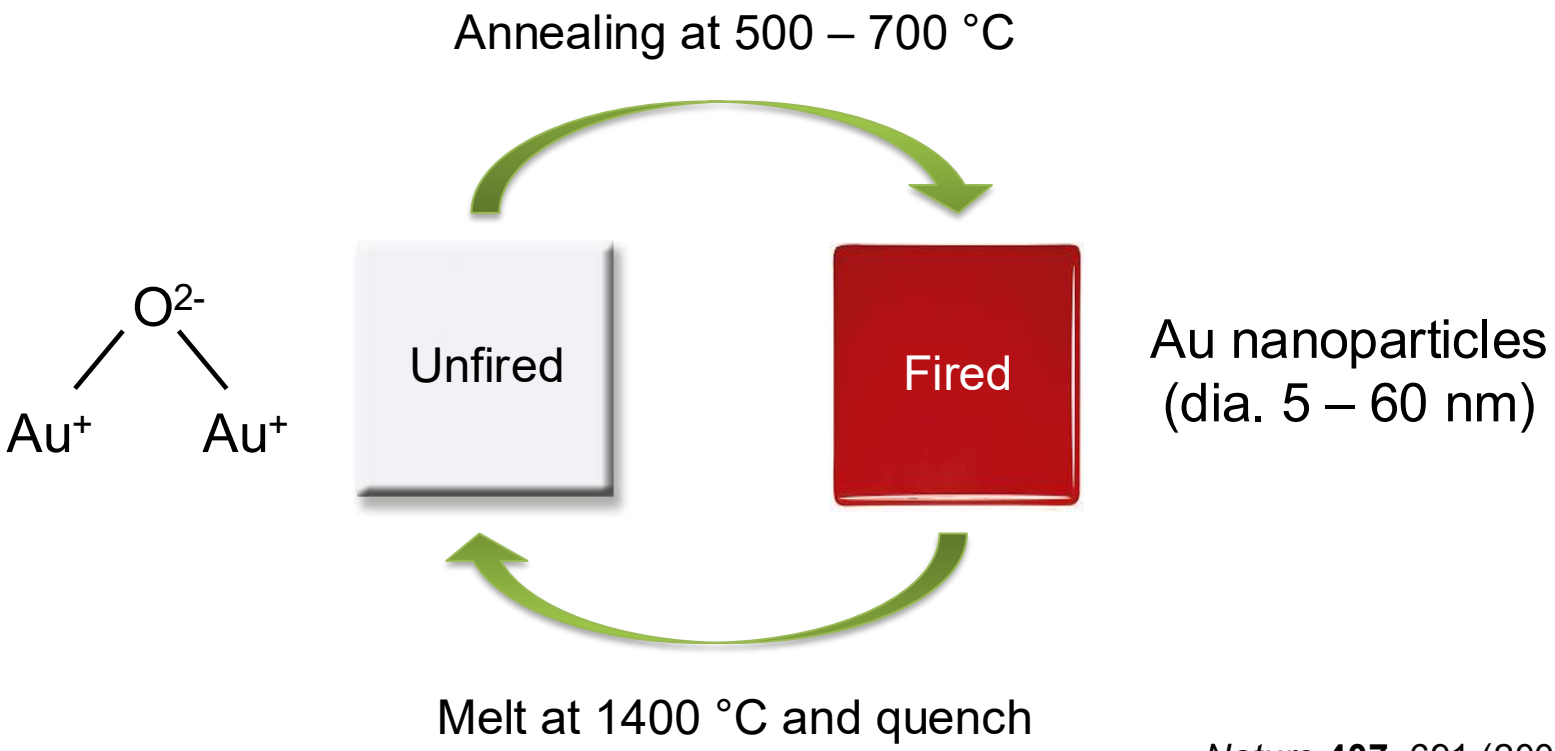
Lycurgus Cup: Au-Ag nanoparticles

Cryolite glass image © unknown. All rights reserved. This content is excluded from our Creative Commons license. For more information, see http://ocw.mit.edu/help/faq-fair-use/.

Images of the Lycurgus Cup courtesy of The British Museum

Striking colors

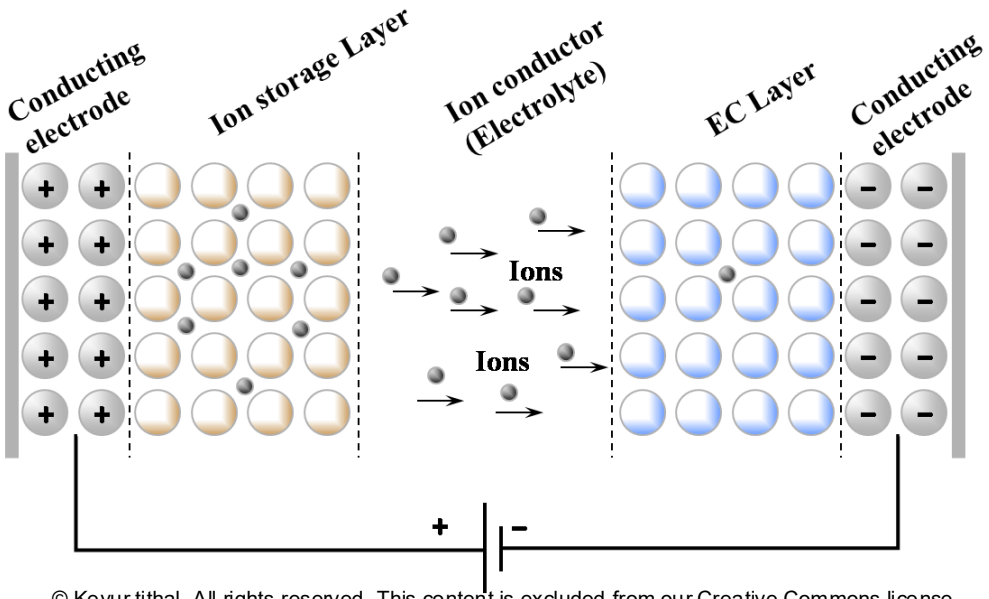
- Coloring of glass via heat treatment
- Example: gold-ruby striking



