

## Chapter 10: Optical Properties

- Glasses are among the few solids that transmit visible light
  - Thin film oxides might, but scattering from grains limit their thickness
  - Mica windows at Acoma Pueblo
- Glasses form the basic elements of virtually all optical systems
  - World-wide telecommunications by optical fibers
- Aesthetic appeal of fine glassware- 'crystal' chandeliers
  - High refractive index/birefringent PbO-based glasses
- Color in cathedral windows, art glass, etc.

### Optical Properties

1. Bulk Properties: refractive index, optical dispersion
2. Wavelength-dependent optical properties: color
3. Non-traditional, 'induced' optical effects: photosensitivity, photochromism, Faraday rotation, etc.

### *Bulk Optical Properties*

- History of optical science parallels the history of optical glass development
    - Ability to tailor the refractive index and dispersion of glass for telescopes and microscopes led to advances in:
      - Modern astronomy
      - Biology
      - Medical sciences
- Each of these sciences depended on the skills of the glassmakers

Modern glass science began with the collaboration (late 1800's) of

- Ernst Abbe: physicist, specialized in optical design
- Otto Schott: glass-maker
- Carl Zeiss: optician/instrument maker

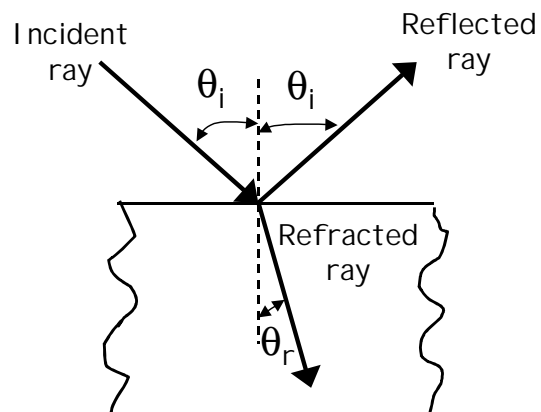
1. *Refractive Index*~(velocity of light in vacuo, or air)/(velocity of light in medium)

Snell's Law:

$$n = \frac{\sin \theta_i}{\sin \theta_r}$$

note: unitless quantity

n (air) =	1.0003
water =	1.33
sapphire =	1.77
diamond =	2.42
f-SiO <sub>2</sub> =	1.458
heavy flint =	1.89



**Internal Reflection:**

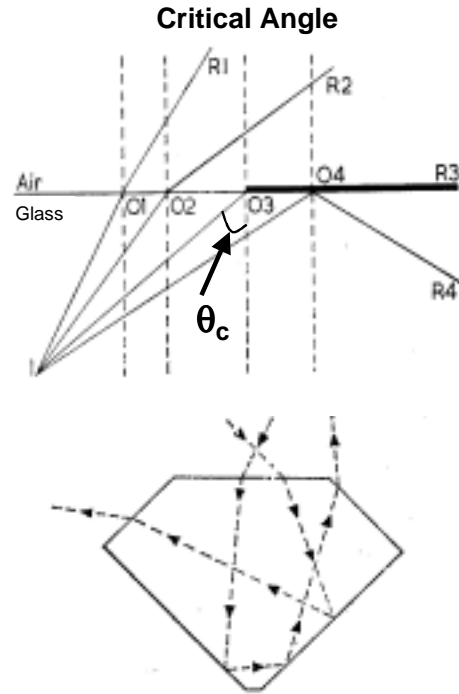
Critical angle (Brewster's angle)  $\theta_c$  below which light is totally reflected:

$$\sin \theta_c = \frac{1}{n}$$

Note: larger  $n$  means greater  $\theta_c$ , and so more light (from a broader distribution of incident angles) will be internally reflected.

High index materials (diamonds, PbO-glasses) look 'brilliant' when facets are cut so that internal reflection returns light from large faces that originally collected the light.

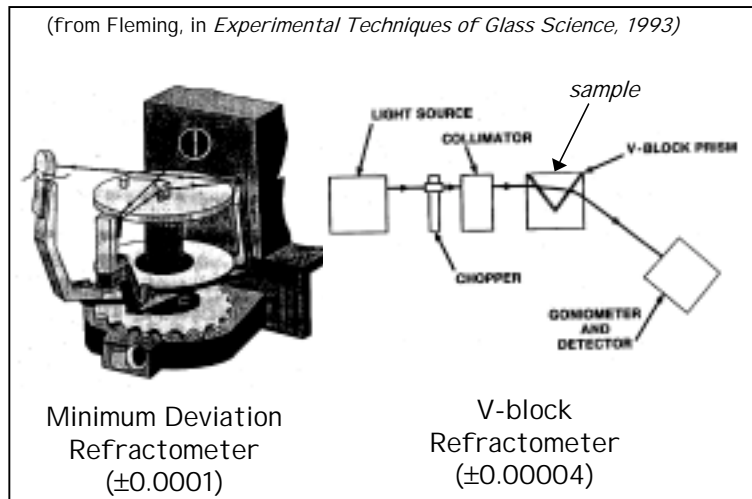
Note too: internal reflection is important for transmission of light down an optical fiber.



Measuring refractive index:

Ray tracing techniques:

- Minimum deviation ( $\pm 0.0001$ ); Fleming Figure 4
- V-block refractometer ( $\pm 0.00004$ ); Fleming Figure 7



**Index Matching Oils ( $\pm 0.001$ )**

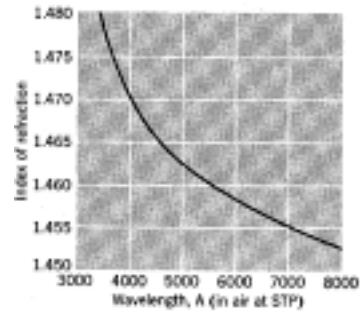
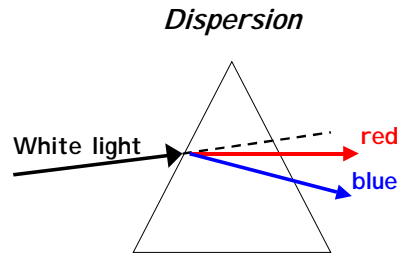
- Compare liquids with known indices to samples with unknown indices
- Samples 'disappear' when indices match
  - Becke line: moves towards *higher* index medium when stage moves *lower*.
- Simple; no special sample cutting/polishing required

Refractive index depends on wavelength.  
This dependence is called *dispersion*  
Short  $\lambda$ : higher index

So, refractive index should be quoted at a specific wavelength:

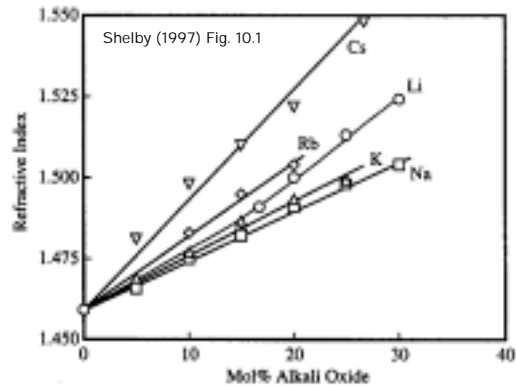
$n_D$ , 589.3 nm, Na-D line emission (yellow)  
 $n_F$ , 486.1 nm, H-F line emission (blue)  
 $n_C$ , 656.3 nm, H-C line emission (red)

