

# Optical and Photonic Glasses

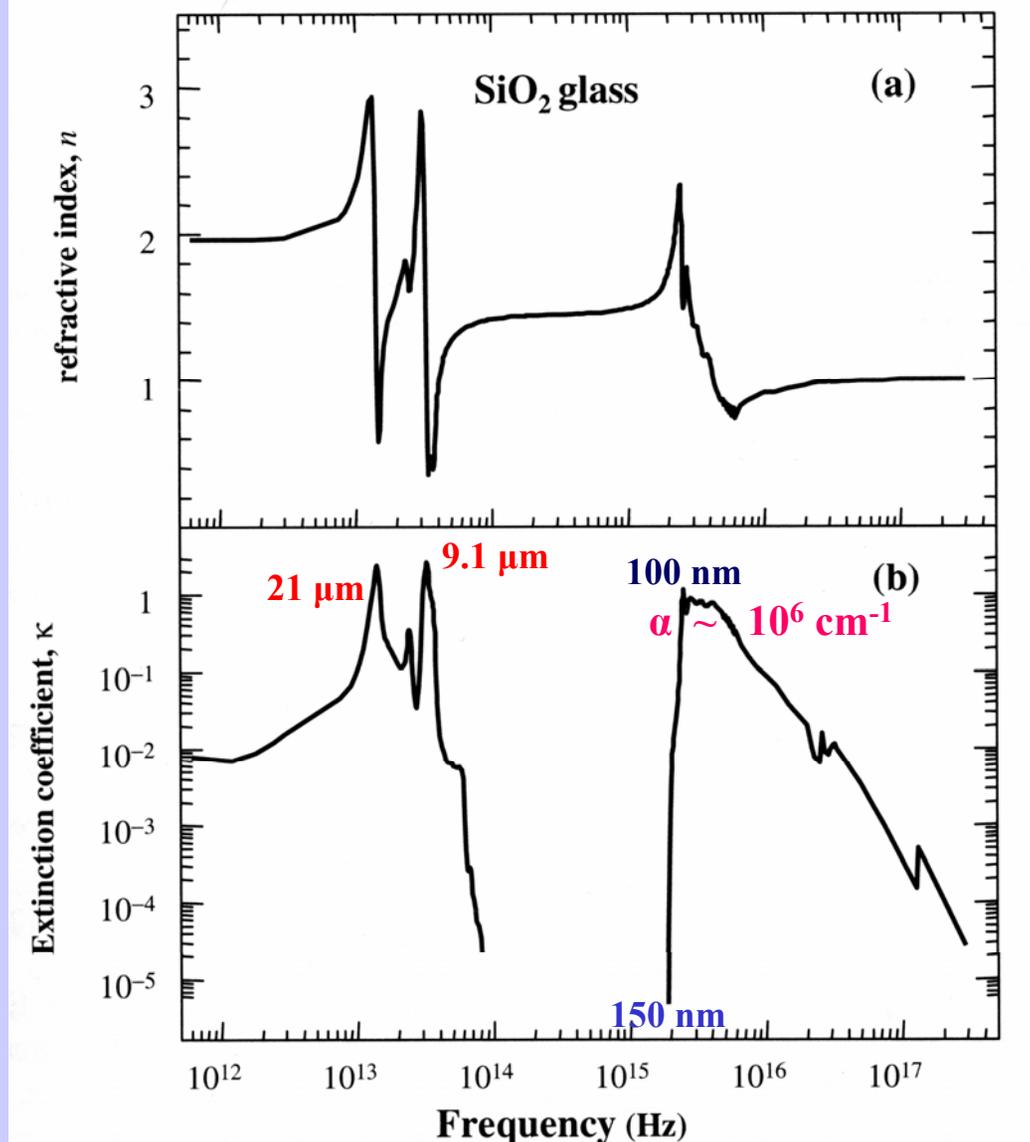
## Lecture 15:

# Optical Properties - Polarization, Absorption and Color

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**For New Functionality in Glass**  
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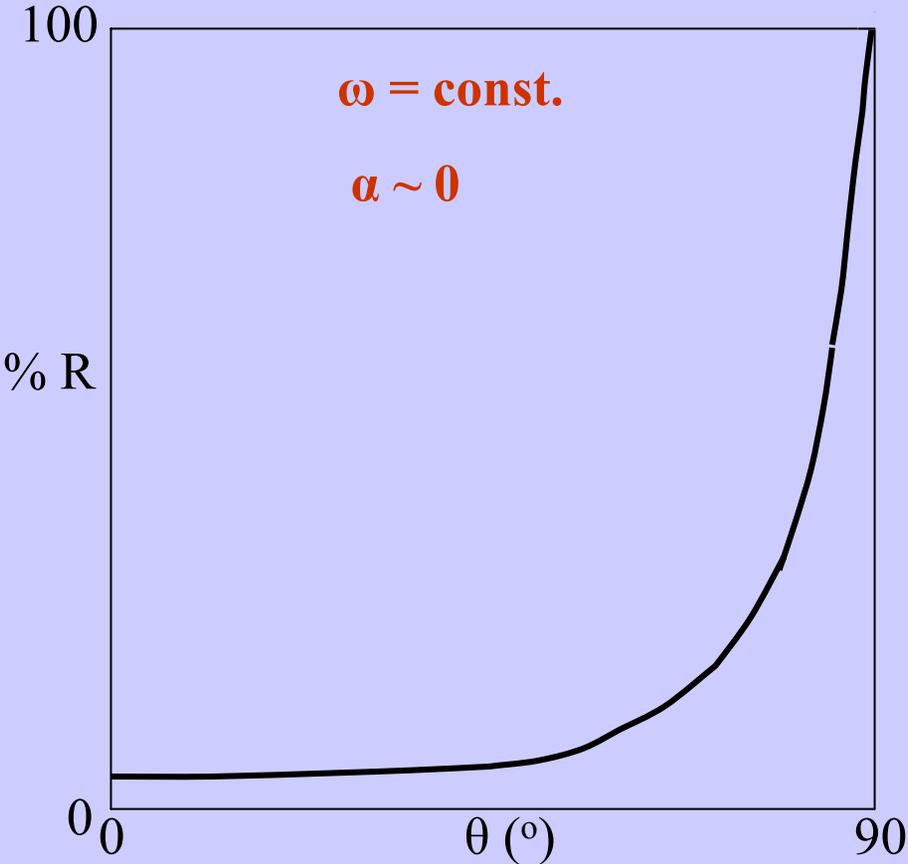




