Optical and Photonic Glasses

Lecture 18:

Rayleigh and Mie Scattering, Colloidal Metals and Photo-elastic Properties

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Colloration due to scattering

Scattering can also cause a glass to become colored. E.g., if a cube of glass containing small particles is traversed by a beam of white light, it may look bluish when viewed from the side, but the light emerging in the beam direction will be reddish, because blue is more strongly scattered than red.

Rayleigh showed that fluctuations of the refractive index cause scattering, designated as *Rayleigh scattering*. If a beam of unpolarized light, I_o, is scattered only once by a spherical (as well as insulating and non-absorbing) particle of diameter $< \lambda/10$, the scattered intensity measured at a distance d from the particle may be expressed as:

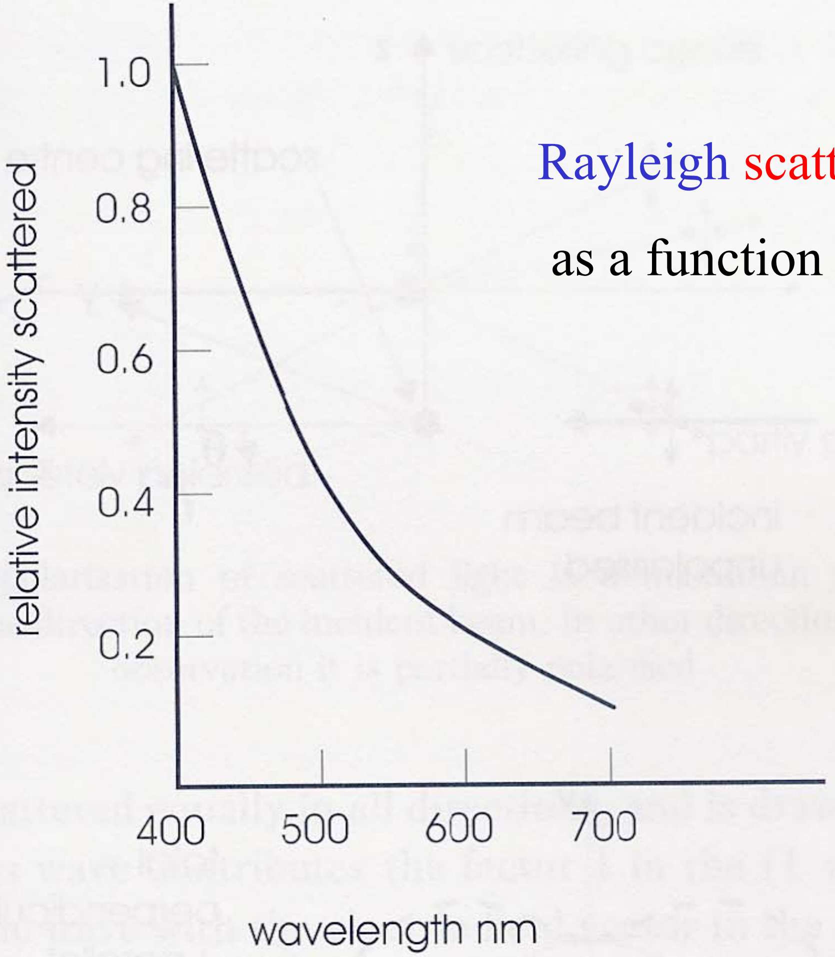
$$I_s = I_o\,(9\pi^2 V^2 / 2d^2\lambda^4)\,[(m^2-1)(m^2+2)]^2\,(1+\cos^2\theta)$$

where V is the particle volume, θ is the angle between the incident and scattered beams and m is the refractive ratio between the particle and the surrounding matrix.

Obviously, shorter wavelengths are much more strongly scattered than the longer ones and this is the reason for the blue color of the sky. Scattering by the molecules of a gas also allowed an estimate of Avogadro's number, N_o.