(More on dispersion later)



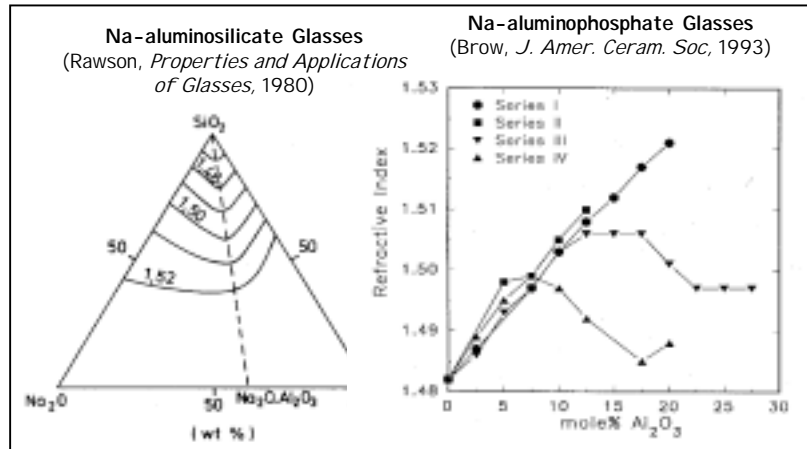
Refractive index represents the interaction of light with electrons of the constituent atoms in a glass.

- 'n' increases with electron density or polarizability.
  - Low 'n': low atomic # ions:  $\text{BeF}_2$  glasses,  $n \sim 1.27$ ;  $\text{SiO}_2$ ,  $\text{B}_2\text{O}_3$ :  $n \sim 1.46$   
low polarizable ions ( $\text{F}^-$  for  $\text{O}^{2-}$ )  
bridging oxygen for nonbridging oxygens; NBO's increase 'n'
- increasing  $\text{R}_2\text{O} \rightarrow$  increase in 'n'
  - 'n' increases even when smaller atomic# ions (Li, Na) replace  $\text{Si}^{4+}$  because of the greater polarizability of NBO's
- note that 'n' increases in the series  $\text{Na} < \text{K} < \text{Li} < \text{Rb} < \text{Cs}$ 
  - the low 'n' for the Li-silicate glasses results from the decreasing molar volume as the glass structure collapses around the small  $\text{Li}^+$  ions



Refractive index is sensitive to other network structural changes

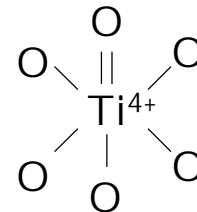
- replacing  $\text{Na}_2\text{O}$  with  $\text{Al}_2\text{O}_3$  in aluminosilicate glasses decreases 'n' because polarizable NBO's are replaced by less polarizable Al-O-Si bridging oxygens (Rawson Fig. 90).
- The Al-CN change in aluminophosphate glasses, from CN=6 to CN=4, replaces a dense structure with a more open network, causing 'n' to decrease (Brow, Fig. 5).



High index glasses contain heavy, polarizable ions: Pb, Bi, Tl, etc.

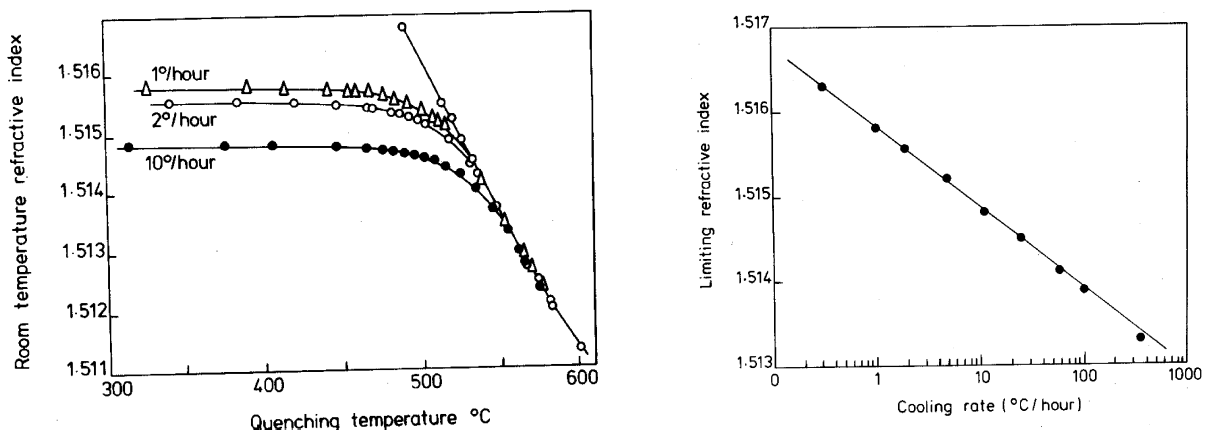
$\text{PbO}\cdot\text{Bi}_2\text{O}_3\cdot\text{Ga}_2\text{O}_3$  glasses: visible light 'n' ~2.7  
 $\text{S}^{2-}$  for  $\text{O}^{2-}$  also increases 'n'

- asymmetric ions also contribute to large 'n'
  - polarizable sites, in addition to polarizable ions
    - Ti-polyhedra: note asymmetry associated with the one short  $\text{Ti}=\text{O}$  bond
      - Non-linear optical applications
      - Basis for PbO-free glassware
      - Nb-polyhedra have similar effects



Fictive Temperature Effects:

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



Note: 'n' varies by ~0.003 for different quench rates for these optical glasses. The required degree of reproducibility (and homogeneity) for many optical applications can be *two orders of magnitude smaller*.

- Must avoid local variations in 'n' caused by poor annealing
- Optical glasses generally require much more careful (fine) annealing schedules than other glass products to avoid local heterogeneities in 'n'

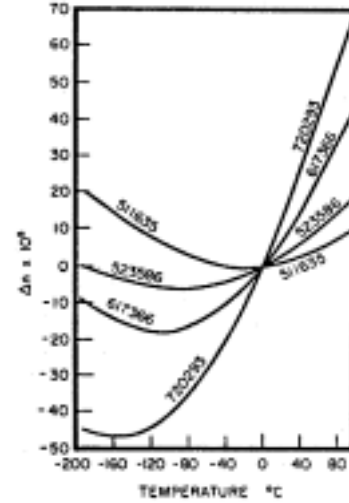
*Temperature Dependence*

- $dn/dT$  depends on composition and properties of the base glass
- CTE affects 'n': longer Me-O bonds, more open structure, lower 'n'
- higher temperature, greater ion polarizabilities, higher 'n'

$dn/dT$  important for a variety of applications

- self-heating of laser elements- increasing 'n' with laser absorption increases self-focusing, runaway damage
- index match for composites

Temperature Effects  
(from W. Vogel, in *Optical Properties of Glass*, 1991)



*Molar Refractivity*: measure of the contribution of constituent ions in a glass to the overall refractive index; dependent on ion polarizability.

$$R_m = V_m \left( \frac{n^2 - 1}{n^2 + 2} \right)$$

where  $V_m$  is the molar volume and 'n' is the refractive index at the  $\lambda$  of interest.