(a) Normal and anomalous dispersion; (b) absorption. From IR to X-ray region.

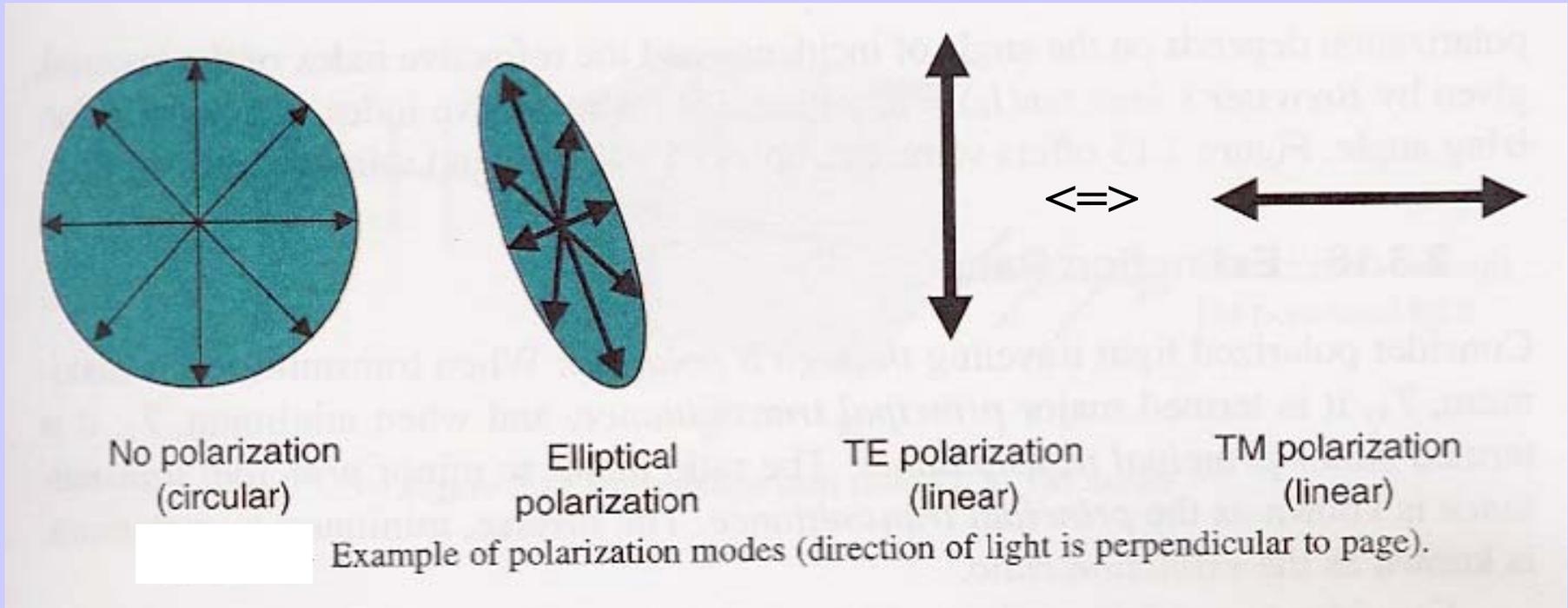
(Adapted from: *Optical Properties of Solids*, M. Fox, 2001)

For a common silicate glass at a visible frequency ( $n \sim 1.5$  and  $\alpha \sim 0$ ),  $R(\theta)$  will have the approximate shape shown below, for external reflection of light. Note that the effect of oblique incidence only becomes important for  $\theta$  higher than  $\sim 45^\circ$  and that external reflection is only total at grazing incidence.