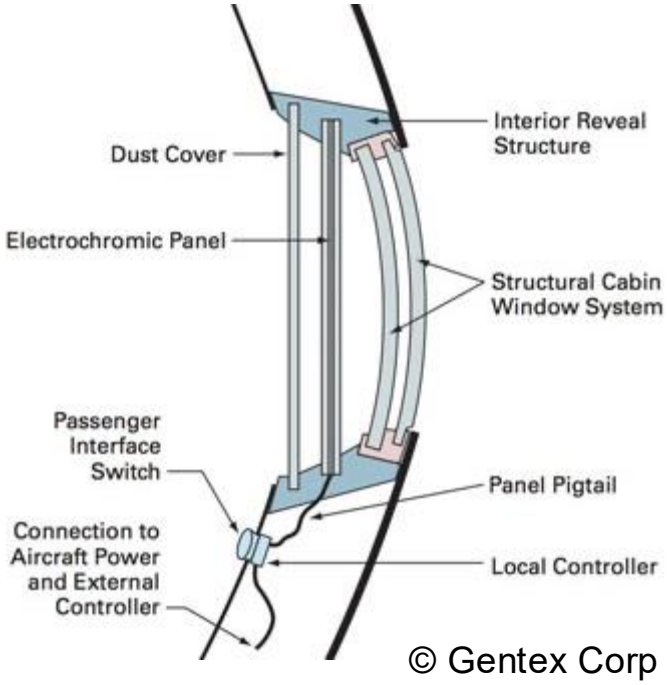
Nature **407**, 691 (2000)

Photochromic and electrochromic glasses

- Optical or electrical control of redox state of ions



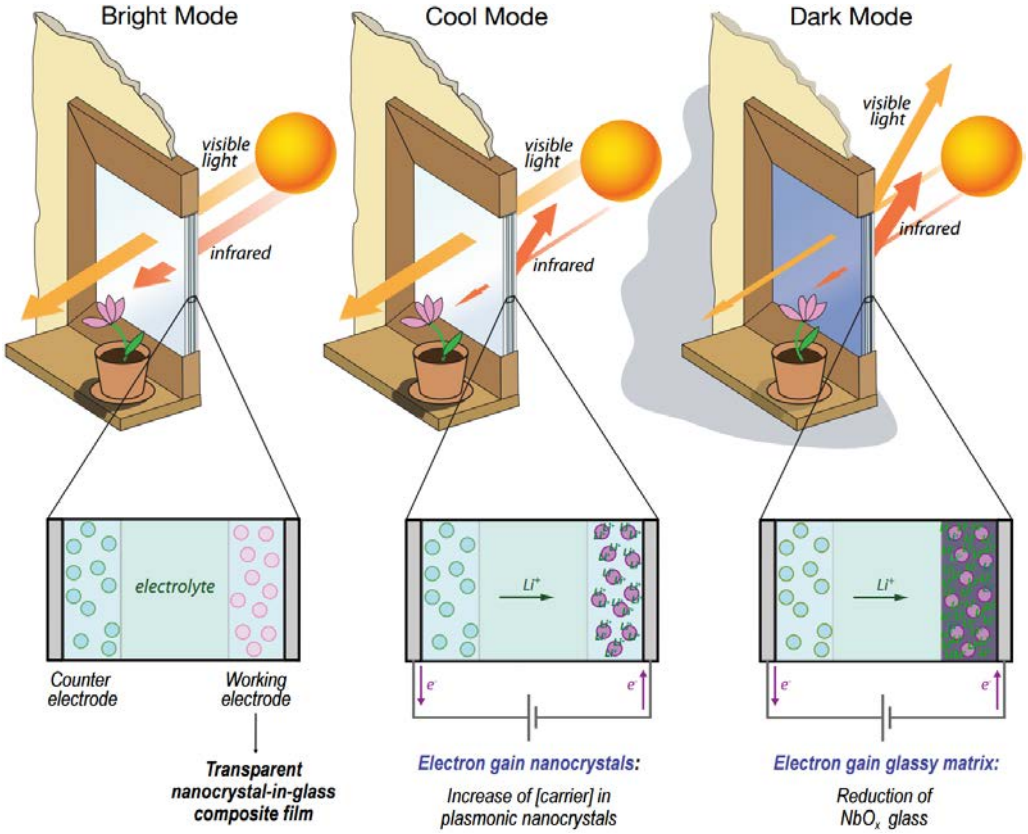
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Photochromic and electrochromic glasses

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



Bleached
transparent

$$Nb_2O_5 + x\ Li^+ + x\ e^- \leftrightarrow Li_xNb_2O_5$$

Colored
brown-gray

Nature **500**, 323 (2013)

'Smart glass' diagram © Heliotrope Technologies. All rights reserved. This content is excluded from our Creative Commons license. For more information, see http://ocw.mit.edu/help/faq-fair-use/

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)

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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

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3.071 Amorphous Materials
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