Molar refractivity is the sum of the individual ionic refractivities ( $R_i$ ):

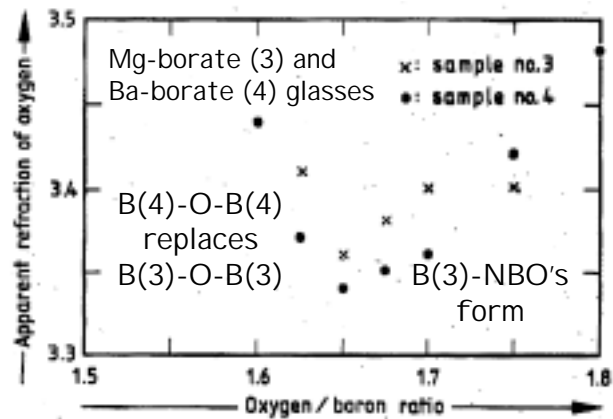
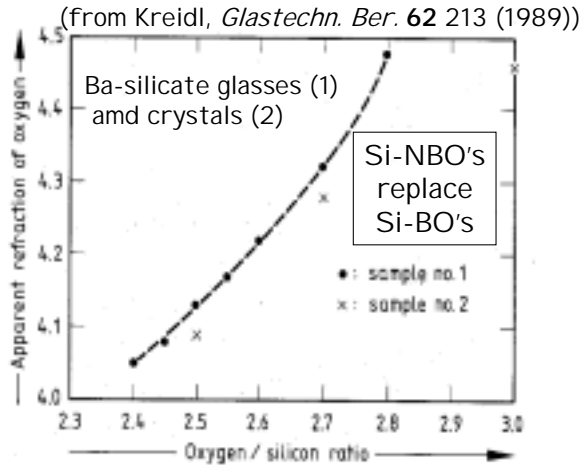
$$\text{for } A_xB_y, R_m = xR_A + yR_B$$

Note: Tables of ionic refractivities (right) are often used to predict the molar refractivity (and so the refractive index) of a glass with a known composition.

- Increasing ion size, increasing ionic refractivity:  $Li^+ < Na^+ < K^+$ ;  $Mg^{2+} < Ca^{2+} < Ba^{2+}$
- Small, highly charged glass-forming ions ( $Si^{4+}$ ,  $P^{5+}$ ) contribute less to the index of refraction than the larger modifiers
- One problem is that  $R_i$  is not a constant; e.g.,  $R_{Oxygen}$  is greater for NBO's than for BO's (Kreidl figure, below).  $R_{ox}$  is sensitive to structural changes.

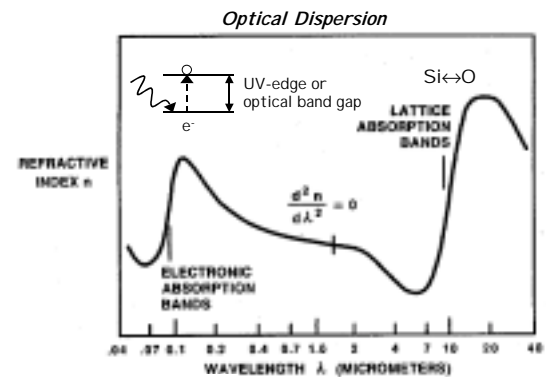
(from W. Vogel, *Chemistry of Glass*, 1985)

Cation	Ionic Refraction
$Li^+$	0.2
$Na^+$	0.5
$K^+$	2.2
$Mg^{2+}$	0.28
$Ca^{2+}$	1.33
$Ba^{2+}$	4.3
$Pb^{2+}$	3.1
$B^{3+}$	0.05
$Al^{3+}$	0.17
$Si^{4+}$	0.1
$P^{5+}$	0.07



**Dispersion:** the variation in index with wavelength:  $dn/d\lambda$

- Associated with the oscillation of electrons coupled to light
  - At short wavelengths, 'n' increases because the photons are absorbed by the promotion of electrons across the optical band-gap; **UV-absorption**
  - At longer wavelengths, 'n' increases because photons are absorbed by phonons associated with molecular-scale vibrations; **IR-absorption**
- $dn/d\lambda$  varies as the  $\lambda$  approaches either the UV- or IR-edges.



(from Fleming, in *Experimental Techniques of Glass Science*, 1993)

Abbe Number is the practical measure of dispersion of visible light:

$$v = \frac{n_D - 1}{n_F - n_C}$$

Note: large Abbe number ( $v$ ) means smaller degree of dispersion; smaller difference index when measured with blue light ( $n_F$ ) vs. red light ( $n_C$ ).

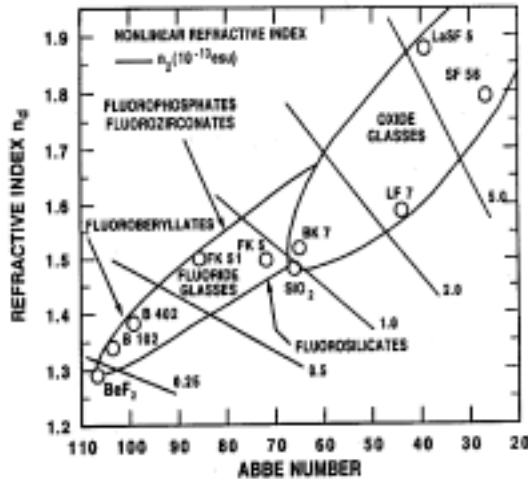


Table III. Some Abbreviations Used for Identification of Optical Glass Groups

Full Name of Glass Groups ('Families')	Abbreviation
Fluor crown	FK
Dense phosphate crown	PSK
Borosilicate crown	BK
Crown	K
Barium crown	BaK
Dense lanthanum crown	LaSK
Extra-light flint	LLF
Flint	F
Dense barium flint	BaSF
Short flint	KzF
Lanthanum flint	LaF

Optical glasses are classified with the *Abbe Diagram*.

Note that, in general, lower 'n' coincides with greater  $v$  (less dispersion). If light doesn't significantly interact with the constituent ions of a glass, then both index and dispersion will be low....