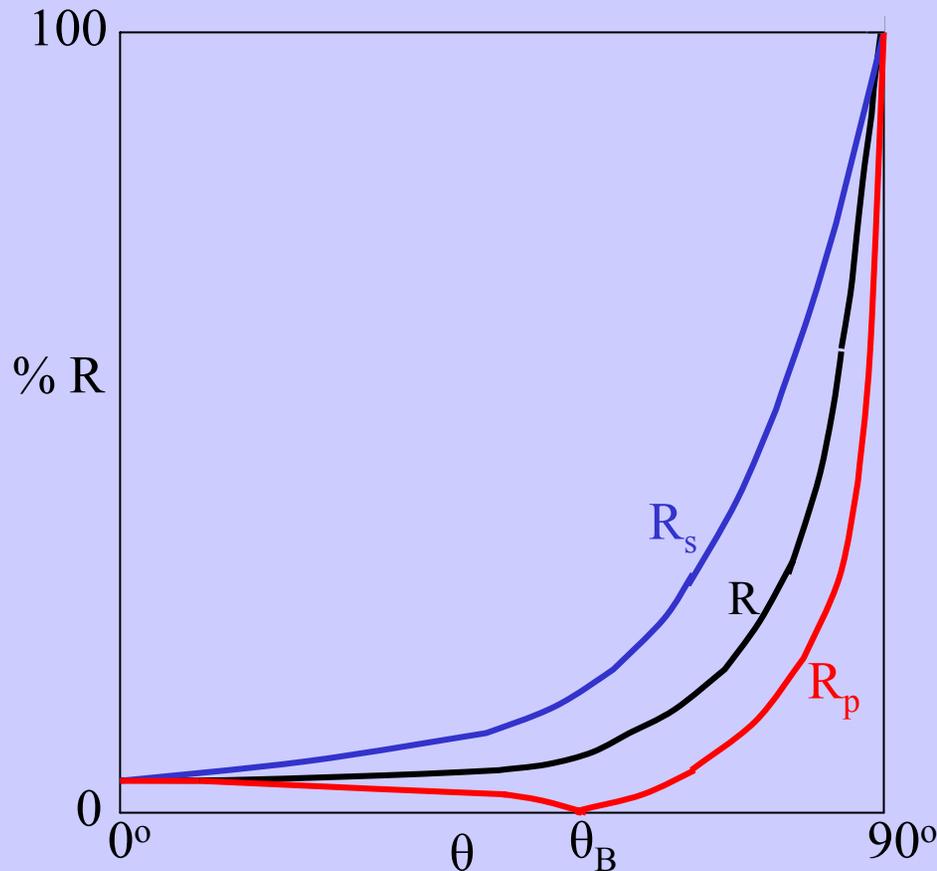
## Reflection with polarized light

For polarized light, the **electric vector** oscillates only in certain, well defined directions, whereas, in unpolarized light, the **E** vector (always perpendicular to the **H** vector) can oscillate in all possible directions with equal amplitude. When natural light impinges on a flat glass surface, its reflected components are linearly polarized and they are called: transverse electric (TE), or **s**, or  $\perp$ , if **E** is perpendicular to the reflection plane; transverse magnetic (TM), or **p**, or  $\parallel$ , when **E** is parallel to that plane.



(Adapted from: *Introduction to DWDM Technology*, S.V. Kartalopoulos, IEEE Press, 2000)

Natural (unpolarized) light can be resolved into two orthogonal components, polarized in perpendicular planes. Therefore, for *external* reflection, one has:

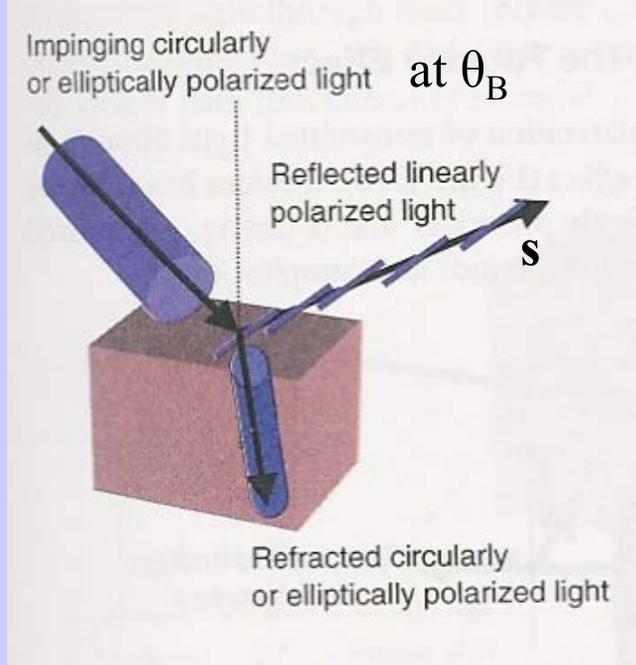


$$R = (R_s + R_p) / 2$$

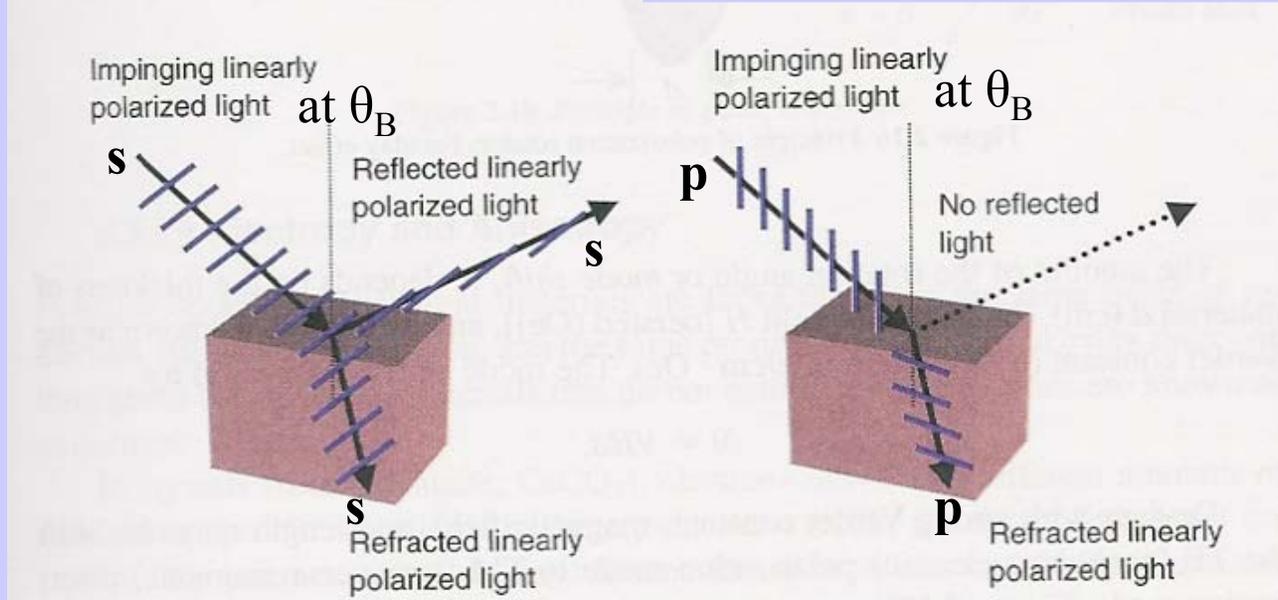
$$\text{Reflection: } R_s > R_p$$

$$\text{Refraction: } T_s < T_p$$

The Brewster angle,  $\theta_B$ , is the angle for which  $R_p$  becomes zero, defined by  $\tan \theta_B = n$ . For common glass ( $n \sim 1.5$ ), one has  $\theta_B \sim 56^\circ$ . Also, from Snell's law, it is possible to show that, when light is incident at the Brewster angle, the reflected and refracted light beams are perpendicular.



Polarization by reflection  
for  
light incident @  $\theta_B$



(Adapted from: *Introduction to DWDM Technology*, S.V. Kartalopoulos, IEEE Press, 2000)

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## Lecture 15:

### Part B – Absorption and Ligand Field Color

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# Absorption of light

## Electronic absorption in the UV and visible regions

While the phenomena of refraction, reflection, interference and polarization of light by a material can be described by Maxwell's classical electromagnetic theory, selective absorption and emission of radiation imply the use of quantum theory.

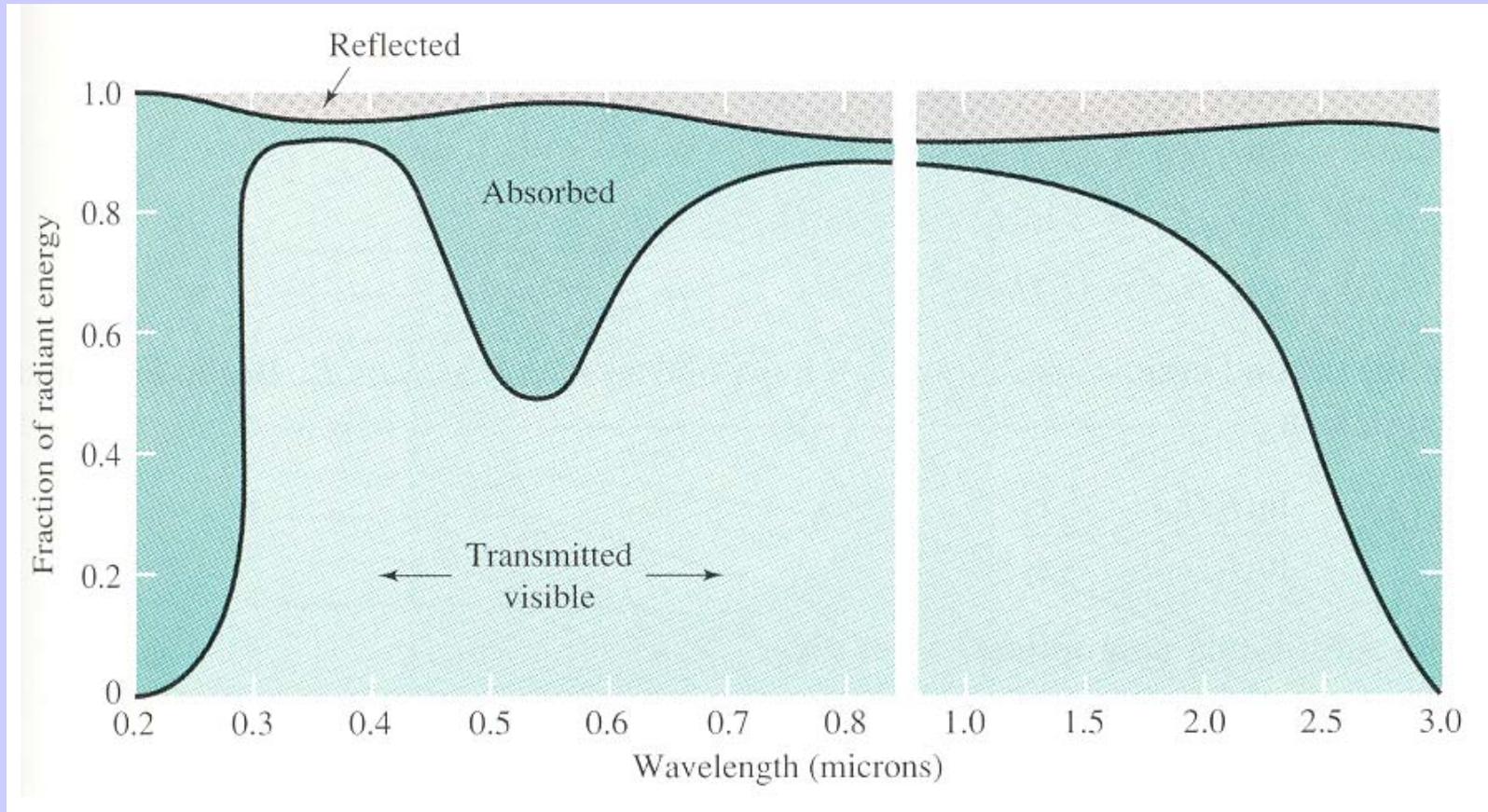
The onset of UV absorption (the Urbach edge) in a glass is due to electronic transitions between the valence and conduction band tails, across the bandgap ( $E_G$ ), corresponding to the wavelength threshold:

$$\lambda \leq h c_0 / E_G \iff \lambda \leq 1240 / E_G$$

when  $E_G$  is expressed in eV and  $\lambda$  in nm units.