Rayleigh scattering

as a function of λ

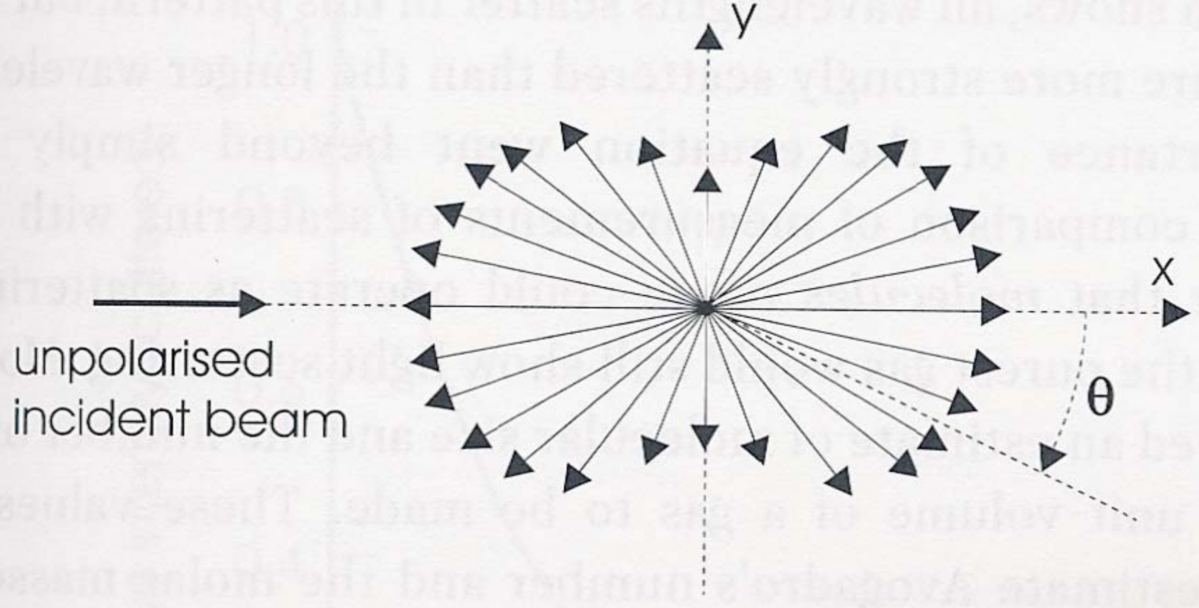


Rayleigh scattering of visible light as a function of wavelength. This is proportional to $1/\lambda^4$, and so violet light is scattered about eight to ten times more than red light

(Adapted from: *Colour and the optical properties of materials*, R. Tilley, John Wiley, 2000)

Rayleigh scattering pattern

Just as much light is scattered backwards as forwards and only half as much intensity is scattered normal to the beam direction. *Rayleigh scattering* also produces strongly polarized light. This is completely p-polarized in the direction perpendicular to the incident beam and partly polarized in all other directions, with the exception of the forward and backward directions, for which the scattered light is unpolarized, just like the incident light beam. In the term $(1+\cos^2\theta)$, 1 corresponds to p-scattered light and $\cos^2\theta$ to the s-scattered component.



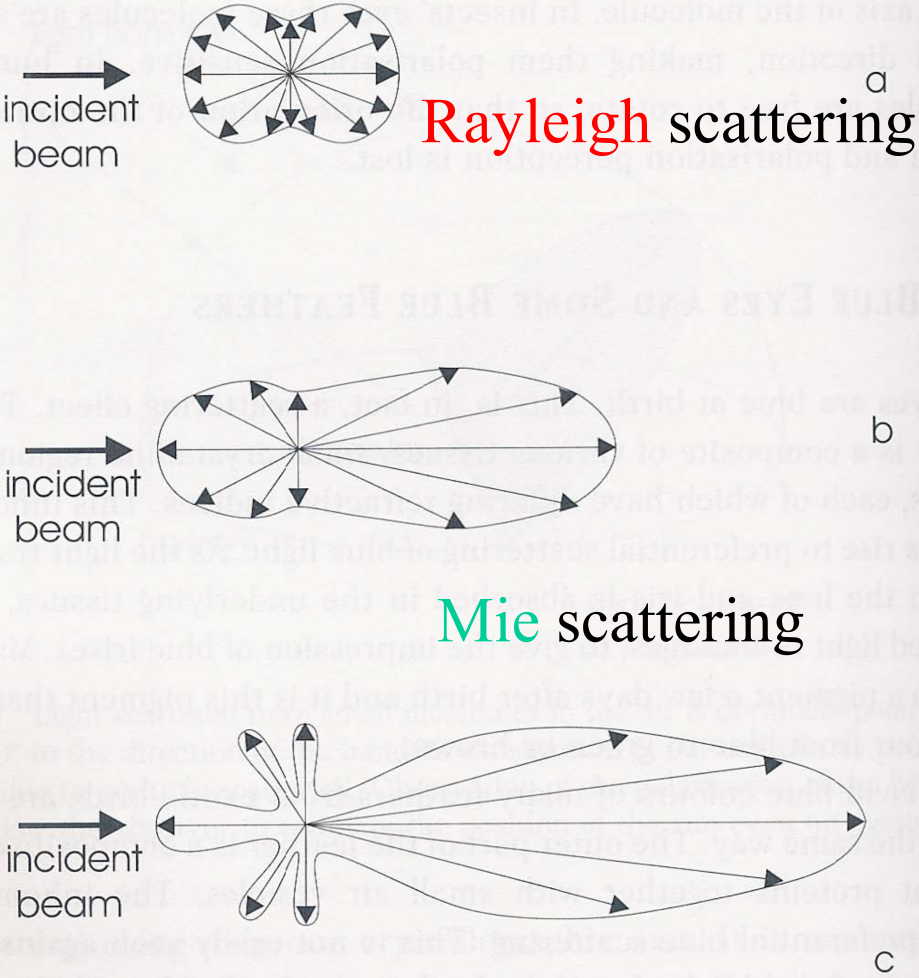
The Rayleigh scattering pattern of unpolarised light from small particles. The lengths of the arrows diverging from the small scattering centre can each be thought of as defining the scattered intensity at a distance d and at an angle θ to the forward direction

(Adapted from: *Colour and the optical properties of materials*, R. Tilley, John Wiley, 2000)

Mie scattering generally refers to scattering by larger particles, with a diameter $\geq \lambda/3$. The scattered intensity becomes proportional to $\sim \lambda^{-2}$. As the particle size increases relatively to λ, the scattering pattern gradually changes from the symmetrical Rayleigh pattern, to a highly asymmetric one, with forward scattering becoming dominant.