This scheme yields different classifications of glasses related to composition:

- **Crown glasses:** soda-lime silicates; low index, low dispersion.  
(named for the British window glass manufacturing process- large blown bubble of glass was transferred to a pontil, opened, then spun into a circular disk by centrifugal force.)
- **Flint Glasses:** lead-containing; high index, high dispersion (low  $v$ )  
(named for the high purity silica from 'flint nodules' found in chalk deposits in SE England)

Schott Glass Classification: second letter K: crown glass  
second letter F: flint glass

first letter represents a type; e.g.,  
BK-7 is a borosilicate crown  
LaF-20 is a lanthanum flint (high n, low  $v$ )

Catalog numbers represent optical properties; first three numbers define ' $n_D$ '  
Last three numbers define ' $v_D$ '

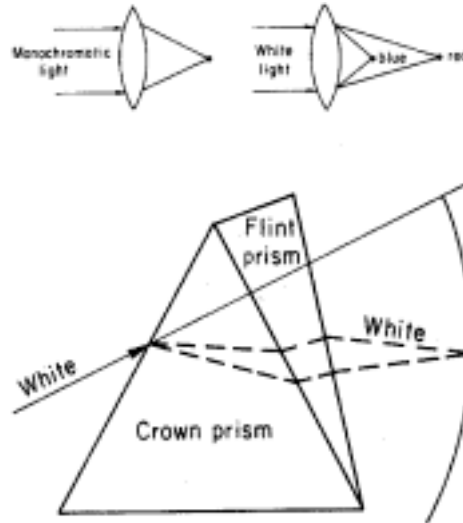
BK-7 (517642): ' $n_D$ '=1.51680;  $v_D$ =64.17  
LaF-20 (682482): ' $n_D$ '=1.68248;  $v_D$ =48.20

- Schott has over 200 glasses in their catalog. Compositions are proprietary, only optical properties are reported. Optical designers don't care; rarely interested in other properties (except for  $dn/dT$ ).

Why be concerned with dispersion? Chromic aberrations.

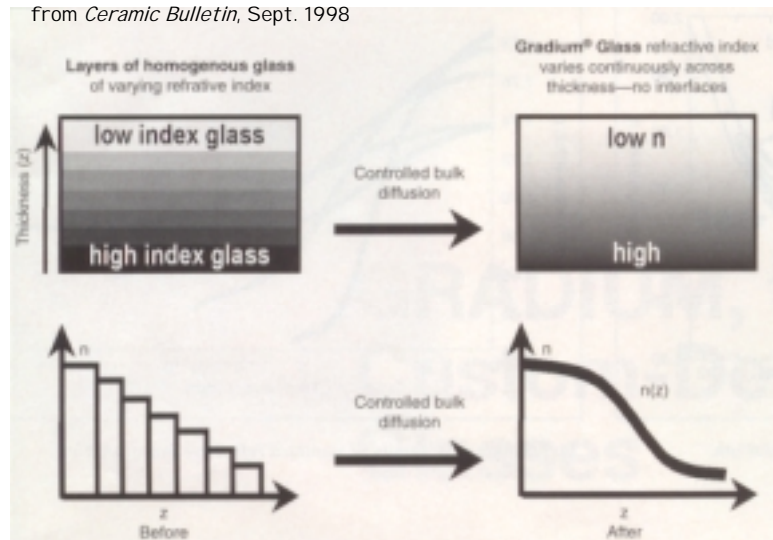
- A lens will focus red light at a different spot than blue
- Multiple optical elements, with different indices and different dispersions, will correct this effect.

(from W. Vogel, *Chemistry of Glass*, 1985)

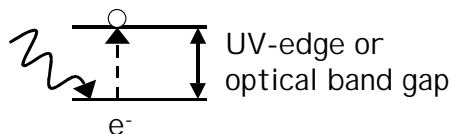


*LightPath Technologies*: diffuse together different glasses to provide the same chromic corrections in a single piece of glass- do not require multiple lenses.

from *Ceramic Bulletin*, Sept. 1998



### Ultraviolet Absorption





- Interband electronic transitions (valence to conduction bands:  $h/\lambda \geq E_{\text{gap}}$ )
- for pure SiO<sub>2</sub>:  $E_{\text{gap}}$  is ~8 eV (0.16 μm)
  - UV-photolithography
- Note: the large increase in 'n' associated with the UV-edge is accompanied by a loss of transmission at these same wavelengths. Ditto for the IR-cutoff. See Fanderlik, figure 41.

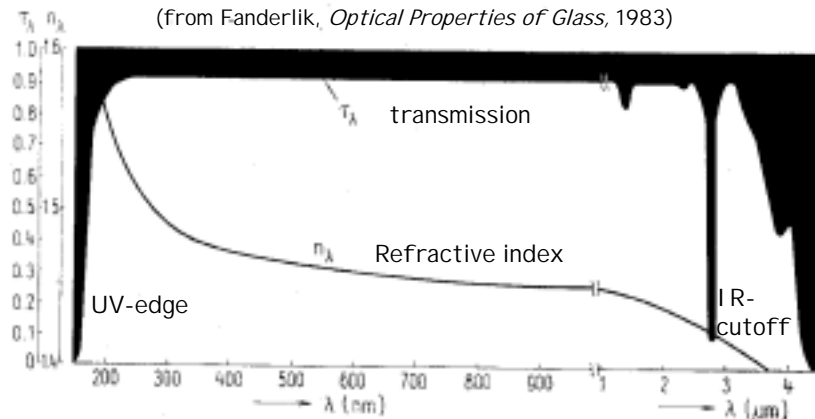


Fig. 41 Dispersion curve of quartz glass compared with its absorption spectrum.

- Adding alkalis reduces the UV-edge energy (moves the edge to longer  $\lambda$ ).
  - The closer the UV-edge is to visible frequencies, the greater the visible dispersion ( $\nu_D$ ).
    - GeO<sub>2</sub> has a smaller  $E_{\text{gap}}$  than other oxide glasses; addition of alkalis pushes the edge close to the visible. Resulting increased absorption causes yellowish color in alkali germanates. Intensity of the color increases with temperature (*thermochromism*) as  $E_{\text{gap}}$  decreases.
- Absolute UV edge is difficult to observe. Small contamination by Fe-impurities lead to intense absorptions due to *charge transfer transitions*, overwhelm the  $E_{\text{gap}}$  transitions

### Infrared Absorption

- transitions associated with phonon vibrations



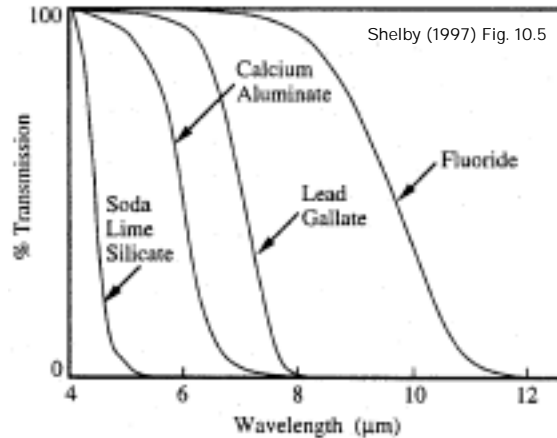
$$\nu = \left( \frac{1}{2\pi} \right) \sqrt{\frac{F}{\mu}}, \quad \text{where } \mu = \frac{m_1 m_2}{m_1 + m_2}$$

$\nu$  is the frequency of the vibrational absorption energy,  $F$ =force constant of the bond (spring) between the two ions and  $\mu$  is the 'reduced mass' of the vibrating entity.

