Advanced Vitreous State – The Physical Properties of Glass

Passive Optical Properties of Glass

Lecture 3:

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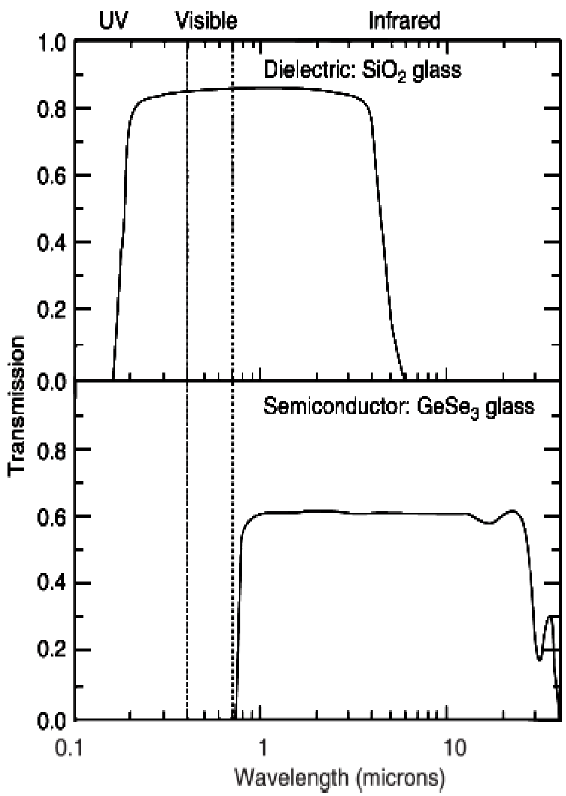
Impurities in Optical Glass:



In a pure glass, the optical window is controlled by intrinsic limitations of the material : the electronic and vibrational transitions of the glass.

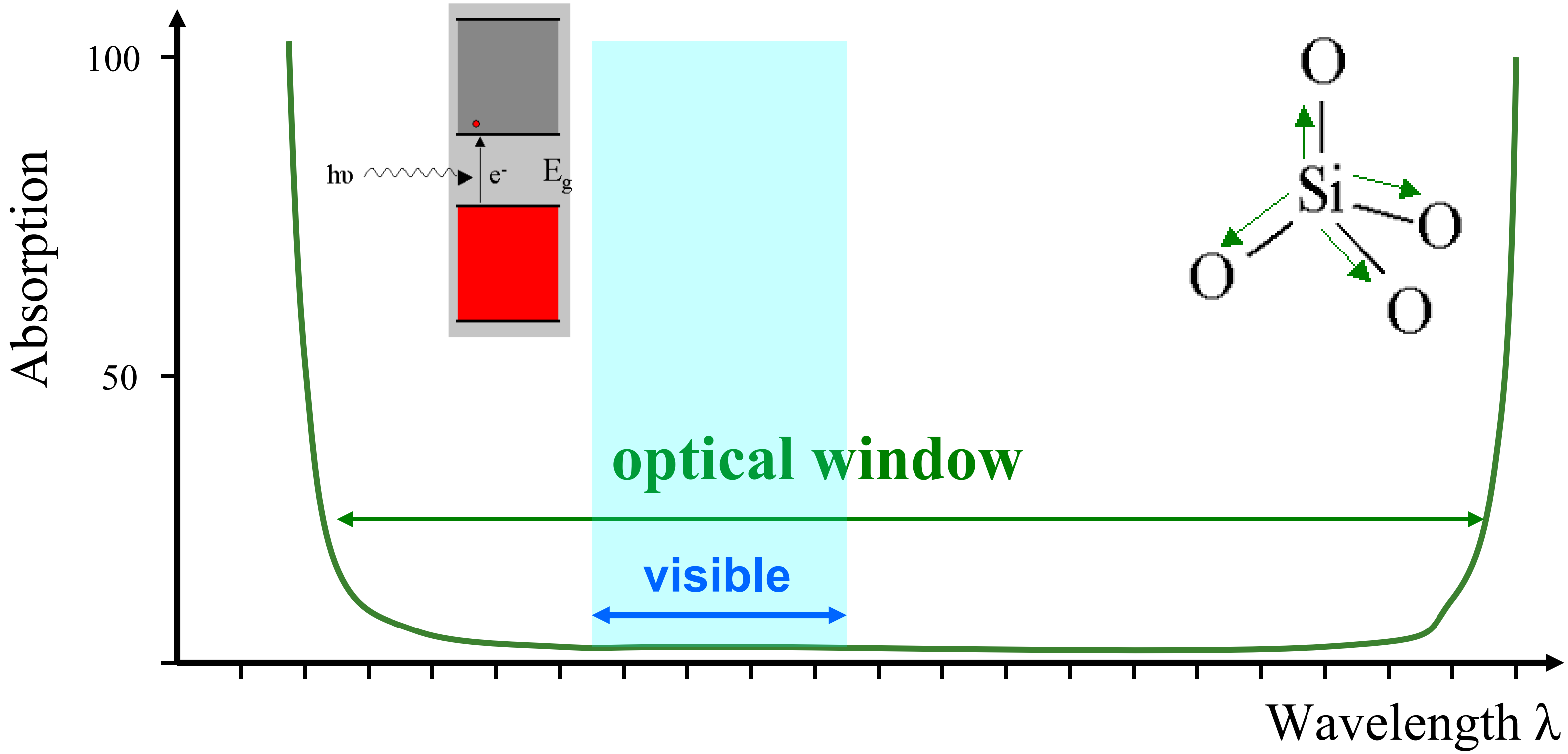
Specific glass compositions are then selected for applications requiring transparency in various ranges of wavelength.

However, if foreign atoms are introduced in the glass (accidentally or purposedly) they can modify the optical window by generating additional:

- Electronic transitions
- Vibrational transitions

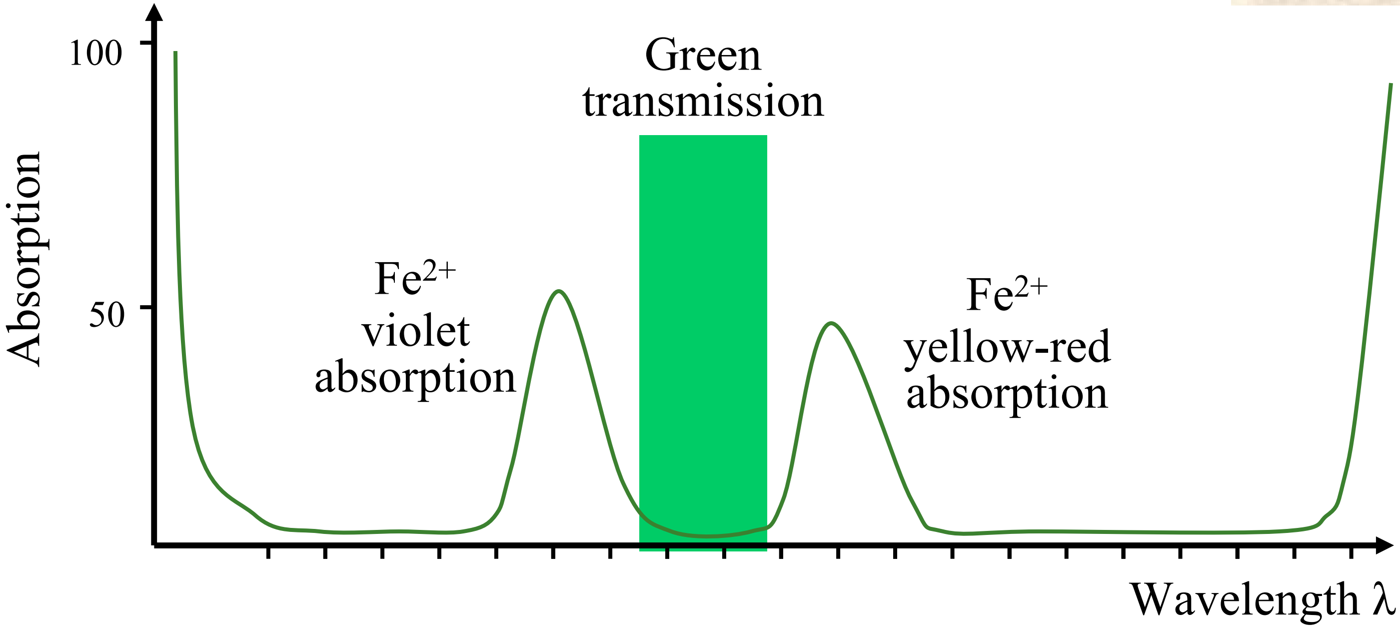
Optical window

- When plotted in Absorption instead of Transmission, the optical window corresponds to the region of zero absorption.
- Absorption is high at short wavelength due to eletronic excitation and high at long wavelength due to vibrational excitations.
- In silicate glasses, the visible wavelengths range is within the window.