When the particle size becomes $>> \lambda$, one has *Tyndall scattering*, which becomes λ-independent and light is then reflected by the large particles evenly in all directions, rather than scattered unevenly.

Scattering patterns



Rayleigh scattering

Mie scattering

Schematic illustration of the patterns of intensity scattered by small particles. (a) Rayleigh scattering from particles much smaller than the wavelength of light. (b) For particles approaching the wavelength of light the scattering becomes pronounced in the forward direction. (c) For particles larger than the wavelength of light lobes of intensity appear which are wavelength dependent and so give rise to colours at specific viewing angles. These are called higher order Tyndall spectra

(Adapted from: *Colour and the optical properties of materials*, R. Tilley, John Wiley, 2000)

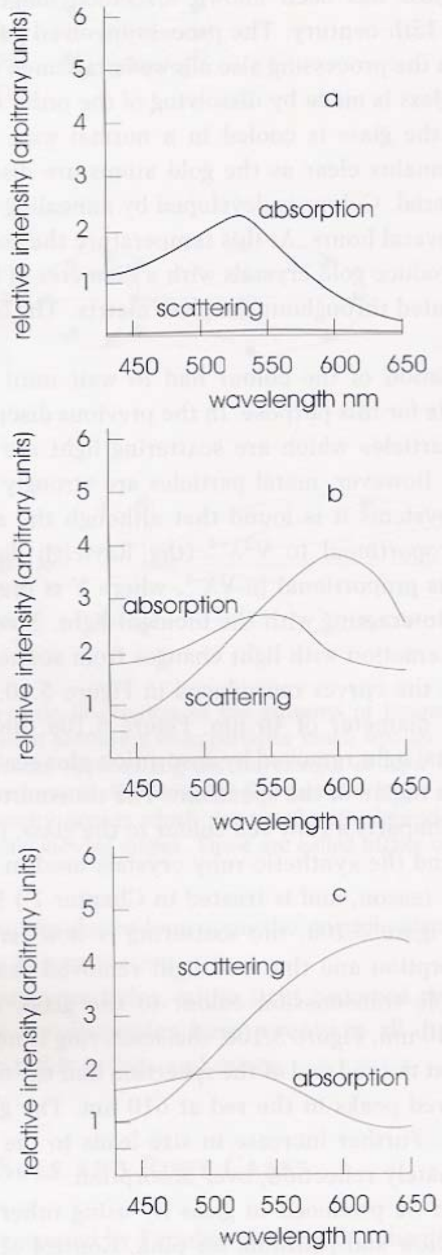
Scattering vs. absorption in glasses with small metal particles

The so-called "ruby glass" owes its red color to the presence of small **gold** particles (as opposed to natural or synthetic ruby crystals, where the red color is due to strong green light absorption by substitutional Cr^{3+} impurities or dopant ions), whereas **silver** and **platinum** yield yellow and pink colors, respectively, for specific particle size ranges.

Although "ruby glass" has been produced since the 15th century, the explanation was only given by Mie in 1908. The previous discussion of Rayleigh scattering assumed insulating, non-absorbing particles. Metal particles, however, are strongly absorbing. For these, although the amount of *scattered* light is still proportional to V^2/λ^4 (the Rayleigh dependence), the amount of *absorbed* light is roughly proportional to V/λ. So, as the volume of the particles, V, becomes smaller, the dominant interaction with the incident light changes from scattering to absorption.

Gold colloids in "ruby glass" are formed by dissolving ~ 0.01% Au in molten soda-lime-silica or borosilicate glass, which is quickly cooled to a clear, colorless glass, since the high temperature solubility of Au **atoms** in the melt is frozen into the glass. However, by reheating the glass to ~ 650 °C for several hours, the lower, equilibrium solubility of Au at this temperature is reached and the atoms aggregate to form colloidal Au crystals with diameters ~ 10-140 nm. The actual colors produced will depend on the Au particle sizes.

Scattering versus absorption for Au particles



Schematic illustration of the way in which scattering and absorption change with radius for spherical gold particles: (a) diameter 40 nm; (b) diameter 100 nm; (c) diameter 140 nm. The intensity scale is in arbitrary units