- Note in the above figure from Fanderlik that these transitions are at much lower energies (longer wavelengths)- for 'clear glasses' these vibrations occur in the IR part of the spectrum.
- Note too that the frequency of the IR-absorption peaks are sensitive to the nature of the Me-O bonds: structural information from vibrational spectroscopies (IR and Raman)

Large ions, weak bonds lead to IR absorptions at longer wavelengths

- IR absorption wavelength increases in the order  $B_2O_3 < SiO_2 < GeO_2$
- Replacing  $O^{2-}$  with  $F^-$ ; weaker bonds, longer wavelength IR cutoff
  - Fluoride glasses are good IR-transmitters
- Chalcogenide glasses are good IR-transmitters ( $S < Se < Te$ )



IR transmitting glasses used in windows to detect IR signals

- sidewinder missiles
- IR lasers ( $CO_2$ ) for surgical applications, etc.

### **Color in Glass**

Color results from selective absorption or scattering of specific (visible) wavelengths. Absorb red, see blue; absorb red and blue, see yellow, etc.

- If all visible wavelengths transmit equally? You'll see clear → gray → black, depending on the *total* transmission (high → low).

Several mechanisms lead to color:

- 1- Absorption; electron transitions; ligand field theory; redox equilibrium rxn.
- 2- Light scattering; colloidal metal or semiconducting particles (Mie scattering)
- 3- Photosensitive glasses
- 4- Fluorescence; lasers

### Absorption Colors

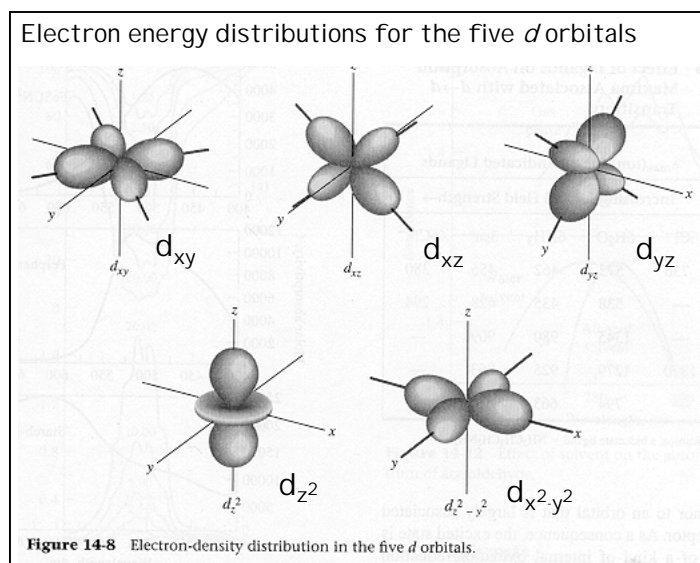
- Absorption by transition metal ions involves the transition of electrons from a *d* orbital of lower energy to one of higher energy.
  - Electron transitions with energies in the visible spectrum:  
 $\Delta E = hc/\lambda$ , 1.77 eV (700 nm, red)  $\leq \Delta E \leq$  3.10 eV (400 nm, blue)
- Noble gas shell ions ( $Si^{4+}$ ,  $O^{2-}$ ,  $Na^+$ ) require large energies for electron transitions
  - $\Delta E > 3$  eV; UV-edge
  - clear glasses

- However, unfilled 3d (transition metals), 4f (lanthanides) orbitals have  $\Delta E$ 's in the visible energy range
- The 3d electrons in transition metal ions are outer shell electrons; participate in bonding; color is sensitive to changes in chemistry.
- The 4f electrons in lanthanide ions are more shielded (by 5s, 5p electrons) and so colors are generally unaffected by compositional variations.

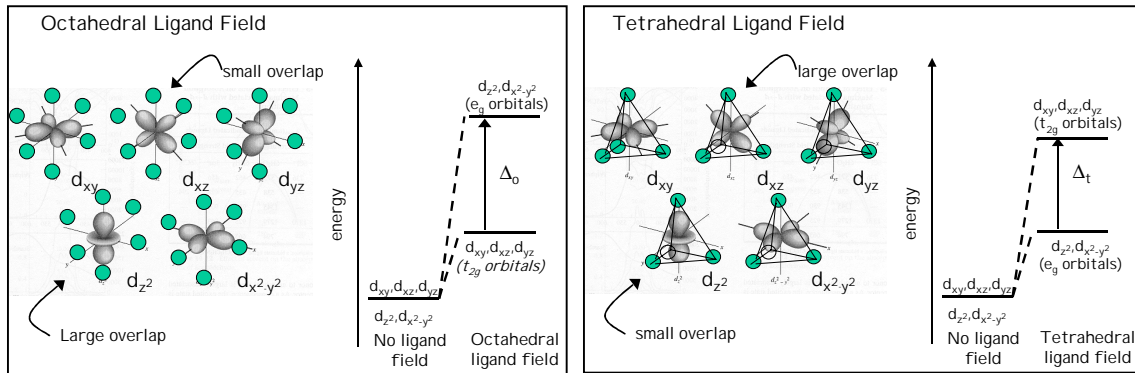
### Ligand Field Theory (Crystal-Field Stabilization)

Consider transition metal ions:

There are five hybrid orbitals for 3d electrons with distinct spatial orientations.

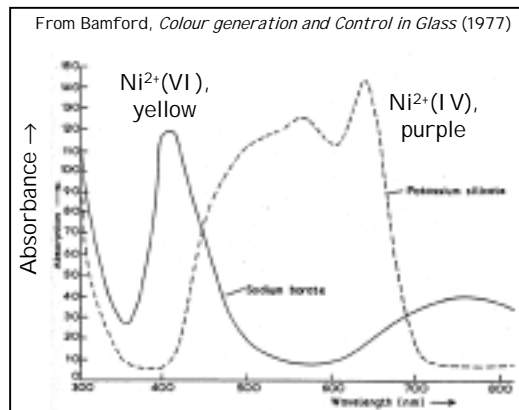


- Energies of  $d$  orbitals in transition-metal ions in different hosts are not identical
  - In the absence of an electric or magnetic field (as in dilute gaseous state), the energies of the five orbitals are identical and so the absorption of a photon is not required for an electron to move from one orbital to another.
  - In the presence of a field (e.g., when the transition metal cation is coordinated by anions) splitting of the  $d$ -orbitals energies results.
    - Electrostatic repulsion between electron pairs from the host (donor) and from the 'central' TM ion.
  - Note that the  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals fill space between the axes, whereas  $d_{x^2}$  and  $d_{x^2-y^2}$  are directed along the axes.
  - If the 'ligand field' (coordination environment) exerted by the host ions overlaps with a particular  $d$  orbital, that orbital will become destabilized to a higher energy.