Absorption due to electronic transition from impurities

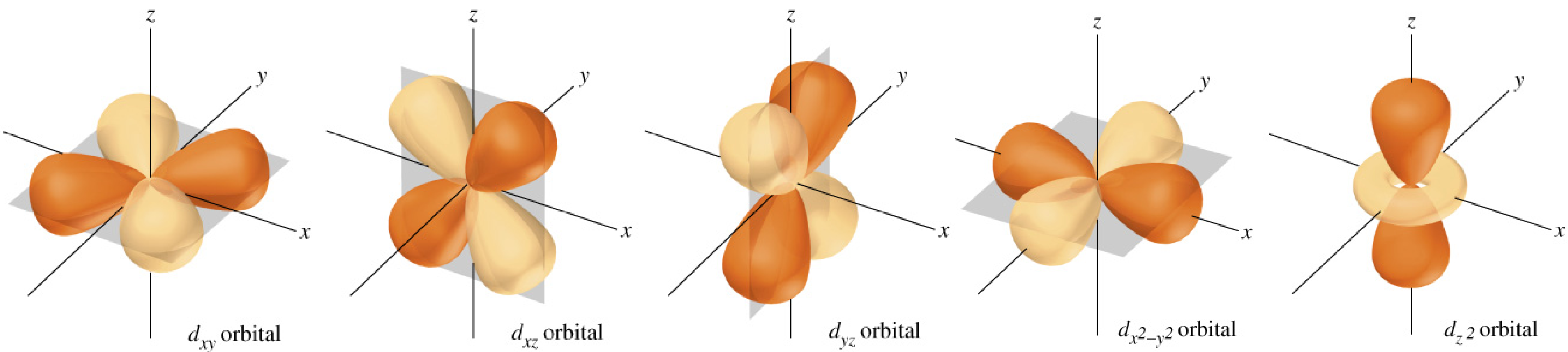
- A glass beer bottle is made of silicate glass which is transparent in the visible, yet it appears colored due to Fe impurities in the glass.



- Because of electronic transitions involving the d orbitals, transition metals absorb visible light within the transparency window and produce colors. They are used as colorant in glasses .

Crystal Field Theory: colors in glass and gems

- Transition metals and have five d orbitals.

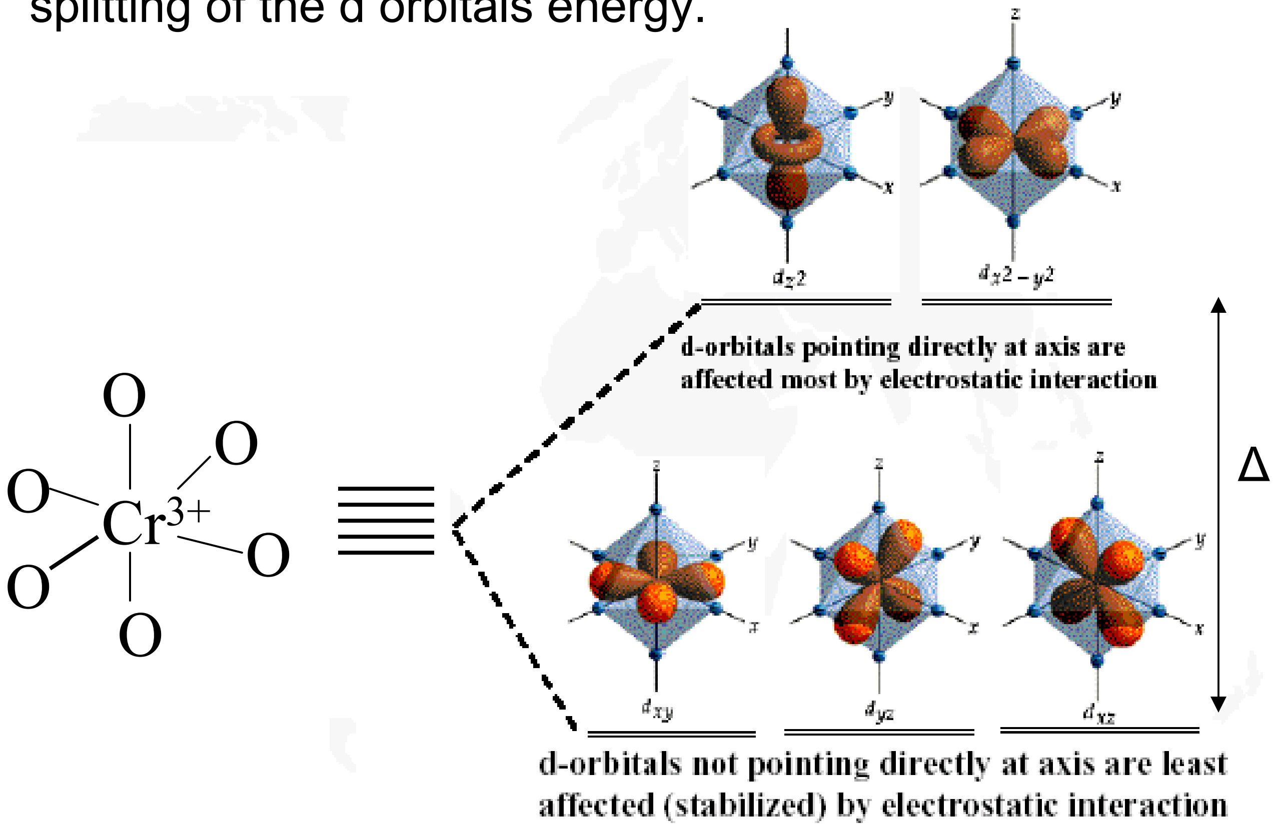


- The 5 d orbitals have different shape but are equivalent in energy and are degenerated in a free (lone) ion.

Cr^{3+} Five d orbitals in lone Cr^{3+} ion

Crystal Field Theory: colors in glass and gems

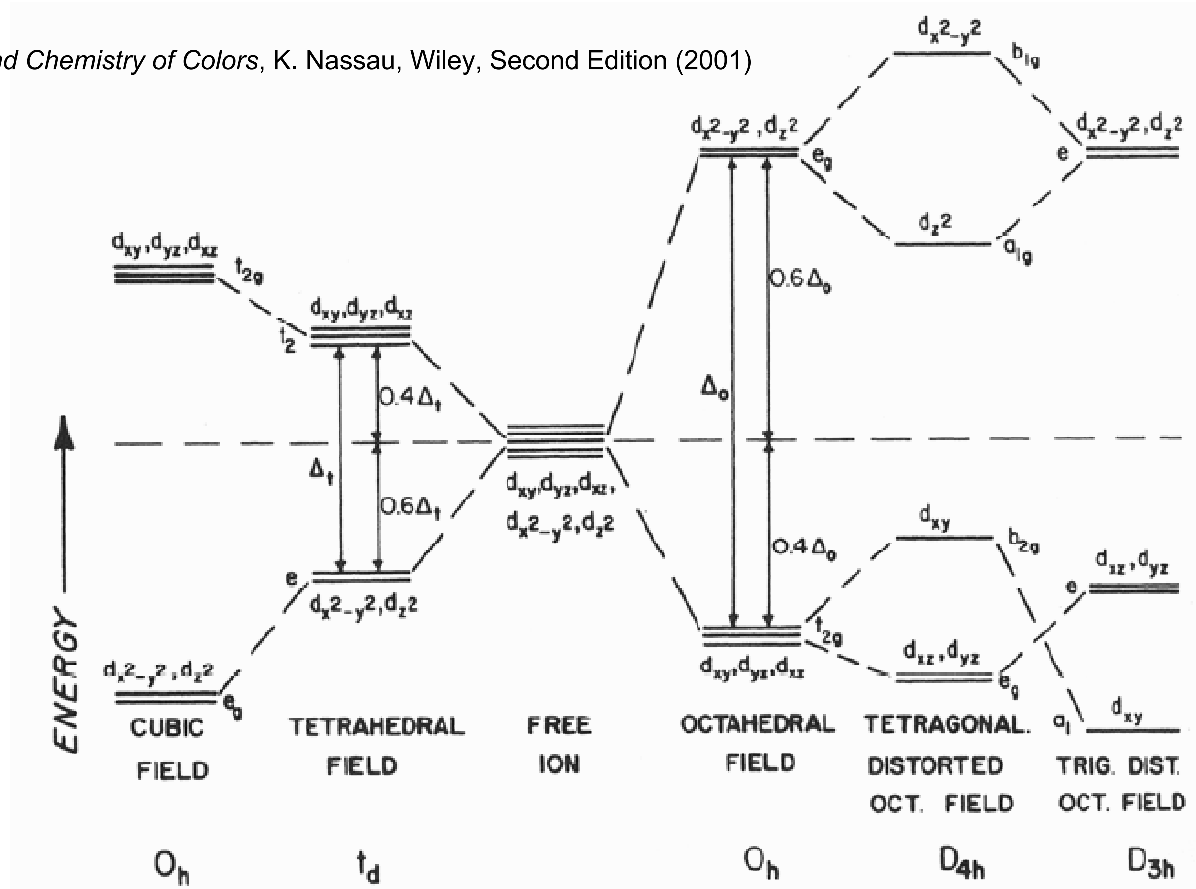
- In solids, transition metals occupy interstitial sites such as tetrahedra or octahedra.
- For example, Cr^{3+} often sits into an octahedra of oxygen.
- Only two d orbitals are pointing to the oxygens and are destabilized. This generates splitting of the d orbitals energy.