For common window glass, e.g., this edge occurs in the near-UV and corresponds to the usual UV cut-off, but for other glasses, such as the chalcogenides, it may lie in the visible or even in the near-IR. For  $v\text{-SiO}_2$ , however,  $E_G \sim 8.9$  eV ( $\lambda \sim 140$  nm), making it an excellent optical glass window for the UV.

Example of the relationship between transmitted, absorbed and reflected light (in the absence of scattering, Kirchoff's law states that  $T + A + R = 1$ ), for the case of a silicate glass of blue color, due to the presence of  $\text{Co}^{2+}$  ions.

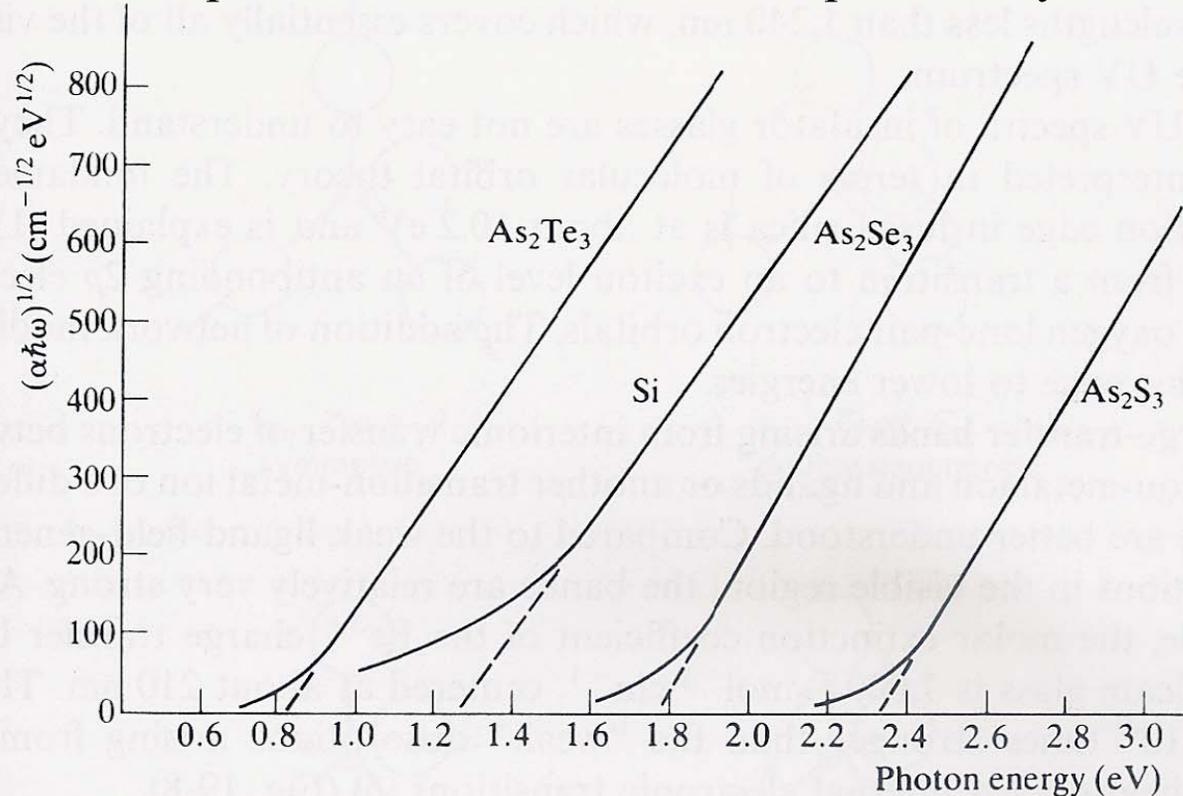


(Adapted from: *The science and design of engineering materials*, McGraw-Hill, 1999)

As-based chalcogenide glasses, e.g., are amorphous semiconductors whose *optical gap* ( $E_0$ ) may be obtained by extrapolation of the linearized form of the Tauc equation:

$$h\nu \alpha(\nu) = B (h\nu - E_0)^2 \quad (\text{for direct bandgap semiconductors})$$

In the Urbach tail, the absorption coefficient,  $\alpha$ , varies exponentially with the photon energy,  $h\nu$ .



Optical absorption edges of some materials. Extrapolation of the linear regime yields the “optical gap.” (After N. F. Mott and E. A. Davis, *Electronic Processes in Non-crystalline Materials*, 2nd Ed. Oxford University Press, 1979. Reproduced with permission of Oxford University Press.)

(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)