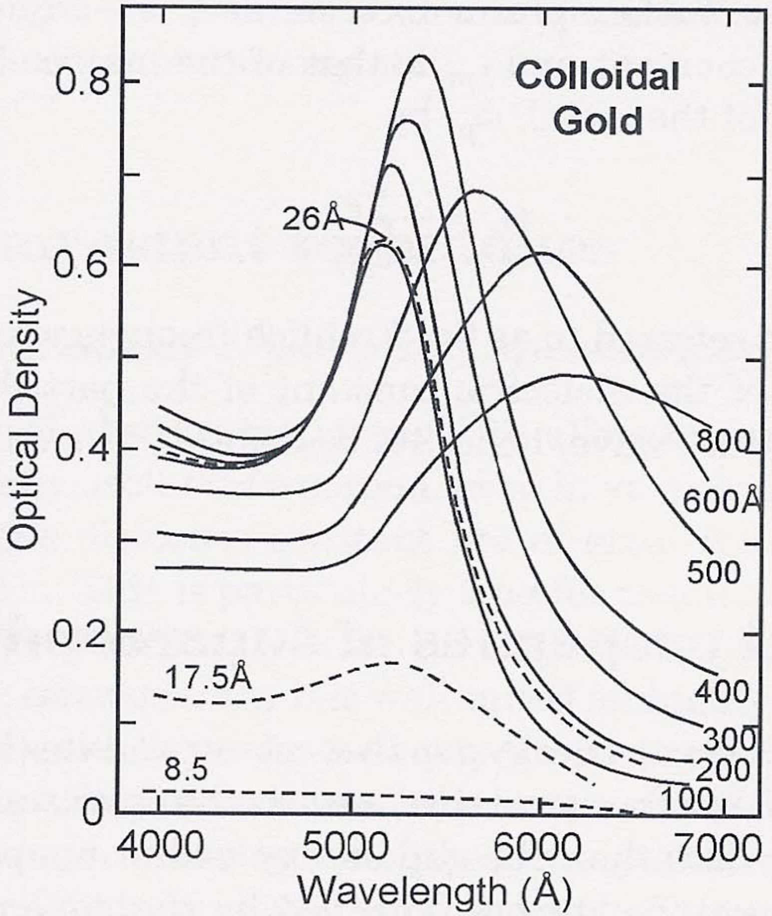
For 40 nm dia. spherical Au particles, green **absorption** dominates and the complementary red ("ruby") color is transmitted.

For 100 nm particles, absorption and scattering are comparable, with non-transmitted light peaking at 580 nm (orange) and the transmitted light giving a purple color to the glass.

For crystallite sizes of 140 nm, **scattering** dominates and peaks in the red, with the non-transmitted light peaking at 610 nm and the transmitted light giving the glass a blue color. (Further increase in size will eventually lead to **reflection** becoming predominant and to the yellow color of bulk gold metal).

(Adapted from: *Color and the optical properties of materials*, R. Tilley, John Wiley, 2000)

Light absorption by colloidal nanoparticles is due to a *surface plasmon resonance* within the bound electron *plasma* oscillations (surface waves). For Au colloids larger than ~ 10 nm (or 100 angstrom, below), the peak red-shifts and broadens, as scattering becomes increasingly dominant over absorption.



Optical absorption of glasses containing gold colloids of different sizes (from Doremus 1964).

(Adapted from: *Optical Materials*, J.H. Simmons and K.S. Potter, Academic Press, 2000)