The energy split Δ=10Dq results from the crystal field and strongly depends on the material's composition and structure.

Crystal Field Theory: colors in glass and gems

The Physics and Chemistry of Colors, K. Nassau, Wiley, Second Edition (2001)

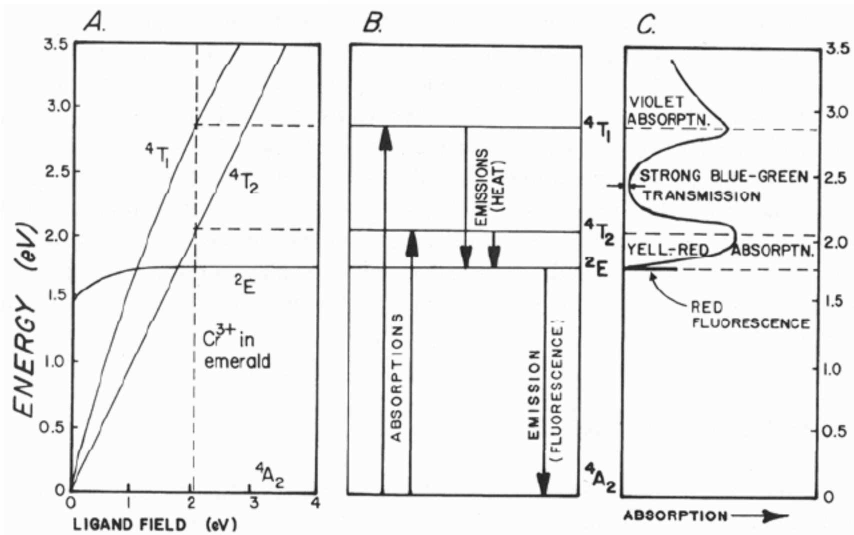


• Many splitting patterns are possible depending on the site geometry and level of distortion (significant in glass).

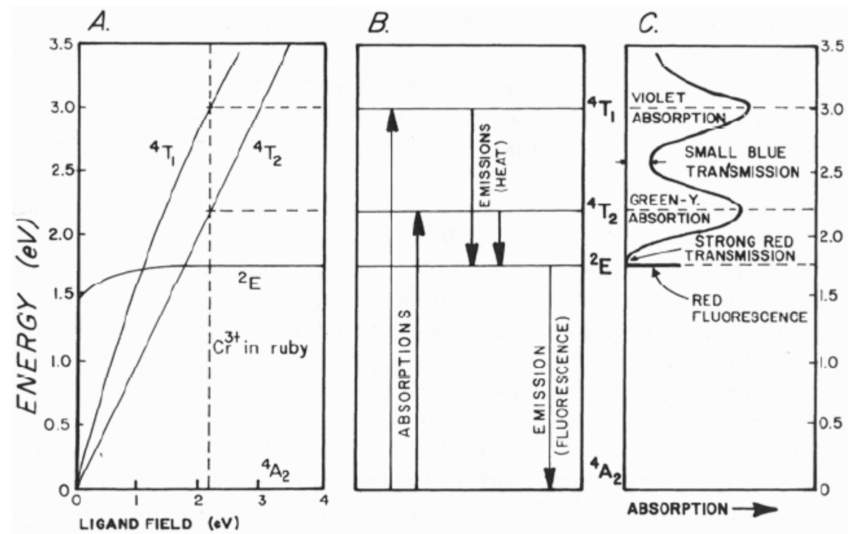
• This results in several possible electronic transitions and absorptions peaks.

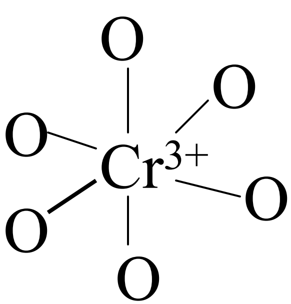
Crystal Field Theory: Chromium Cr^{3+} in Ruby and Emeralds

Emerald



Ruby

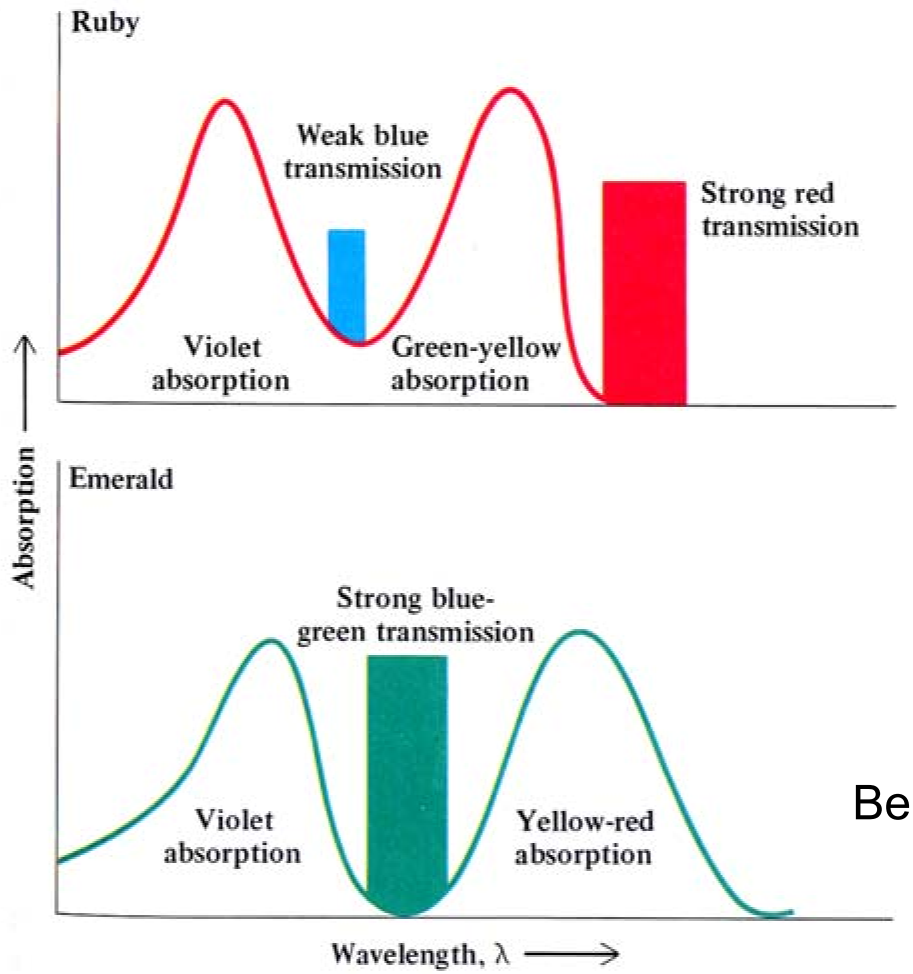




- The energy of electronic levels is also highly dependent on the strength of the crystal field.
- While Cr^{3+} is in octahedral sites in both gems, the crystal field is slightly lower in emerald (2.05eV) than in ruby (2.23eV).
- This results in distinctly different absorptions and bright colors.

The Physics and Chemistry of Colors, K. Nassau, Wiley, Second Edition (2001)

Crystal Field Theory: Ruby and Emeralds



Al_2O_3 with 1% of Cr impurity substituting Al in octahedral sites.

Beryl ($Be_3Al_2Si_6O_{18}$) with 1% of Cr impurity substituting Al in octahedral sites.