## Electronic absorption in the visible due to chromophores

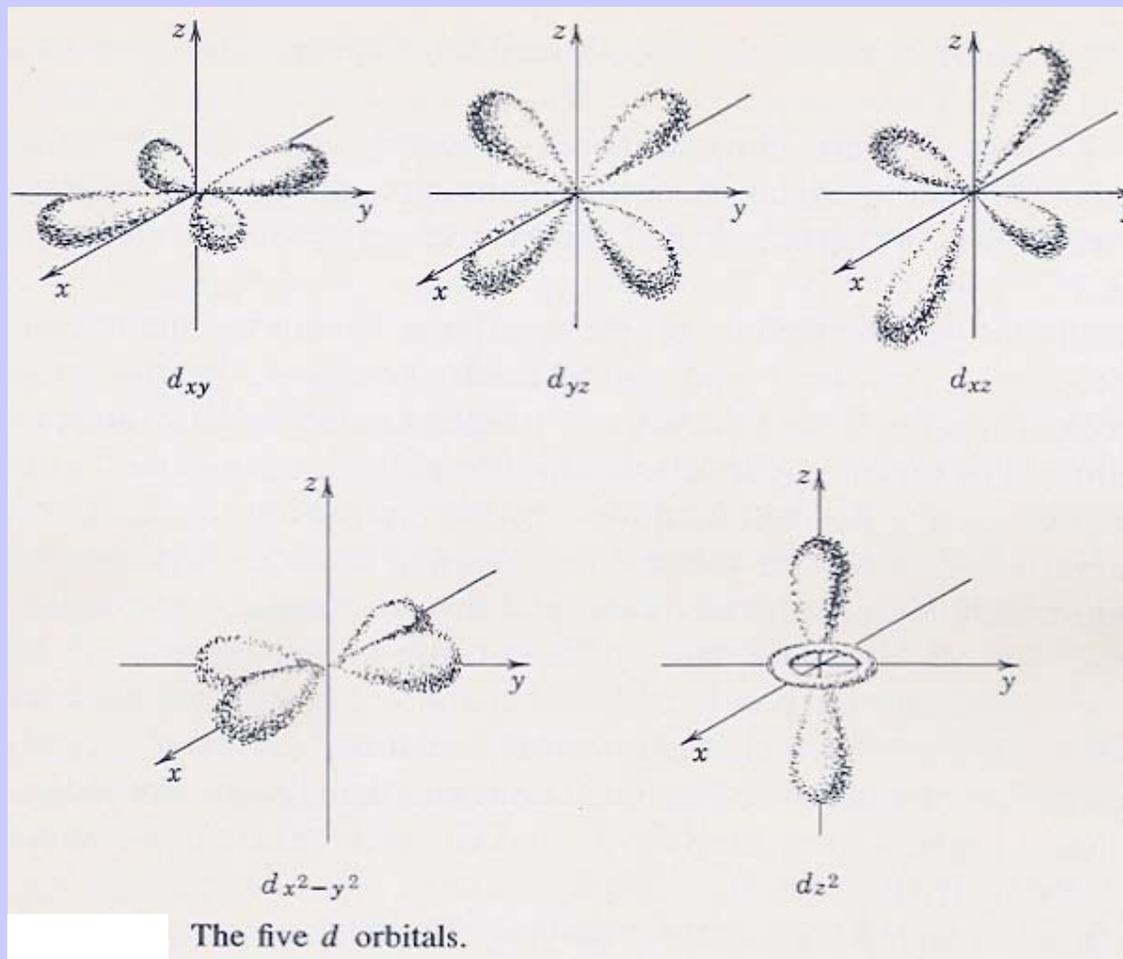
The *color* of glass is due, in most cases, to the presence of transition metal (TM) ions, with partly filled **d** shells, or rare-earth (RE) ions, with partly filled **f** shells, which introduce localized electronic energy levels within the gap of an otherwise colorless material (usually with  $E_G > 3.1$  eV, corresponding to the visible limit @  $\lambda \sim 400$  nm).

As colorants, however, RE ions do not allow a good control of the final color and are more expensive, when compared to the TM ions, which are normally used.

The color obtained is usually a function of:

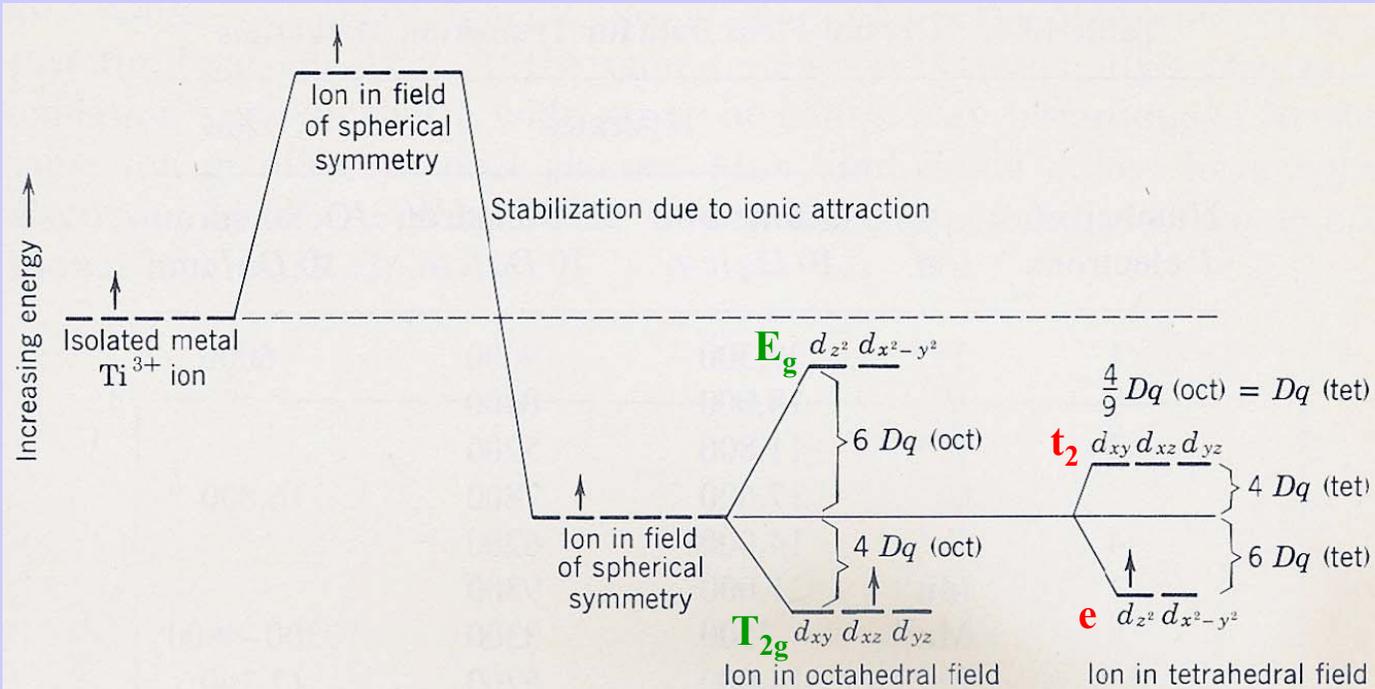
- the TM ion present (e.g.  $V^{4+}$ ,  $Cr^{3+}$ ,  $Mn^{2+}$ ,  $Fe^{3+}$ ,  $Co^{2+}$ , ...)
- its oxidation state (e.g.  $Fe^{2+}$  or  $Fe^{3+}$ )
- the type and number of *ligands* around it (e.g.  $O^{2-}$ ,  $S^{2-}$ ,  $Cl^-$ ,  $H_2O$ , ...)