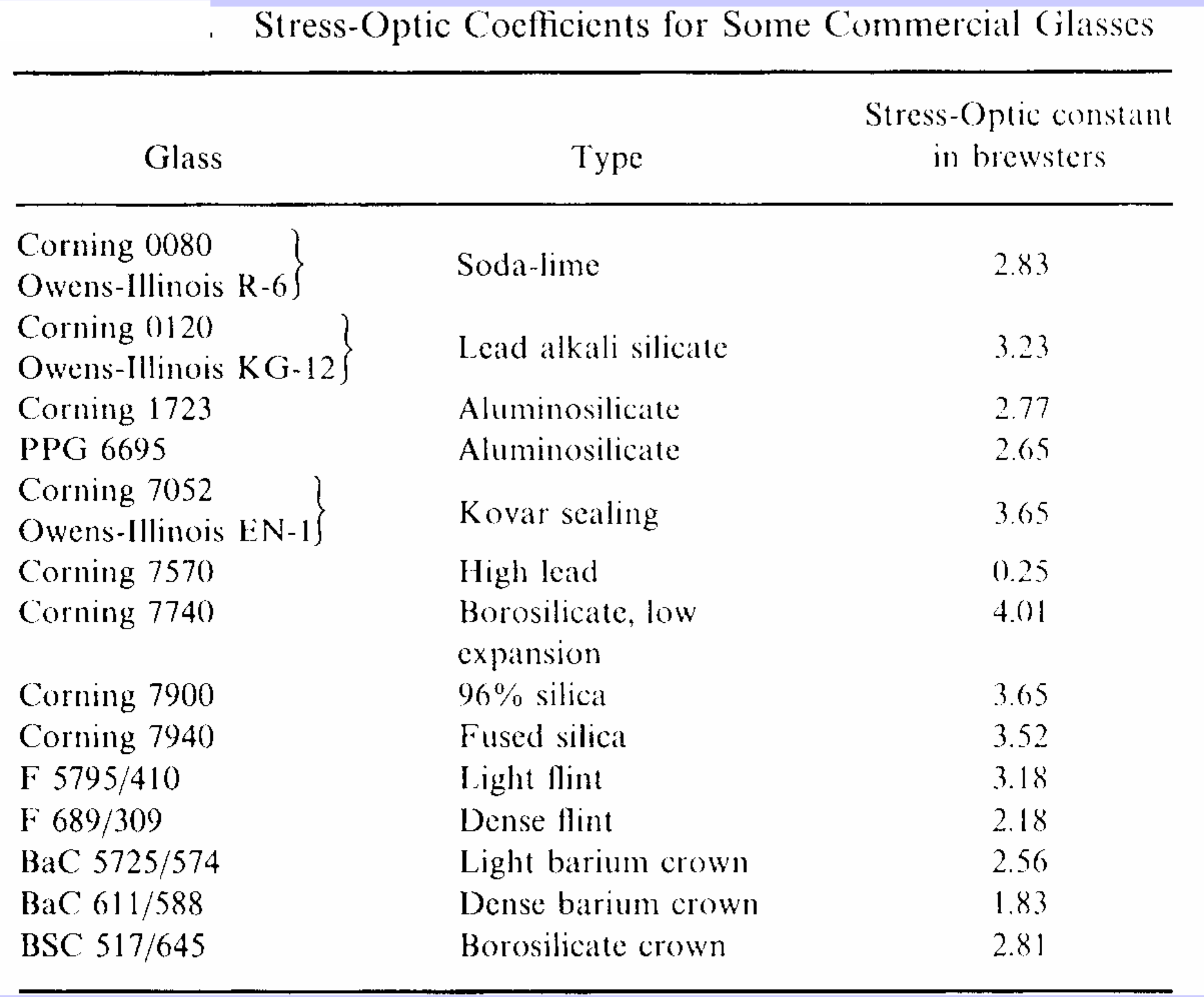
Photoelastic properties of glass

Well annealed glass is homogeneous and isotropic. However, in glasses with residual stresses, the s- and p-components of unpolarized (natural) light will travel at different speeds, corresponding to a birefringence, Δn, equal to the difference between the *principal indices* of the "ordinary" and "extraordinary" rays (n_e-n_o). This birefringence, positive for most glasses under tension, is a function of the residual stress, σ:

$$\Delta n = C\,\sigma$$

where C is the photoelastic (or stress-optic, Pockel's) coefficient. For example, if C = $3\mathrm{x}10^{-12}$ Pa^{-1} for a typical silicate glass and $\sigma = 1$ MPa, then $\Delta n = 3 \times 10^{-6}$. (Note that C is also sometimes called Brewster's constant and 10^{-12} Pa^{-1} = 1 brewster). For high lead, HMFG and ChG, C ~ 0 and sometimes even negative (negative birefringence).

The photoelastic effect is the basis for determining residual stresses in glasses. If linearly polarized light is allowed to impinge on a glass piece with residual stresses, then a rotating polarization analyzer is used as a birefringence compensator and the optical retardation (or optical path difference between the ordinary and extraordinary rays) is thus measured. The observation of interference fringes between the two rays also allows an easy visual determination of the presence of residual stresses in a glass object.



Stress-Optic Coefficients for Some Commercial Glasses

Glass	Type	Stress-Optic constant in brewsters
Corning 0080	Soda-lime	2.83
Owens-Illinois R-6		
Corning 0120	Lead alkali silicate	3.23
Owens-Illinois KG-12		
Corning 1723	Aluminosilicate	2.77
PPG 6695	Aluminosilicate	2.65
Corning 7052	Kovar sealing	3.65
Owens-Illinois EN-1		
Corning 7570	High lead	0.25
Corning 7740	Borosilicate, low expansion	4.01
Corning 7900	96% silica	3.65
Corning 7940	Fused silica	3.52
F 5795/410	Light flint	3.18
F 689/309	Dense flint	2.18
BaC 5725/574	Light barium crown	2.56
BaC 611/588	Dense barium crown	1.83
BSC 517/645	Borosilicate crown	2.81