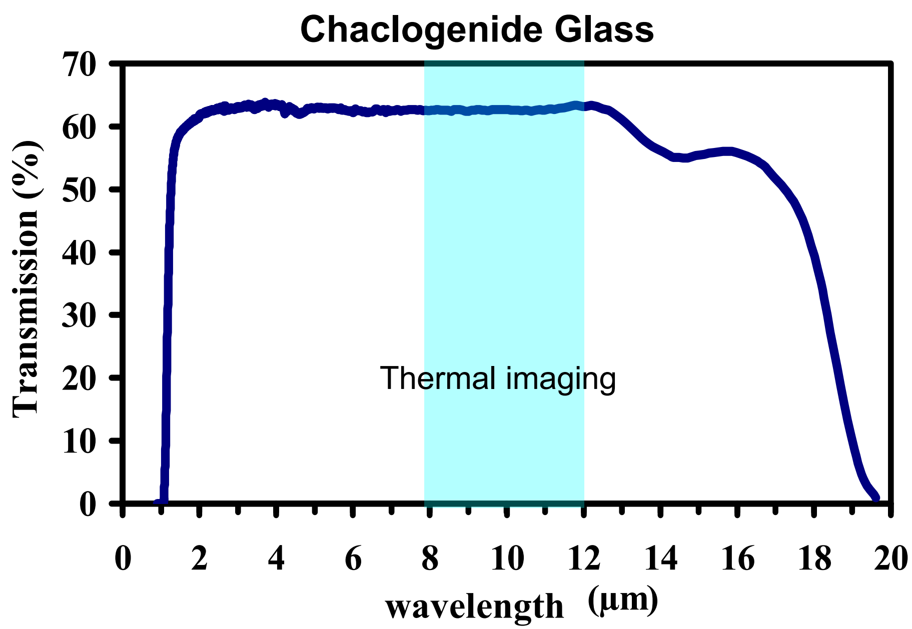
Colors in glass

Colorant	Host glass	Concentration (wt%) for 0.1 OD	Color or shade	Source of color
CoO	Silicates	0.0018	Cobalt blue	$Co^{+2}(3d^7)$
	Borates		Pink	
NiO	Silicates	0.0078	Neutral grey	$Ni^{+2}(3d^8)$
	Borates		Blue	
Se		0.0250	Pink	Se^{+4}
Cr_2O_3	Most compositions	0.0324	Serpentine green	$Cr^{+3}(3d^3)$
CuO	Silicates (oxy)	0.116	Blue	$Cu^{+2}(3d^9)$
Cu_2O	Silicates (red)		Red	$Cu^{+1}(3d^{10})$
MnO	Silicates	0.207	Violet	$Mn^{+3}(3d^4)$
	Silicates		Pale yellow	$Mn^{+2}(3d^5)$
U_3O_8		0.381	Pyrethrum (yellow with green fluorescence)	U^{+6}
Fe_2O_3	Silicates (oxy)	0.384	Yellow brown	$Fe^{3+}(3d^5)$
FeO	Silicates (red)		Blue green	$Fe^{+2}(3d^6)$
V_2O_3	Silicates	0.655	Serpentine green	$V^{+3}(3d^2)$
VO_2	Silicates		Blue	$V^{+4}(3d^1)$
Nd_2O_3	Silicates	0.92	Purple with red fluorescence	Nd^{+3}
Pr_2O_3	Silicates	2.38	Greyish green with yellow fluorescence	Pr^{+3}
Ti_2O_3	Phosphates		Violet-brown	$Ti^{+3}(3d^1)$
$TiO_2 + CeO_2$	Silicates	6.6	Yellow	$TiO_2 + CeO_2$

Table 3.5: Coloring agents in glasses. *Optical Materials*, J. H. Simmons, K. S. Potter, Accademic Press (2000)

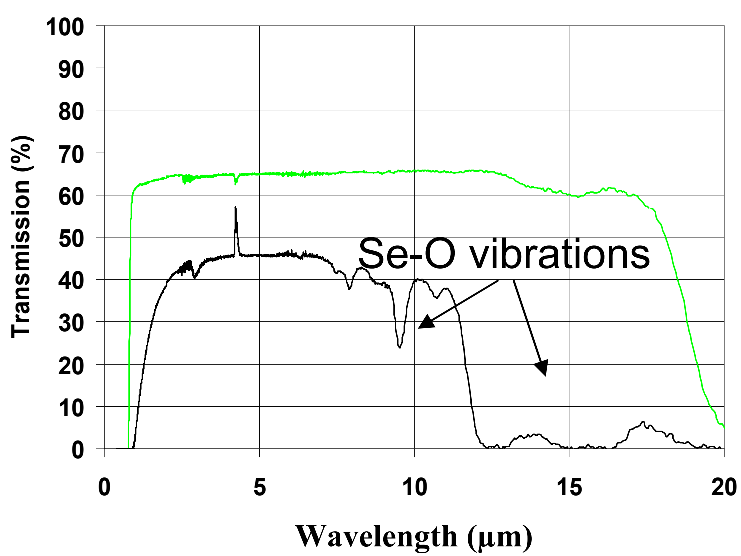
Glasses Transparent in the Infrared

Thermal imaging requires high transparency in the infrared region around 10 microns



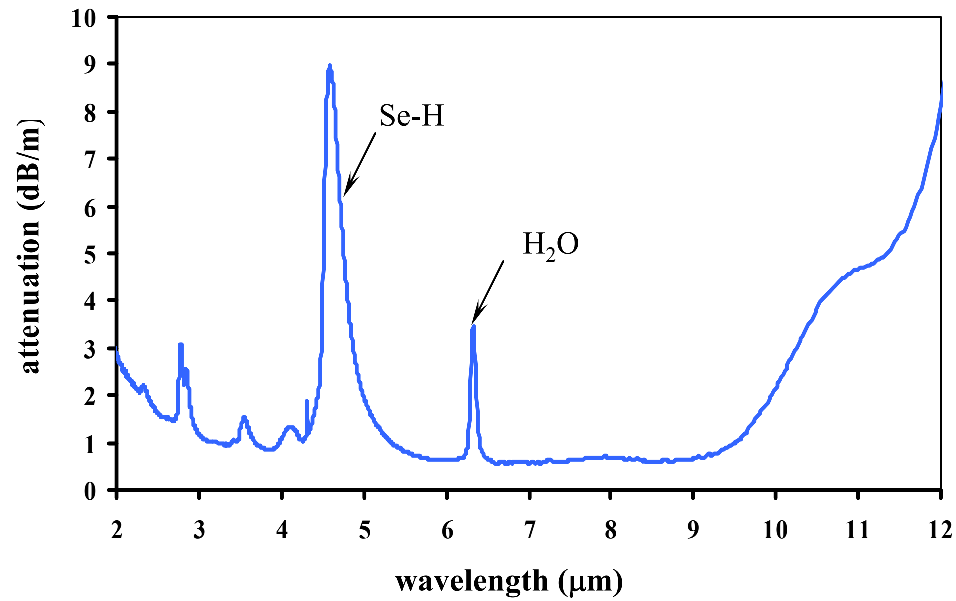
Absorption due to vibrational transition from impurities:

$Te_2As_3Se_5$



non-purified glass
purified glass

$Te_2As_3Se_5$ fiber



$$\omega = \frac{1}{2\pi}\sqrt{k\left(\frac{1}{m_1}+\frac{1}{m_2}\right)}$$

• Low mass impurities such as O or H generate phonon absorption peaks at lower wavelength within the transmission window of chalcogenide glasses.

Optical losses

- The fraction of absorbed light is a function of the path length ℓ through the sample and the absorption coefficient α of the material.

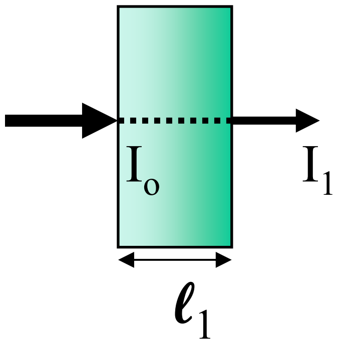
$$\frac{I}{I_o} = e^{-\alpha \ell}$$

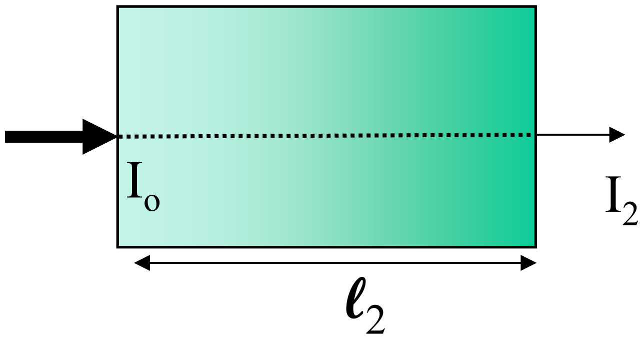
- The higher the concentration of [Fe^{2+}] colorant, the higher the absorption coefficient α and the lower the transmitted intensity.

  A glass window contain minute amount of Fe^{2+} and appears clear while a beer bottle contains a significant amount of Fe^{2+} and appear distinctly green.