The influence of the ligands on the d-levels of the transition metal ion is explained in the framework of the *ligand field* theory.



(Adapted from: *Introductio to ceramics*, W.D. Kingery et al., John Wiley, 1976)

For the  $d$  electrons to avoid the stronger ligand field regions of the TM ion nearest neighbor coordination, they preferentially occupy those orbitals whose spatial lobes are farther away from the ligand coordination positions, with a simultaneous energy splitting ( $\Delta$ ) of the five otherwise degenerate orbital energy levels.

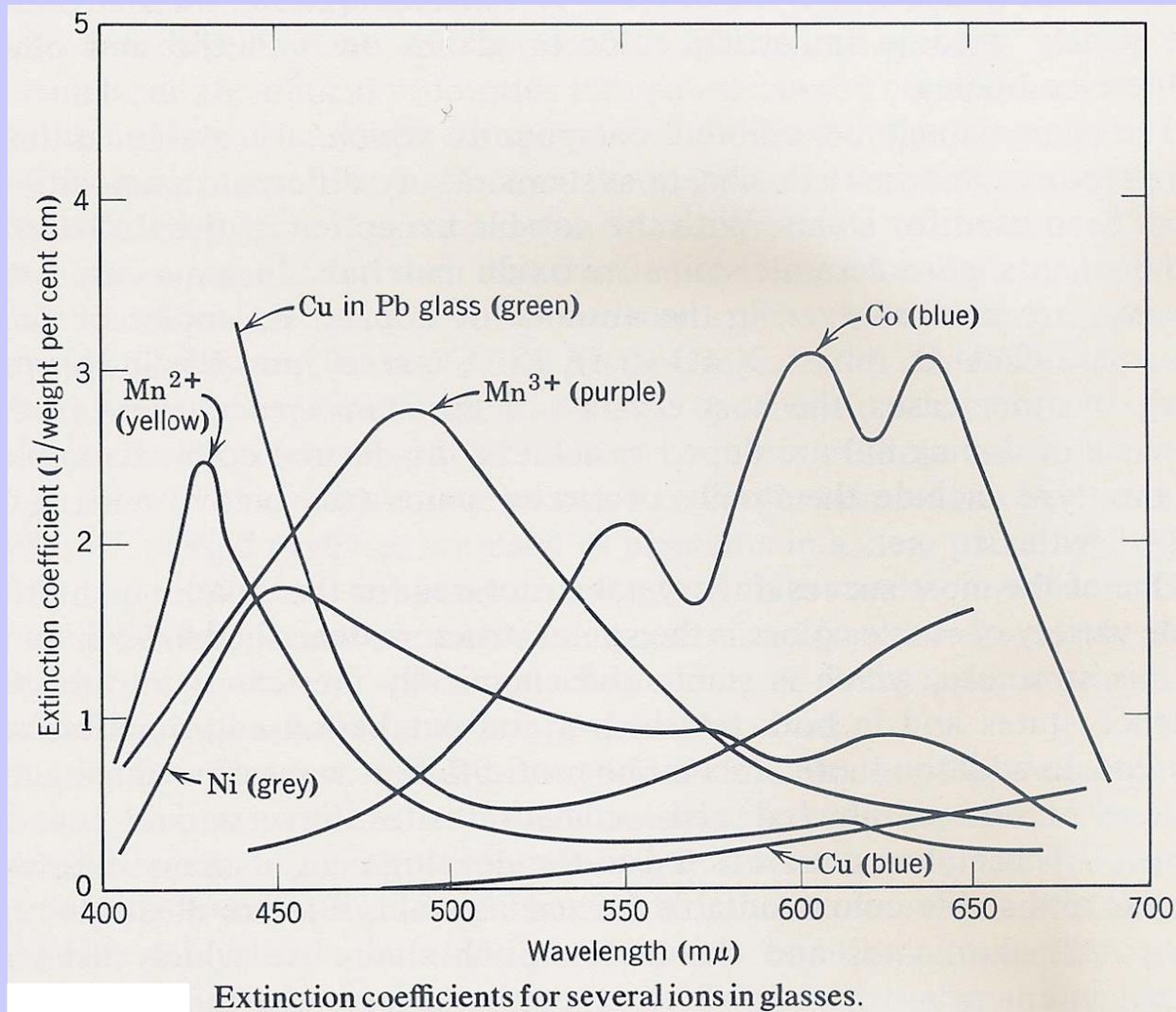


Crystal field energy relationships for  $Ti^{3+}$  ion in an octahedral and tetrahedral field.