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

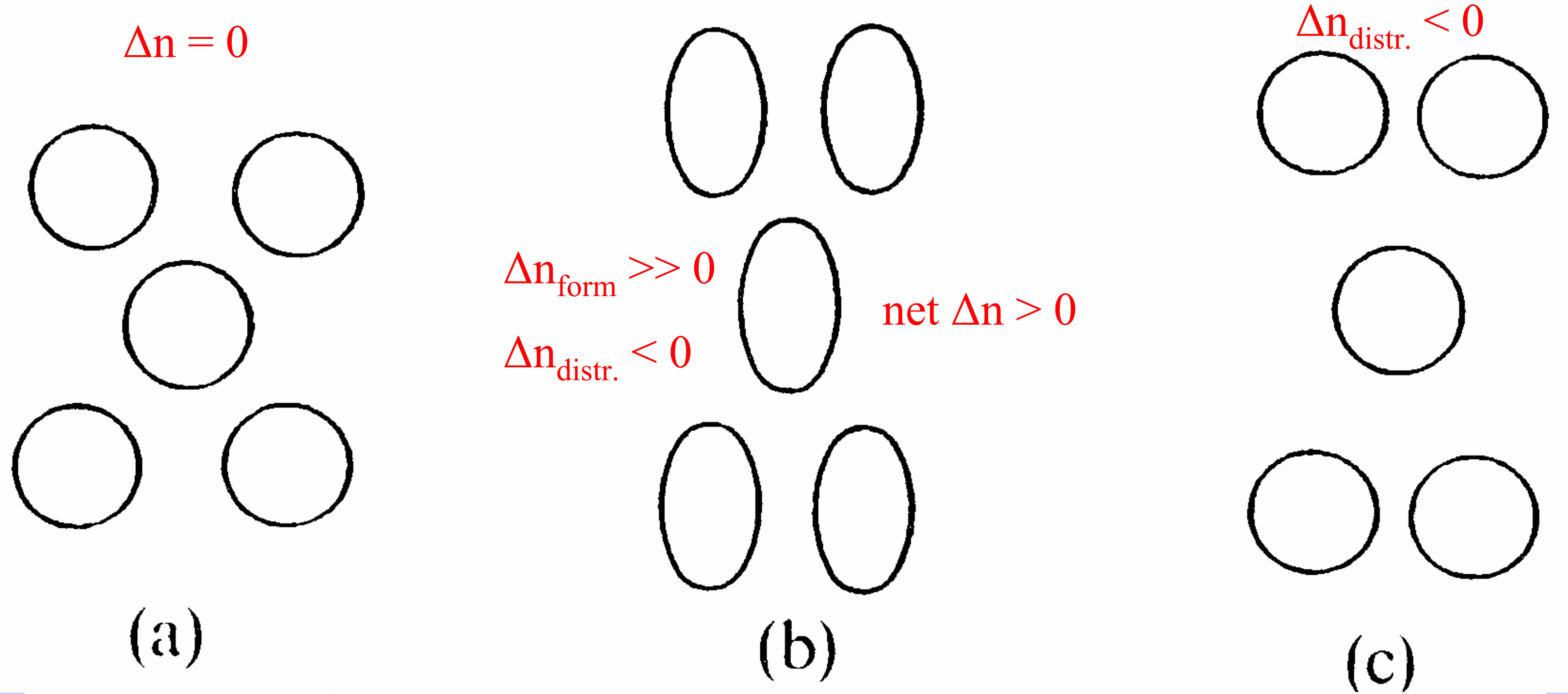
Anomalous birefringence

This is the birefringence (or double refraction) observed in *phase separated* glasses, even in the absence of any internal or external stress.

Particularly in those glasses which exhibit droplet-like phase separation, the presence of non-spherical droplets gives rise to **form birefringence**, whereas an anisotropic spatial distribution of the particles will give rise, in addition, to **distribution birefringence**.

A borosilicate glass was given a phase separation treatment, leading to the precipitation of borate-rich particles in a continuous, silica-rich matrix.

unstretched | stretched @ $\eta \sim 10^9$-10^8 Pa.s | post annealed



$\Delta n = 0$

$\Delta n_{form} >> 0$

$\Delta n_{distr.} < 0$

net $\Delta n > 0$

$\Delta n_{distr.} < 0$

Schematic representation of microstructures. (a) The unstretched specimen is isotropic. (Note: The body-centered cubic arrangement shown is merely incidental.) (b) After stretching, the form as well as the distribution become anisotropic. (c) After a post-pulling annealing treatment, the particles spheroidize; however, the distribution remains anisotropic.