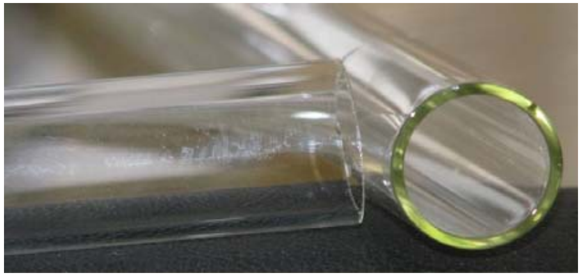
  α=c[Fe^{2+}], Beer's law is often used to measure concentrations when ℓ is fixed.

- The longer the path length through the sample ℓ, the lower the transmitted intensity.





- The edge of a transparent glass tube appears greenish because of the longer path length $\ell_2 < \ell_1$

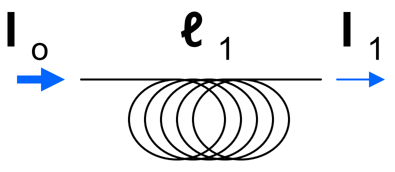


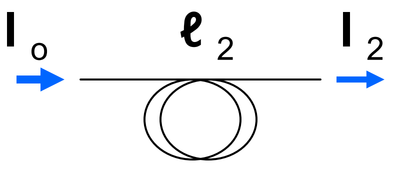
Optical losses in fibers

- In fibers, the path length ℓ is extremely long. In return the absorption coefficient α of the material must be extremely low.

$$\frac{I}{I_o} = e^{-\alpha \ell}$$

- α is measured using the cut-back method: $\ell_1 > \ell_2$





$$\alpha = \frac{1}{\ell_2 - \ell_1} \ln \frac{I_2}{I_1}$$

- In the optical fiber industry the decrease of transmitted intensity is expressed in terms of losses rather than absorption coefficient. It is reported in decibel (dB) per unit length: dB/km or dB/m.

The decibel is defined as: dB = $10\log_{10}(I_1/I_0)$ where I_1 is the output power and I_0 is the input power.

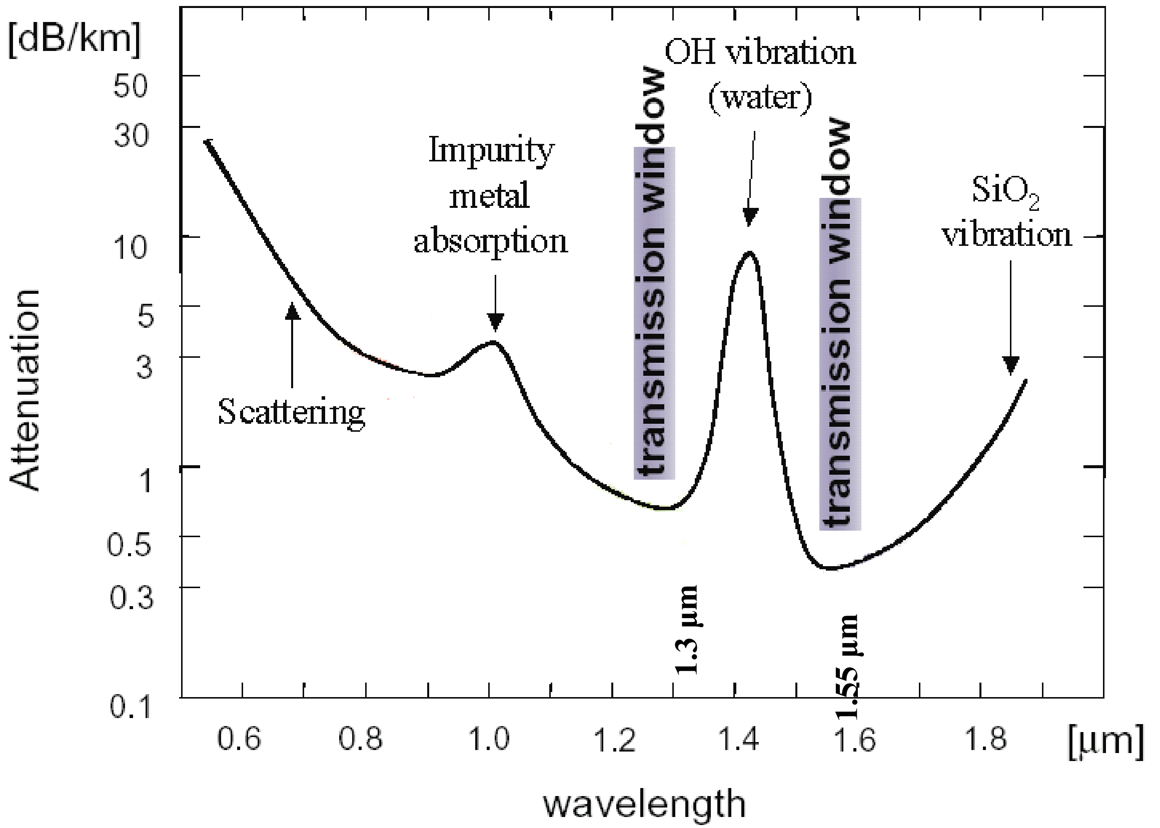
$$loss(dB) = -10\log_{10}(I/I_o)$$

$$loss(dB/m) = \frac{-10\log_{10}(I/I_o)}{\ell(m)}$$

A loss of 1 dB corresponds to about 80% transmission. Losses of silica telecom fibers are below 1dB/km.

Attenuation in silica fibers

- Because the light is transmitted through a very long path length in the fiber, all the light loss mechanisms become important.



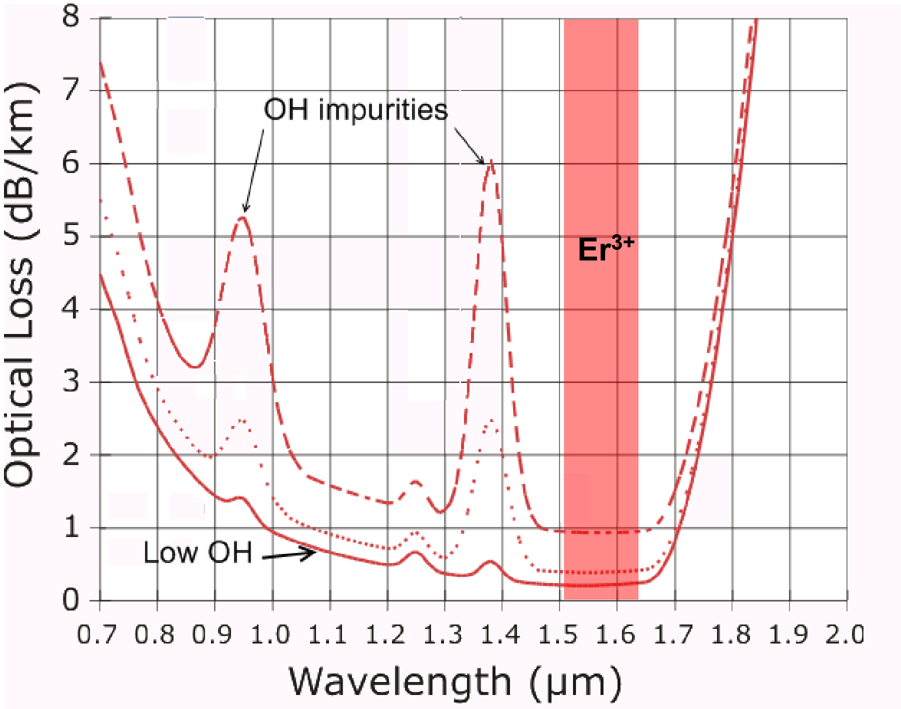
Attenuation due to

- scattering,
- transition metals absorption
- water vibrations
- SiO_2 network vibrations

leaves only two small transmission windows for efficient long distance transmission of light:
1.3 µm and 1.55 µm

Low-OH fibers

- Nowadays, state of the art fibers contain very low OH-impurities and the optical window is extended from 1.1 to 1.7 microns.



This wide window is advantageous for **wavelength-division multiplexing** (**WDM**).

In WDM, laser pulses of different wavelength carry different signals.

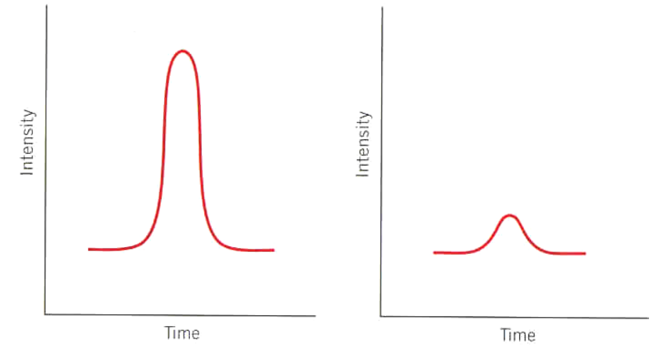
More than 100 channels can transmitted at once with wavelength only 0.2 nm apart (25Ghz).