Compare the octahedral and tetrahedral ligand fields:

- In an octahedral ligand field, there is a greater overlap of the  $d_{x^2}$  and  $d_{x^2-y^2}$  orbitals (the  $e_g$  orbitals- so-named from group theory) with the ligand orbitals, and so these will have greater energies than the  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals (the  $t_{2g}$  orbitals).
  - Photons that possess the gap energy (the energy difference between the different d-orbitals,  $\Delta_o$ ) will be absorbed as they excite electrons from the lower energy orbitals to the higher energy orbitals.
    - $Ti^{3+}$ /octahedral CN:  $[Ar]3d^1: t^1_{2g}e^0_g \rightarrow t^0_{2g}e^1_g$  transition
      - Purple color in phosphate glass
  - In a tetrahedral ligand field, there is a greater overlap of the  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals with the ligand orbitals, and so these will have greater energies than the  $d_{x^2}$  and  $d_{x^2-y^2}$  orbitals.
    - Photons that possess the gap energy (the energy difference between the different d-orbitals,  $\Delta_t$ ) will be absorbed as the excite electrons from the lower energy orbitals to the higher energy orbitals
  - In general,  $\Delta_t \sim (4/9)\Delta_o$ 
    - *Transition metal ions with different CN's will produce different colors.*
      - Consider  $Ni^{2+}$ : ( $[Ar]3d^8$ )
        - Li-Ca-silicate:  $Ni^{2+}(VI): t^6_{2g}e^2_g \rightarrow t^5_{2g}e^2_g$ : pale yellow glass
        - K-Ca-silicate:  $Ni^{2+}(IV): e^4_{gt^4}_{2g} \rightarrow e^3_{gt^5}_{2g}$ : purple glass



- Different TM-ions will have different  $\Delta_{t,o}$  and will produce different colors

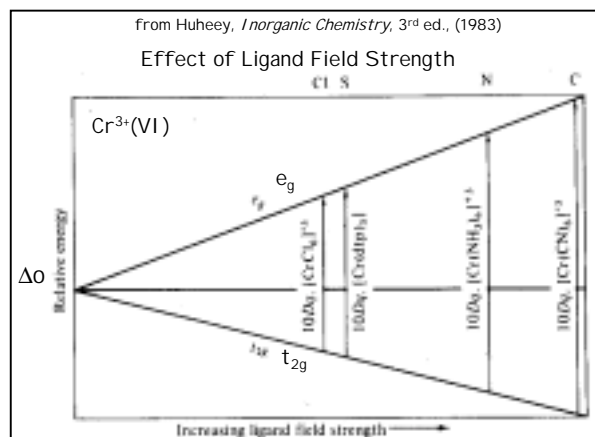
Table 2 Visible Optical Absorption in Soda-Lime Silicate Glasses of Transition Metal Ions

Ion	No. of d electrons	Abs. max. ( $\mu$ )	Coordination no. with oxygen	Color of glass	Remarks	Refs.
$\text{Cr}^{3+}$	1	0.66 0.45	6	Green		44
$\text{Ti}^{3+}$	1	0.57	6	Purple	Borosilicate glass	4
$\text{V}^{4+}$	1	1.12	6?	Red		45
$\text{V}^{3+}$	2	0.645 0.425	6	Green		45
$\text{Mn}^{2+}$	4	0.90	6	Purple		4
$\text{Mn}^{3+}$	5	0.435	4, 6?	Brown		4,51,52
$\text{Fe}^{3+}$	5	0.41	4?	Green	Potassium silicate	46,47
$\text{Fe}^{2+}$	6	1.30	4, 6?	Blue		46,53
$\text{Co}^{3+}$	7	0.56	6	Blue	Low alkali borate	48,50
		0.60	4		High alkali borate	
$\text{Ni}^{2+}$	8	1.33 0.76 0.42	6	Purple, grey	Low alkali borate	48 50 50a
		1.19	4		High alkali borate	
$\text{Cu}^{2+}$	9	0.79	6	Blue		45

(from Doremus, Glass Science, 1973)

What else effects color?

- Ligand field strength; different *anions* will produce different  $\Delta_{t,o}$ 
  - In general,  $\Delta$  increases in the series  $\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{F}^- < \text{OH}^- < \text{O}^{2-} < \text{NO}_3^- < \text{CN}^-$ 
    - Absorbing wavelength becomes shorter (red  $\rightarrow$  blue).



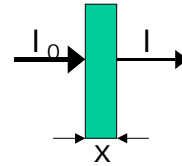
- Shelby:  $\text{Co}^{2+}$  in Na borate is dark blue
  - Adding NaCl for  $\text{Na}_2\text{O}$ : light blue-green
  - Adding NaBr for  $\text{Na}_2\text{O}$ : green
  - Adding NaI for  $\text{Na}_2\text{O}$ : red-brown

Effects of TM-concentration:

- Recall Beer-Lambert Law

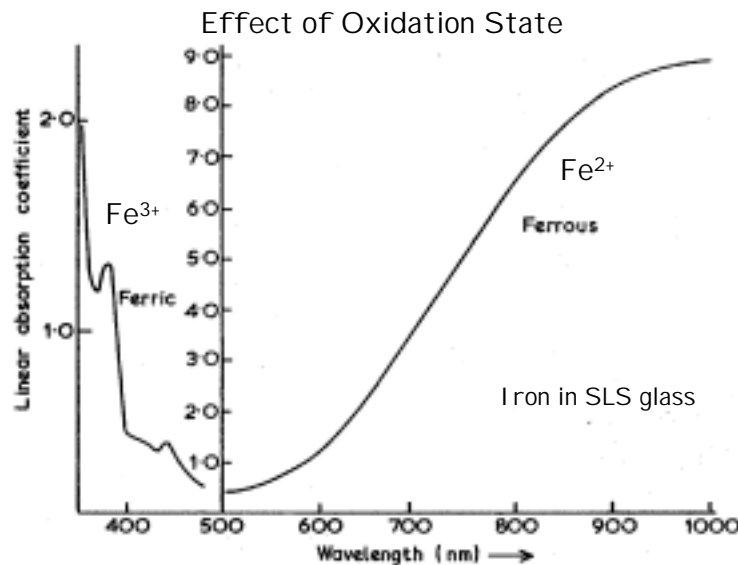
$$\frac{I}{I_0} = e^{-\epsilon c x}$$

Where  $c$  is molar concentration,  $\epsilon$  is molar extinction coef. (absorptivity) and  $x$  is the sample thickness



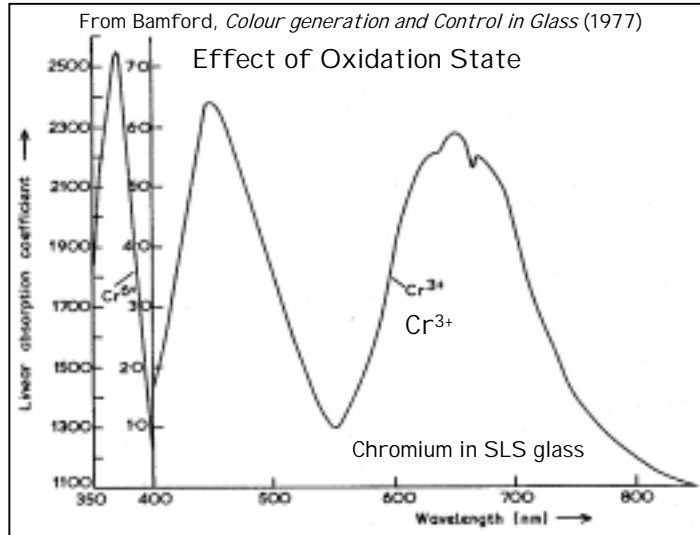
- Weak, *intra-cation transitions* (3d splittings):  $\epsilon \sim 0.01-200$
- charge-transfer absorption*: electron-transfer from a donor complex (SCN<sup>-</sup>) to an acceptor orbital (Fe<sup>3+</sup>)
  - very large molar absorptivities ( $\epsilon > 10^3$ )
    - often mistaken for UV-edge
    - used in analytical chemistry
- Oxidation state affects color*
  - In general, greater valence  $\rightarrow$  greater  $\Delta \rightarrow$  absorption at shorter  $\lambda$ 
    - e.g., V<sup>4+</sup> is red (absorbs blue); V<sup>3+</sup> is green (silicate glasses)
    - Fe<sup>2+</sup>/Fe<sup>3+</sup> colors; Fe<sup>3+</sup> absorbs UV/blue, Fe<sup>2+</sup> absorbs IR/red, leaving a greenish tinge; look at the edge of a window glass to see color effects of Fe-contamination- demonstrates the effect of 'x' in Beer-Lambert law
      - Fe<sup>2+</sup>/Fe<sup>3+</sup> IR & UV absorption used for 'heat control' in automobile window glasses