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

New optical glasses

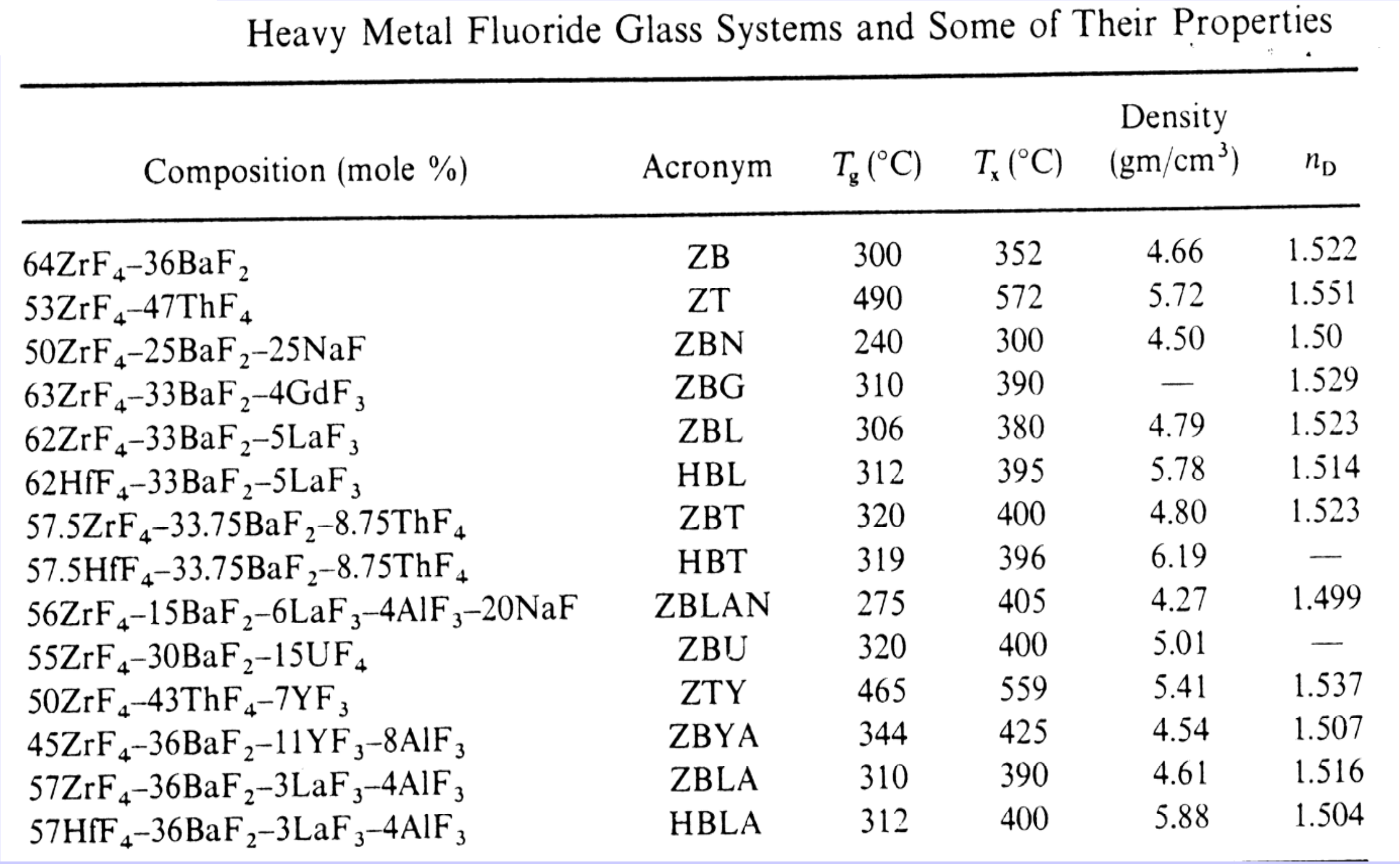
Glasses like the halides (namely **fluorides,** like the HMFG) or the **chalcogenide** glasses (ChG) have very interesting optical properties, namely an extended IR transmission and a large solubility for RE elements (Nd, Pr, Er, …), which, coupled with the characteristic low vibrational frequencies responsible for the extended IR transmission, lead to important photonic applications to be considered in the third part of the course.

In this second part of the course, we will be concerned mostly with the IR properties of such glasses.

While oxide glasses have intermediate ionic character (of the order of ~ 50%), fluoride and chalcogenide glasses are on opposite sides with respect to ionicity. While HMFG are highly ionic in character (e.g. of the order of ≥ 80%), thus having large cation CN, ChG are generally quite covalent, with only ~ 4 - 5 % ionicity in most cases, having therefore small cation CN.

One of the consequences of this is the **extent of the glass-forming regions**, which tends to be **large for ChG**, but **small for** most halide glasses, namely the **HMFG**.