Erbium doped fiber amplifiers (EDFAs), are effective for wavelengths between approximately 1525 nm - 1565 nm (C band), or 1570 nm - 1610 nm (L band).

Much research is currently underway to develop amplifiers for the remaining window.

Telecom systems

Picosecond pulses

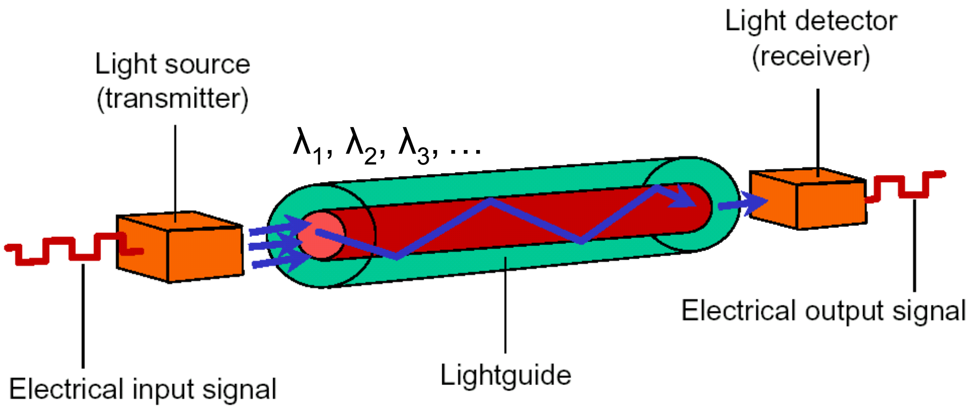


• Optical telecommunication networks use a digital encoding scheme, or binary format, a high power pulse of laser light correspond to a “one” and a low power pulse to a “zero”.

• This signal can be modulated at a rate of 100 Gb/second in a signal channel.

• About 100 channels can be transmitted through a single fiber using WDM.

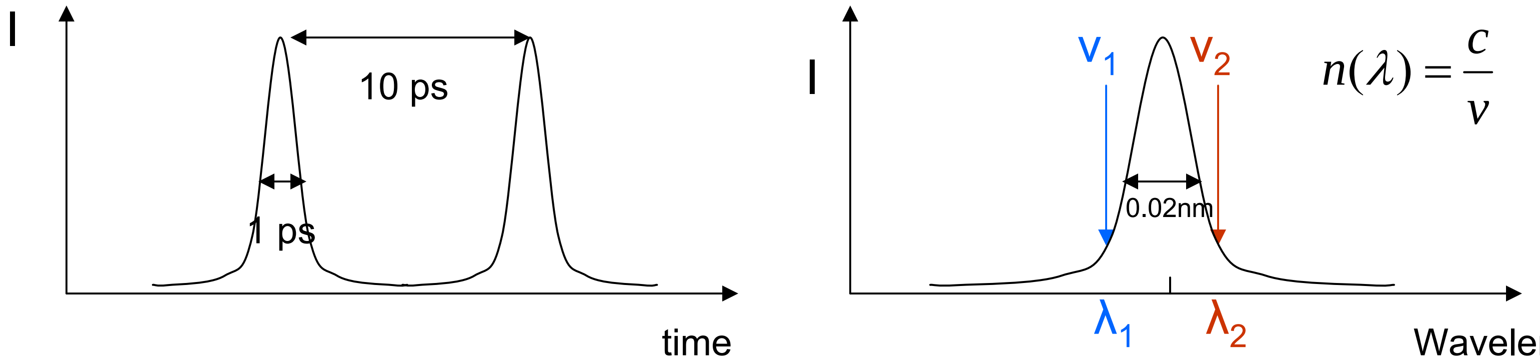
• This results in a transmission capacity of more than 10 Tb/second (10^{13} bits).



The current limitation to transmission rate is due to electronic signal routing which is slower than optical.
All optical systems are therefore being developped.

Dispersion

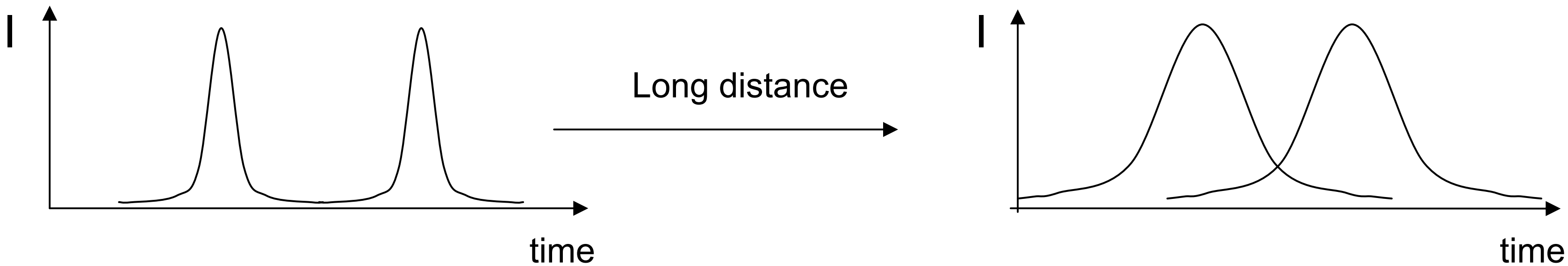
• The transmission distance in a telecom fiber system is limited not only by losses but also by spreading of the pulse-width due to dispersion.



$$n(\lambda) = \frac{c}{v}$$

• Light pulses have a finite width in time (pulse length) but also a finite width in wavelength (not exactly monochromatic).

• Due to the wavelength dependence of the index, the beginning of the pulse travels slower than the end of the pulse.



•This results in temporal broadening of the pulses which can become indistinguishable

Light waveguide:

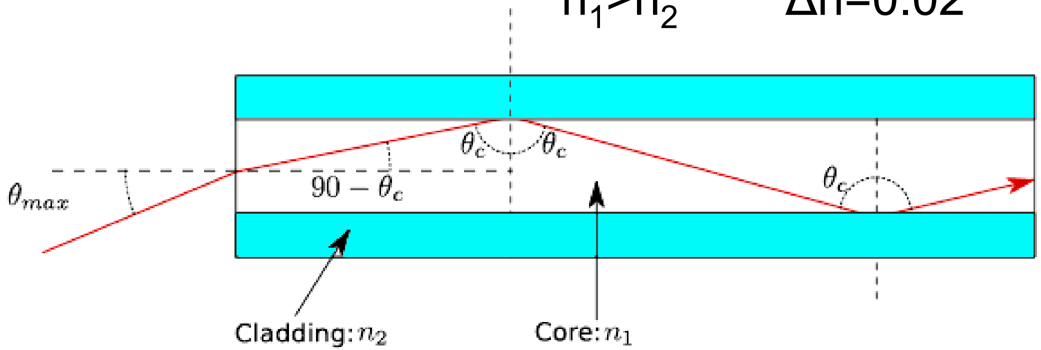
- Propagation of light in fibers in based on the total internal reflection principle.

$n_1 > n_2$ $\Delta n = 0.02$

The critical angle is $\sin\theta_c = \dfrac{n_2}{n_1}$

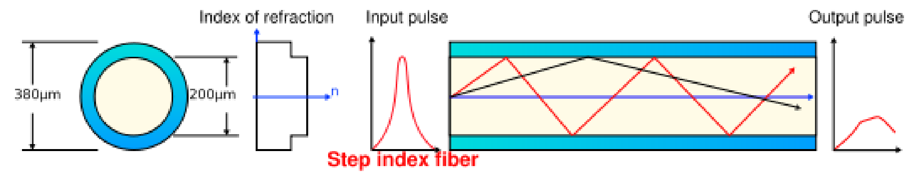
Hence the maximum angle for coupling incident light is:

$$\sin\theta_{\max} = \sqrt{n_1^2 - n_2^2}$$

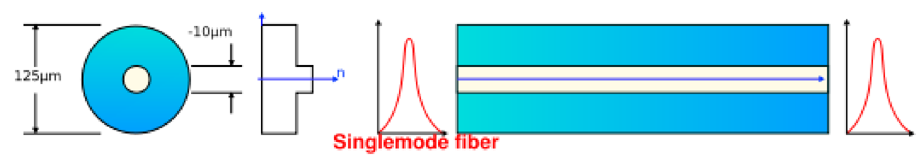


$\sin\theta_{max}$ is called the numerical aperture NA.

- Fibers with large core diameter transmit multiple modes while fiber with narrow core are monomode.