From Bamford, *Colour generation and Control in Glass* (1977)

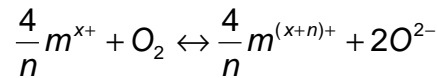


- Cr<sup>3+</sup>/Cr<sup>6+</sup> used for green glass used in containers. (NiO or CoO sometimes added for darker green found in champagne bottles vs. emerald green of some beer bottles.)

- $\text{Cr}^{3+}$  is emerald green;  $\text{Cr}^{6+}$  is yellowish (broad absorption tail in blue; also possesses red absorption band that is not shown below). Vary the  $\text{Cr}^{3+}/\text{Cr}^{6+}$  ratio to change the yellow-green tints.



- Redox effects in glass melts: TM valence sensitive to the oxygen partial pressure in the melt:



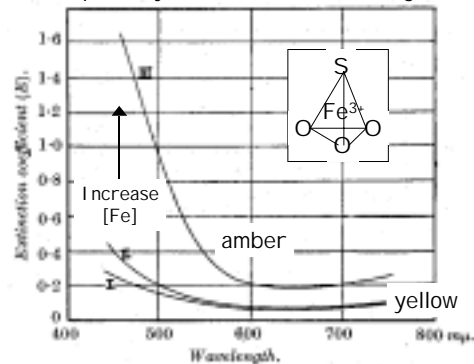
$[\text{O}^{2-}]$  depends on

- $\text{P}_{\text{O}_2}$  over the melt
- melt temperature
- $[\text{M}^{x+}]$  concentration
- glass 'basicity'
- presence of reducing agents in the melt
- use of fining agents or oxidizing raw materials
- ( $\text{As}_2\text{O}_5 \rightarrow \text{As}_2\text{O}_3 + \text{O}_2$ ;  $\text{KNO}_3 \rightarrow \text{K}_2\text{O} + \text{NO} + \frac{1}{2}\text{O}_2$ )

### Amber Glass: $\text{Fe}^{3+}$ -S chromophore

- Blocks UV to protect against spoilage (pharmaceuticals and adult beverages)
- Tricky to make:
  - $\text{P}_{\text{O}_2} < 10^{-10}$  atm,  $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$
  - $\text{P}_{\text{O}_2} > 10^{-8}$  atm,  $\text{S}^{2-} \rightarrow \text{SO}_4^{2-}$
  - Glass turns green
- Controlled by carbon-additions to the melt; hence 'carbon-sulfur' amber
- Replace  $\text{S}^{2-}$  with  $\text{Se}^{2-}$  to form a black chromophore

Absorption by 'carbon-sulfur' amber glass



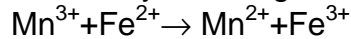
from W.A. Weyl, *Colored Glasses* (1951)



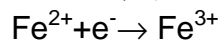
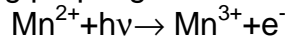
Decolorizing- clear glasses.

- Eliminate all transition metals; used to be expensive
- Add decolorizing agents to alter 'internal' oxidation state:

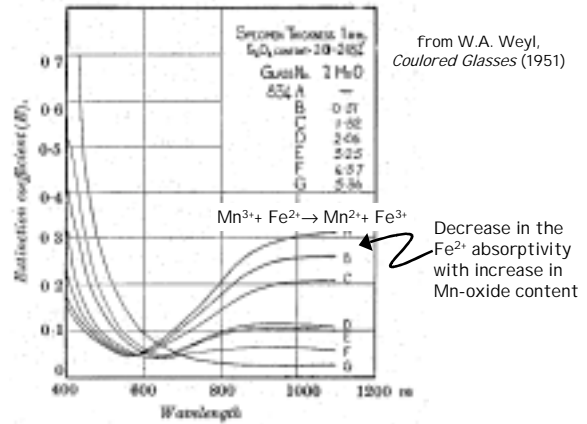
Mn-oxides were once added to SLS glass to counteract the effects of significant Fe-contamination by oxidizing  $Fe^{2+}$ :



Produced clearer glasses, however unanticipated interactions with sunlight (solarization) altered the redox conditions, forming purple glasses:

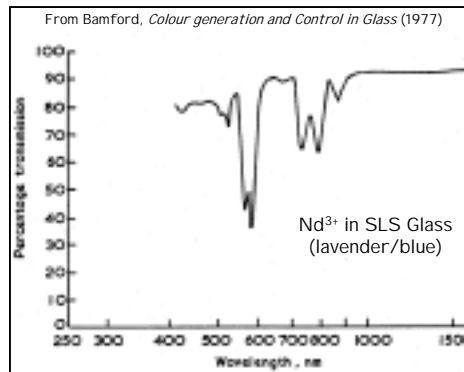


Old windows and doorknobs have purple tint



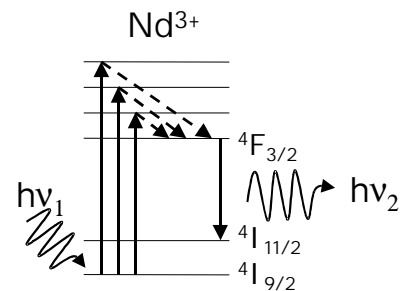
Absorption by Rare-earth ions

- Electronic transitions in 4f orbitals
  - Generally sharper absorption bands than those associated with Transition Metal 3d orbitals
    - More effectively shielded from 'chemical variations' by outer 5s/5p electrons
    - Much smaller ligand field effects
    - Much weaker absorption coefficients



More important consequence of RE-ions is *fluorescence* colors

- UV absorption ( $h\nu_1$ ), excite electrons from the ground state ( $4I_{9/2}$ ) to excited states
- Non-radiative transfer to 'longer-lifetime excited state ( $4F_{3/2}$ )
- Fluorescence by de-excitation back to the  $4I_{11/2}$  ground state- emission of visible light ( $h\nu_2$ ) depends on energy level differences.
  - Emitted in phase, same direction as incident photon





- Fluorescence spectra from a series of  $\text{Nd}^{3+}$ -doped glasses.
  - Note the dependence on host chemistry.
- Fluorescent light at different  $\lambda$  than absorbed light.
  - RE-doped glasses will have different (apparent) colors depending on light-source
  - $\text{Nd}^{3+}$  is pinkish in sunlight, blue under fluorescent lights
    - Alexandrite- naturally-occurring RE-doped gemstone