HMFG compositions

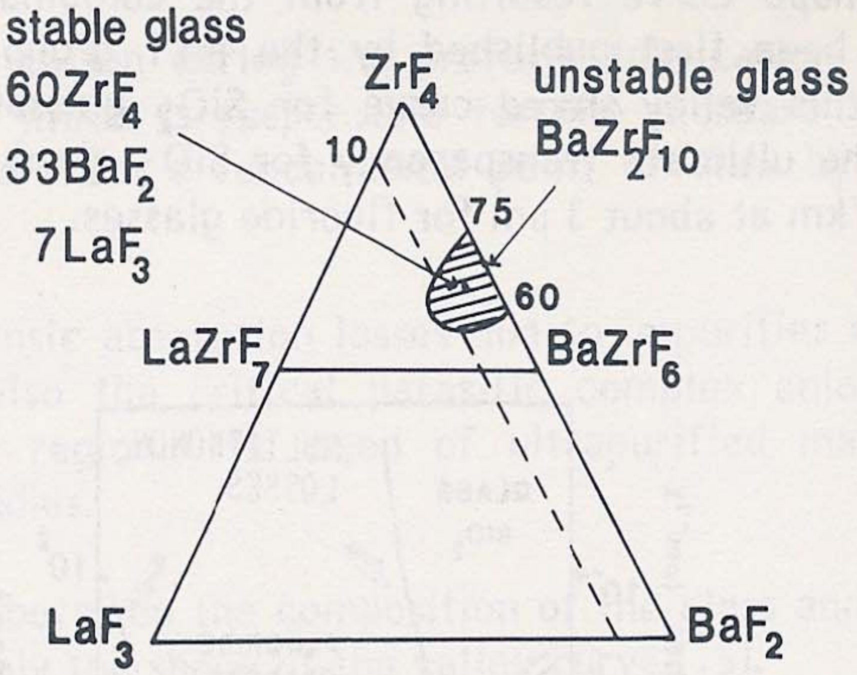


Heavy Metal Fluoride Glass Systems and Some of Their Properties

Composition (mole %)	Acronym	T_g (°C)	T_x (°C)	Density (gm/cm^3)	n_D
$64ZrF_4$–$36BaF_2$	ZB	300	352	4.66	1.522
$53ZrF_4$–$47ThF_4$	ZT	490	572	5.72	1.551
$50ZrF_4$–$25BaF_2$–$25NaF$	ZBN	240	300	4.50	1.50
$63ZrF_4$–$33BaF_2$–$4GdF_3$	ZBG	310	390	—	1.529
$62ZrF_4$–$33BaF_2$–$5LaF_3$	ZBL	306	380	4.79	1.523
$62HfF_4$–$33BaF_2$–$5LaF_3$	HBL	312	395	5.78	1.514
$57.5ZrF_4$–$33.75BaF_2$–$8.75ThF_4$	ZBT	320	400	4.80	1.523
$57.5HfF_4$–$33.75BaF_2$–$8.75ThF_4$	HBT	319	396	6.19	—
$56ZrF_4$–$15BaF_2$–$6LaF_3$–$4AlF_3$–$20NaF$	ZBLAN	275	405	4.27	1.499
$55ZrF_4$–$30BaF_2$–$15UF_4$	ZBU	320	400	5.01	—
$50ZrF_4$–$43ThF_4$–$7YF_3$	ZTY	465	559	5.41	1.537
$45ZrF_4$–$36BaF_2$–$11YF_3$–$8AlF_3$	ZBYA	344	425	4.54	1.507
$57ZrF_4$–$36BaF_2$–$3LaF_3$–$4AlF_3$	ZBLA	310	390	4.61	1.516
$57HfF_4$–$36BaF_2$–$3LaF_3$–$4AlF_3$	HBLA	312	400	5.88	1.504

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

Typical HMFG glass-forming region

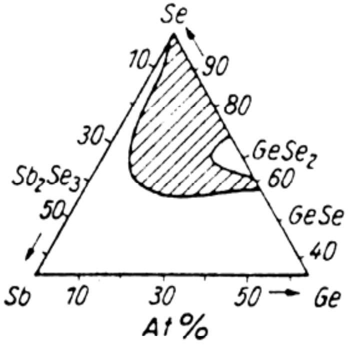


One of the first diagrams where fluorozirconate glasses have been isolated
The binary glasses BaF_2/ZrF_4 are of interest for structural investigations.

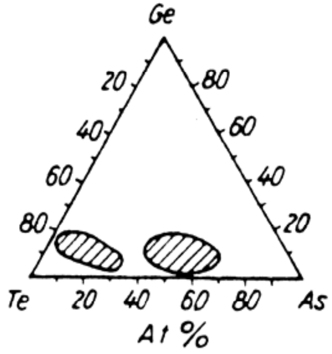
(Adapted from: *J. Lucas, in: Halide Glasses for Infrared Fiberoptics*, ed. R.M. Almeida, Martinus Nijhoff, 1987)

ChG glass-forming regions

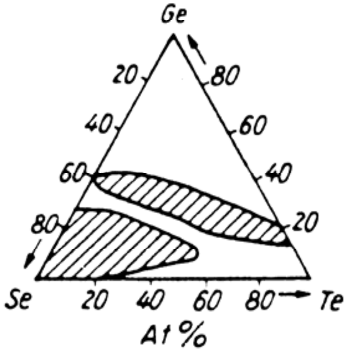
Ge–Sb–Se



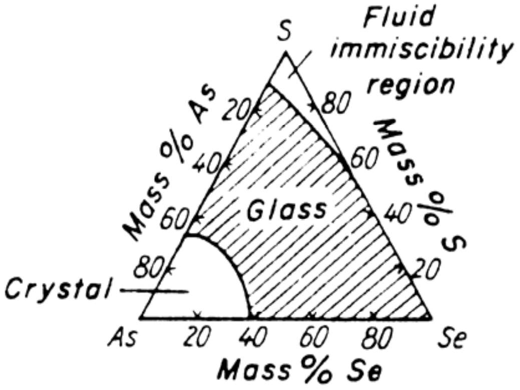
Ge–As–Te



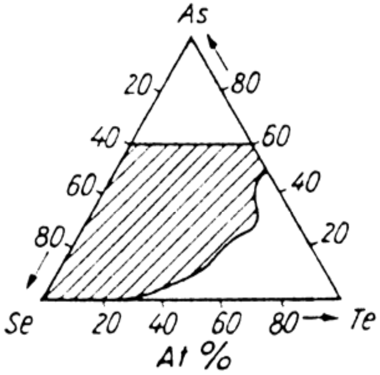
Ge–Se–Te



As–S–Se



As–Se–Te



Glass formation region shown shaded in the Ge-Sb/As-S/Te ternary diagrams. (From W. Vogel, *Chemistry of Glass*, pp. 184–190. Amer. Ceram. Soc., 1985. Reproduced with permission of the publisher.)

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