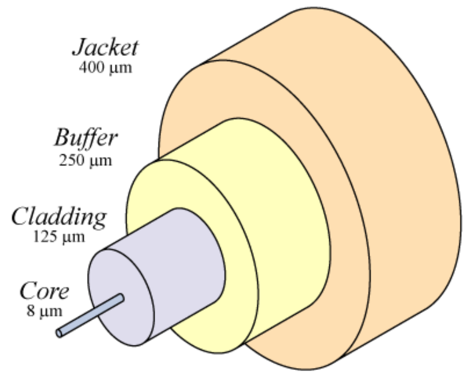
- Telecom fibers must be monomode to prevent pulse broadening due to multiple optical path.

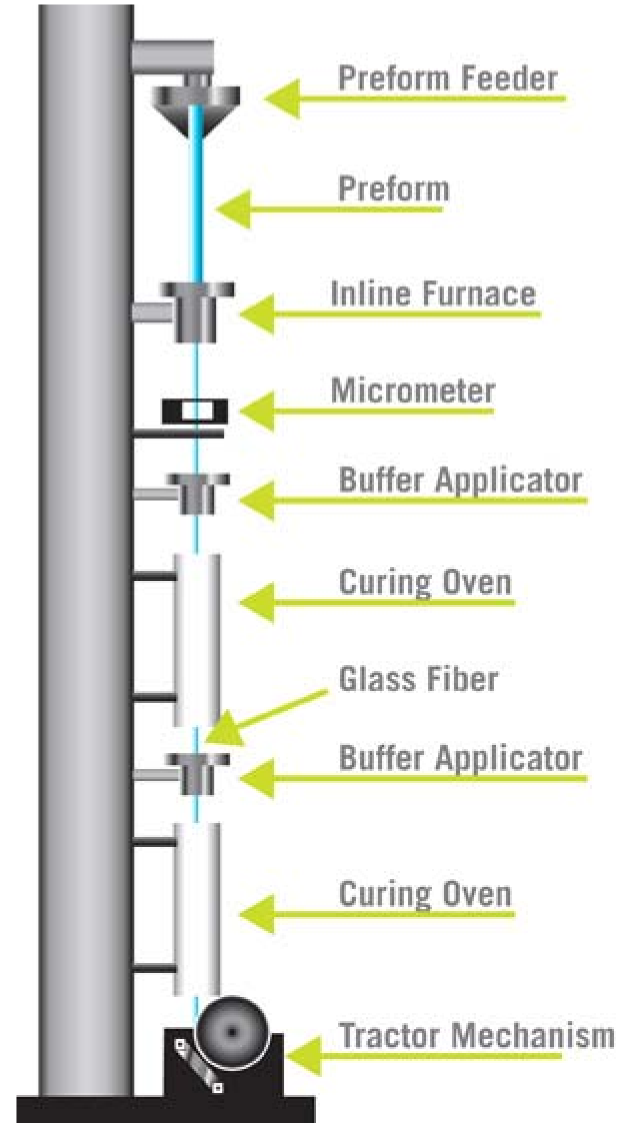


Synthesis: fiber drawing

In theory a monoindex fiber can work as a waveguide. But for practical reasons commercial fibers have several layers.

- All these layers are applied in line during the fiber drawing process.

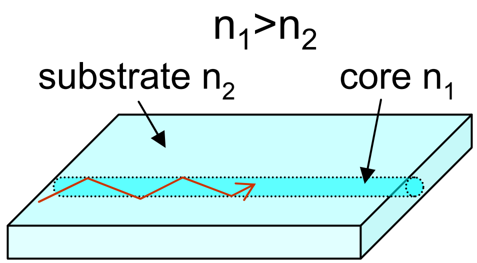




- Monomode core would be too fragile (8microns)
- Cladding prevents evanescent wave coupling.
- Buffer protects from surface oxidation, damage (potentially drastic loss in mechanical properties).
- Jacket protects from mechanical abuse (excessive bending, etc)

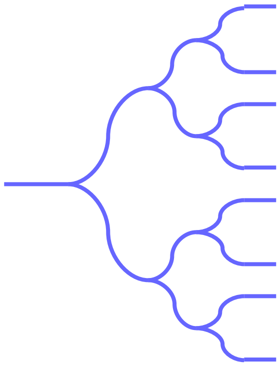
Planar waveguides and Integrated Optics

- Waveguides can be manufactured in planar substrate based on the same principle of TIR.
- A local index increase will confine light.

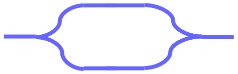


- Local refractive index change can be produced by:
  - Ion exchange (mask + salt bath)
  - laser modification (photo-writing)

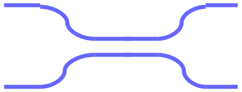
- Planar optical circuits permit to design compact devices for telecom network routing, optical sensing etc.. combining many optical components:



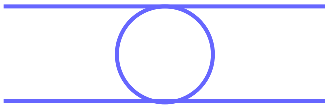
multiplexer



interferometer

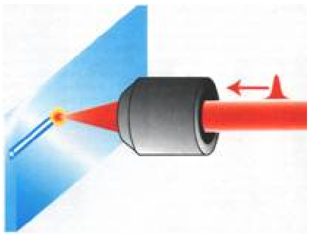


coupler



ring resonator

Photo-writing:



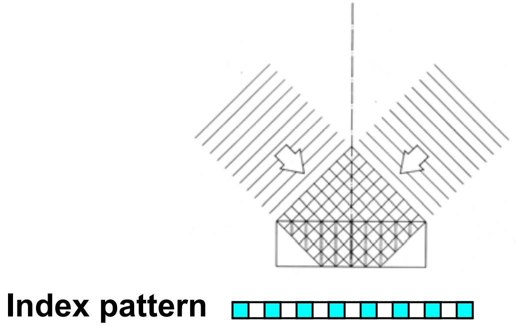
• Photo-writing in silicate glass substrates is performed with Ti-sapphire femtosecond pulsed laser at 800nm.

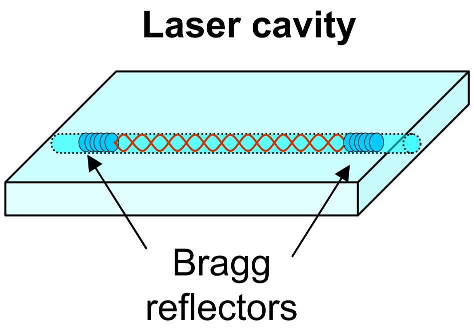
• 800nm is below bandgap for SiO_2 (9eV) but high energy pulses lead to nonlinear multiphoton absorption that generates electron plasma and local microexplosion in the glass which traps the structure into a higher fictive temperature state.

• SiO_2 has an abnormal behavior and will actually contract and its index increase with higher T_f therefore producing a waveguide (see Steve Martin).

• This is not the case for phosphate glass for example.

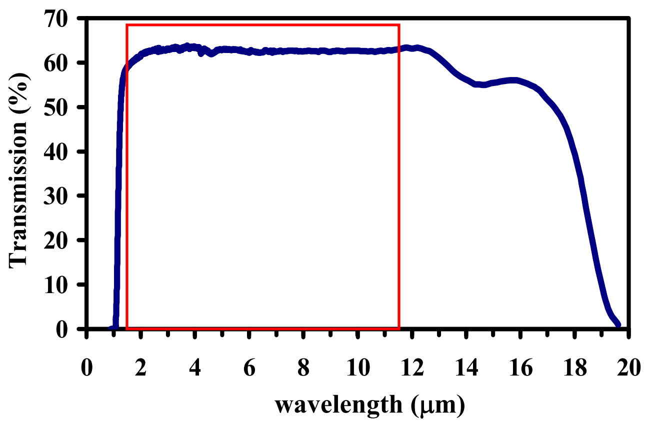
• Index patterns can also be holographically photo-inscribed to produce gratings, reflectors, laser cavities etc...