(from Weber, *J. Non-Cryst. Solids*, 123 208 (1990))

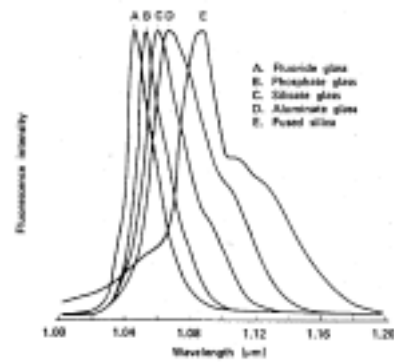
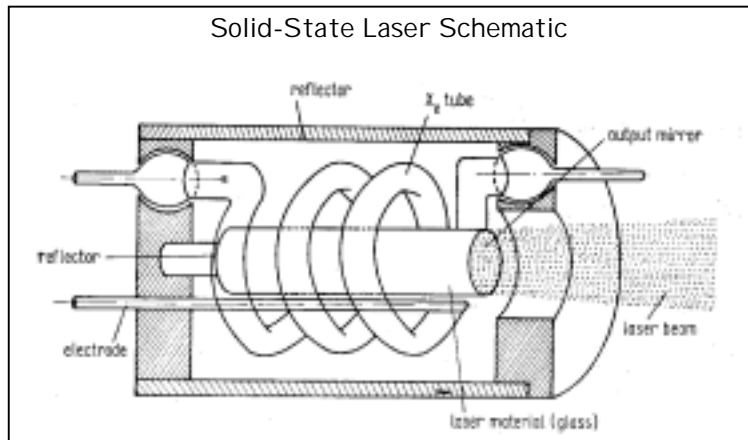


Fig. 1.  ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$  fluorescence spectrum of  $\text{Nd}^{3+}$  in different glasses at 300 K. Compositions (mol%): A 47 $\text{ReF}_2$ , 27 $\text{KF}$ , 14 $\text{CaF}_2$ , 10 $\text{AlF}_3$ , 2 $\text{NaF}$ ; B 55 $\text{P}_2\text{O}_5$ , 38 $\text{Li}_2\text{O}$ , 10 $\text{CaO}$ , 4.3 $\text{Al}_2\text{O}_3$ , 0.7 $\text{Nd}_2\text{O}_3$ ; C 99.9 $\text{SiO}_2$ , 27.5 $\text{Li}_2\text{O}$ , 10 $\text{CaO}$ , 2.3 $\text{Al}_2\text{O}_3$ , 1.8 $\text{Nd}_2\text{O}_3$ ; D 33 $\text{Al}_2\text{O}_3$ , 53 $\text{CaO}$ , 10.2 $\text{SiO}_2$ , 3 $\text{BaO}$ , 0.5 $\text{Nd}_2\text{O}_3$ ; E 99.9 $\text{SiO}_2$ , 0.1 $\text{Nd}_2\text{O}_3$ .

- *Population Inversion*: greater population of electrons in the excited state (depends on the fluorescence decay lifetime) than in the ground state, the then the incident light will be amplified- *LASER* (Light Amplification by Stimulated Emitted Radiation)



Operation:

1. Optically pumped by pulses from Xe flash-lamps; mirrors concentrate pump light onto the lasing rod at center
2.  $\text{Nd}^{3+}$  ions absorb pump energy, electrons excited to higher energy levels
3. Excited ions decay (non-radiatively, through phonons) to the  ${}^4F_{3/2}$  excited state.
4. The de-excitation transition from the  ${}^4F_{3/2}$  level to the  ${}^4I_{11/2}$  level is triggered (stimulated) by a photon, accompanied by the emission of a 1.06  $\mu\text{m}$  photon.
5. This fluorescent photon is emitted at all angles from the ion. The laser cavity is designed to focus these photons along the axis of the laser rod, where intensity increases until a pulse of coherent light is emitted through the partially reflecting mirror (right side of above schematic).

- Glass lasers generally have broader distributions of energy levels (20-30X broader) than crystal lasers. (Due to the broader distributions of local bond arrangements around the RE ion in a glass than in an ordered crystal lattice).
- Glass laser materials are easier to manufacture than crystal laser materials
  - More opportunities for varying the host properties
  - Easier to manufacture a variety of shapes-
    - glass fiber lasers
    - large plates of laser glass for fusion experiments (LLNL)
  - Lower thermal conductivity of glass is a disadvantage (problem with heat dissipation in high power lasers)

Emitting wavelength from RE-doped solid state lasers is dependent on the 4f energy levels. (See Weber's collection of levels).

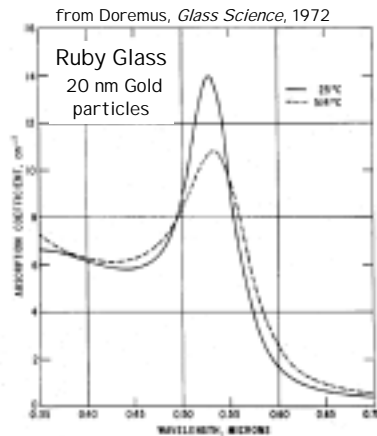
Other mechanisms for color in glass:

### 1. Colloidal Colors

#### 1.1. Metal Particles

*Mie Scattering*: red light is reflected more efficiently than blue light from metal particles with diameters  $< \lambda$  of the light.

*Striking glasses*: heat treatments above  $T_g$  nucleate/grow the colloidal metal particles. Color is 'struck' when particles reach the right size to scatter light; e.g., the gold 'Ruby' glass.



These glasses are generally more difficult to process than TM (or RE) doped 'absorption' colors.

- $K_2O \cdot CaO \cdot SiO_2$ ,  $K_2O \cdot PbO \cdot SiO_2$  base
- 0.003-0.1wt% Cu, Ag, Au-salts
- reducing agent:  $SnCl_2$ ,  $SnO$ ,  $Sb_2O_3$
- nucleating agent:  $CeO_2$

#### 1.2. Semiconducting particles

Color arises from absorption across the band gap (visible ranges from 3.35 eV to 1.61 eV):

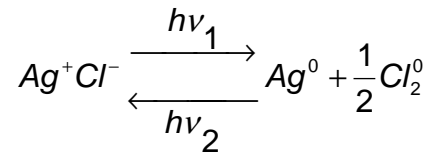
CdS	2.42 eV	yellow 'ruby'
CdSe	1.73 eV	red 'ruby'
ZnS	3.53 eV	UV cut-off filter

VG from 401 showing the phase separated particles and the absorption spectra of striking glasses

## 2. Photochromic Glasses

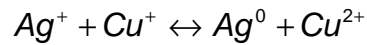
Reversible darkening; photographic film chemistry

- Ag-halides in borosilicate matrices



Where  $h\nu_1$  is generally an UV-photon, and  $h\nu_2$  is thermal energy.

- AgX particles (4 nm, colorless) are present in the glass after controlled heat treatments; phase separated and crystal nucleated material.
- Ag-metal particles form on irradiation at  $h\nu_1$ ; sensitizers are often added



- metal particles then Mie-scatter the light