(Adapted from: *Introduction to ceramics*, W.D. Kingery et al., John Wiley, 1976)

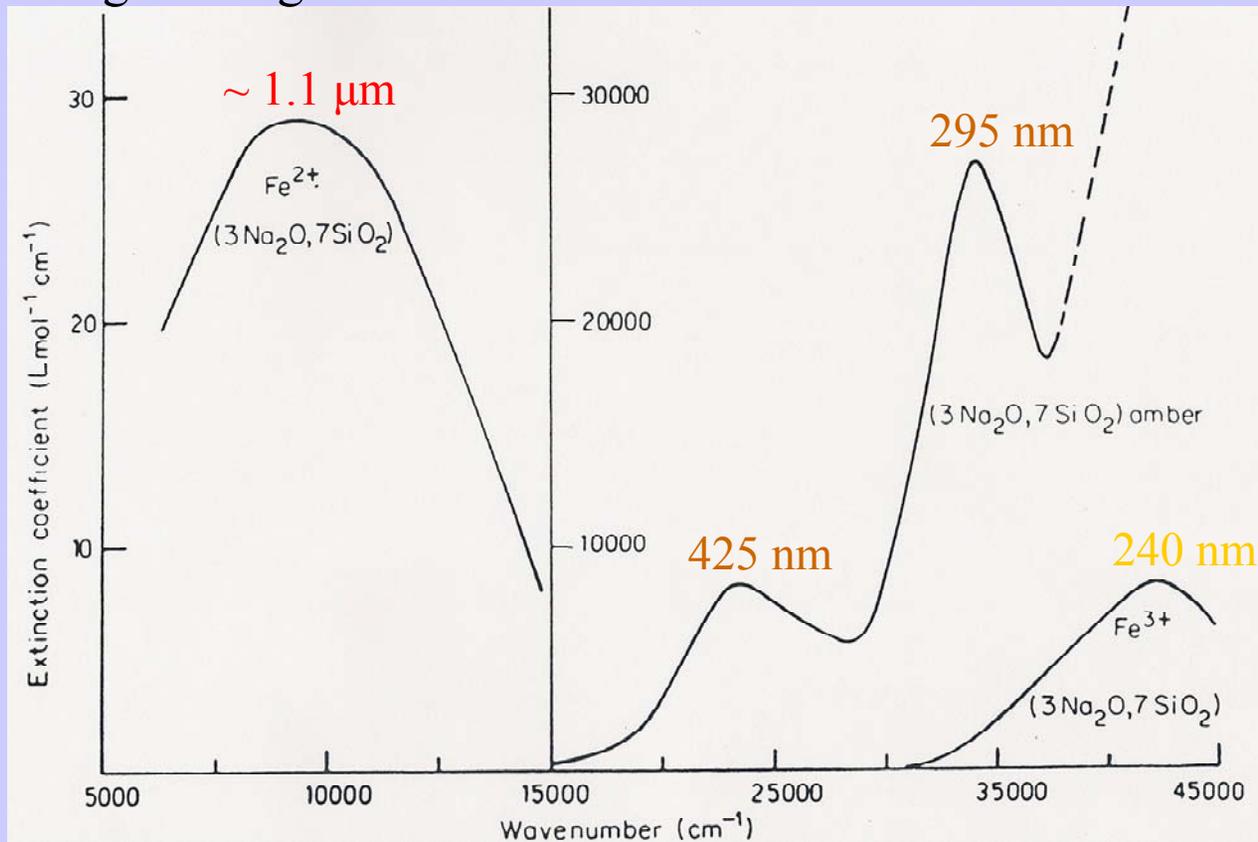
$Ti^{3+}$  has one 3d electron only. The values of  $\Delta_{\text{oct}}$  or  $\Delta_{\text{tet}}$ , usually represented as  $10 Dq$  and larger in the octahedral case, are of the order of 1-2 eV for most TM ions. (Note that the visible region lies between  $\sim 1.8$ -3.1 eV). Therefore, an electronic transition between the  $T_{2g}$  and the  $E_g$  levels (in the octahedral case), or between the  $e$  and  $t_2$  levels (tetrahedral case), for a  $Ti^{3+}$ -containing glass, causes light absorption in the visible and makes the glass colored. For ions with more than one d electron, one has to consider the relationship between the electron coupling energy and  $\Delta$ . (E.g., high field ligands form coordinated complex ions of low spin and vice-versa).

Examples of different colorations in glass due to selective absorption by TM ions:



(Adapted from: *Introduction to ceramics*, W.D. Kingery, John Wiley, 1976)

E.g., octahedrally coordinated  $\text{Fe}^{2+}$  in silicate glass has a weak absorption band near  $1.1 \mu\text{m}$ , which extends into the red and is the source of bluish-green color in many glass products.  $\text{Fe}^{3+}$ , on the other hand, has a very strong charge transfer band near  $240 \text{ nm}$ , which extends into the visible (blue absorption) and gives the glass a yellowish coloration. Since these two colors are  $\sim$  complementary, a proper  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio may lead to decolorizing of the glass.



Absorption spectra of  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , and “carbon-sulfur amber.” (After Paul [7], Fig. 9.31, p. 330. Reproduced with permission of Chapman & Hall.)

(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, John Wiley, 1976)

The **amber** color of beer bottles, e.g., is obtained from  $\text{Fe}_2\text{O}_3$  plus  $\text{Na}_2\text{SO}_4$  and is due to two intense charge transfer bands at 295 nm and 425 nm. The *chromophore* in this case is believed to be a complex consisting of an octahedrally coordinated  $\text{Fe}^{2+}$  ion, a tetrahedrally coordinated  $\text{Fe}^{3+}$  ion with one of the oxygens replaced by a  $\text{S}^{2-}$  ion and a  $\text{SO}_4^{2-}$  group.

**Charge transfer** bands usually occur at higher frequencies, compared to the intra-cation transitions between ligand field-split levels and they may take place between cations (e.g., cation-to-cation charge transfer between  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ ), from a cation to an anion ligand, or from an anion ligand to a cation.