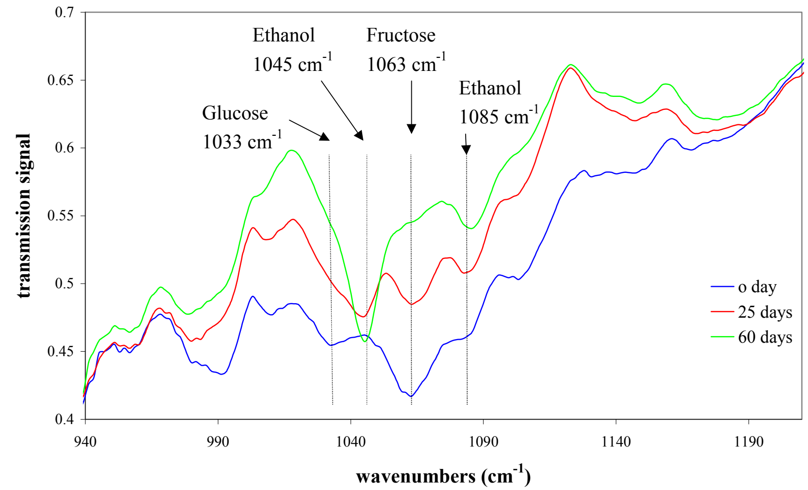


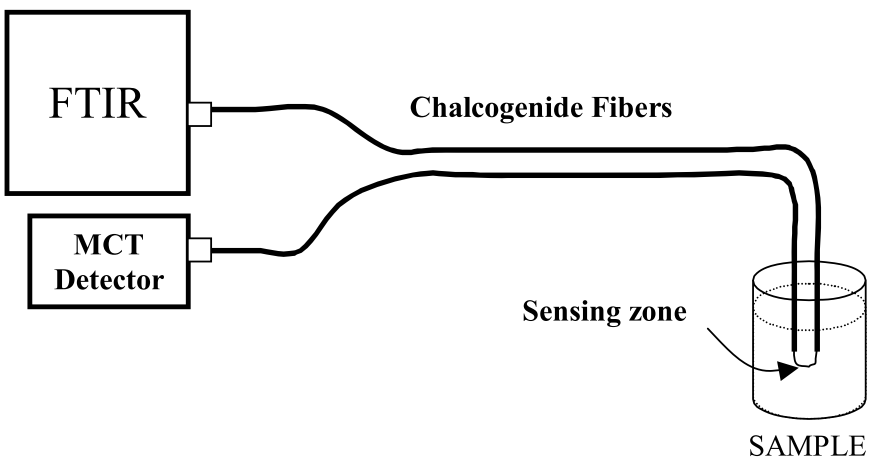


Infrared fibers

- Chaclogenide glasses are transparent in the domain where the vibrational signature of most molecules lies: 2-12 microns.



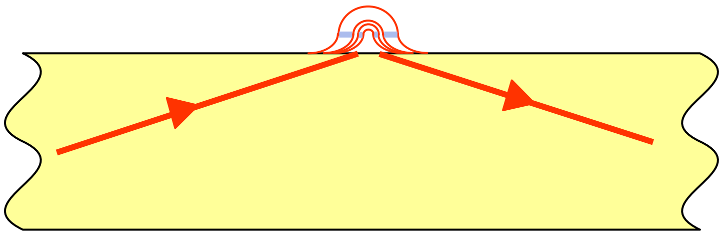


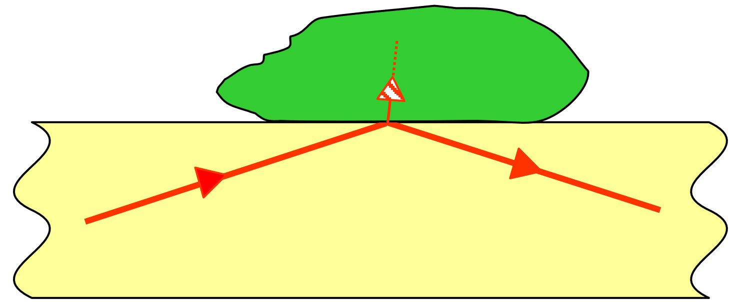


- Infrared fibers can be used to carry the optical signal from the spectrometer to the sample and back to the detector

Evanescent wave spectroscopy

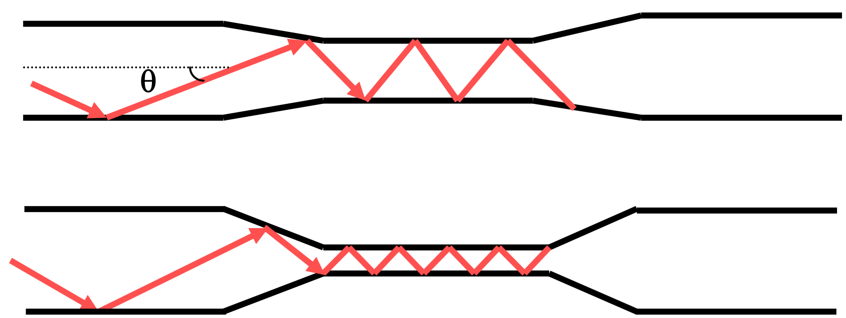
- The electric field of a lightwave confined into a fiber extends about 0.5 microns above the surface.





- If a absorbing molecule is in contact with the fiber surface, it will couple with the evanescent field and absorb the light.

- Reducing the fiber diameter improves the sensitivity by increasing the number of reflections



N: number of reflections

$$N(\theta,d,L) = L * \frac{\tan(90-\theta)}{d}$$

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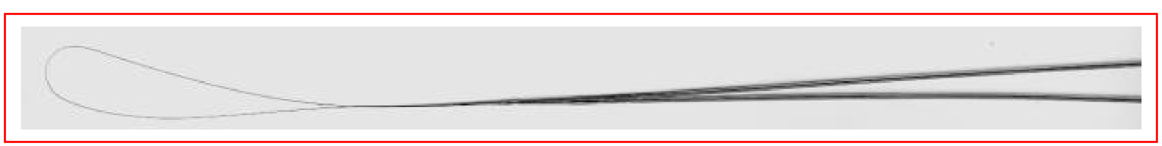
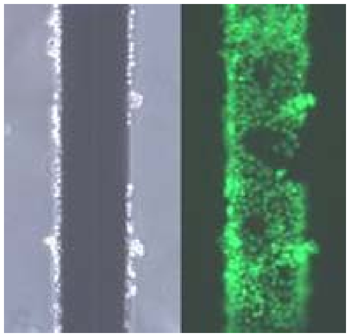
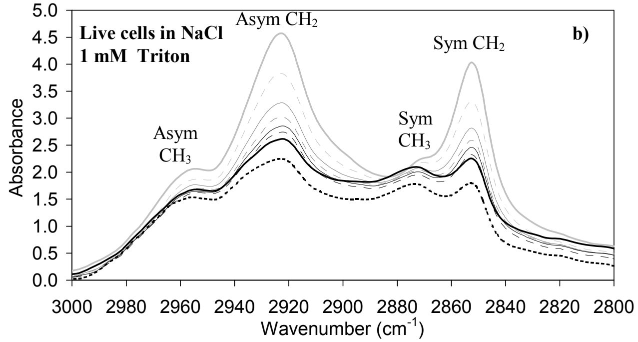
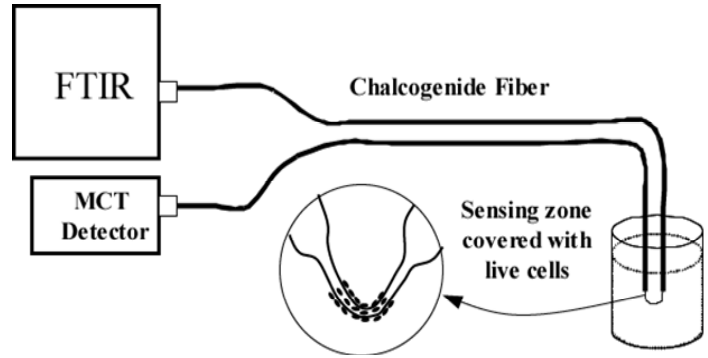
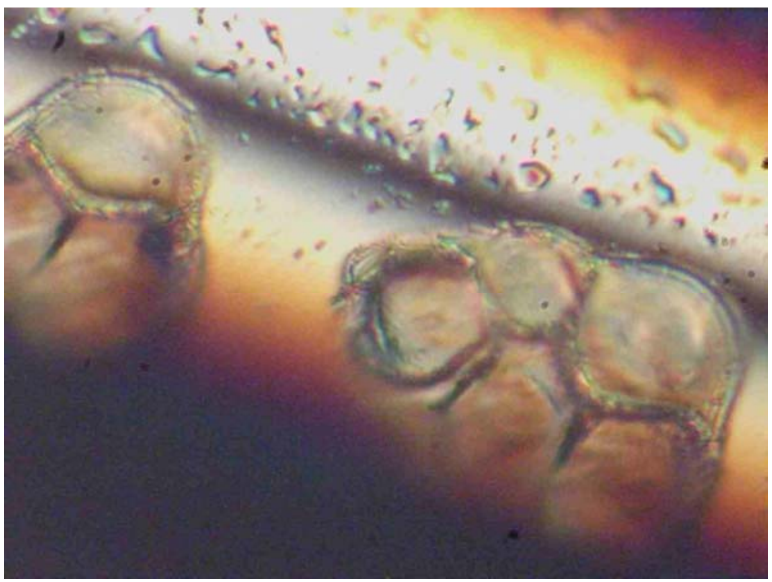


Evanescent wave spectroscopy: biosensing









- Biological molecules and microorganism have strong signature in the mid-infrared.
- Hence FEWS is an effective method for optical bio-sensing.

- Here, human lung cells are coated on the surface of an IR fiber and there spectrum is monitored during exposure to toxic agents.