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Refractive index of glass and its dispersion for visible light

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Abstract. The classification of optical glass and empirical relations between the refractive index and its dispersion are discussed in terms of moments of the glass's IR and UV absorption spectra. The observed linear dependence of index on dispersion within glass families is shown to arise primarily from the approximately linear superposition of the electronic absorptions of glass former and glass modifiers. The binary classification into crown and flint glasses is also based primarily on electronic spectra: Crown glasses are "wide-gap" materials with excitation energies greater than ~12.4 eV, while flint glasses are their "narrow-gap" counterpart.

1. Introduction

The search for glasses to minimize chromatic aberrations in transmission optics has spurred extensive studies of the refractive index and its dispersion for optical glass for more than a century [1-6]. Traditionally, these quantities are summarized within the framework of empirical relations [1, 4, 7-8] that are suitable for lens design, but give little insight into processes determining the index. Here we employ a moment-analysis procedure [9, 10] based on the Kramers-Kronig relations to explore the physics underlying both the empirical relations and the common classification scheme used for optical glass. Specifically, the index and dispersion of various glass families trace out separate straight lines on plots of index *vs.* mean dispersion [4, 11]. We show that this is a consequence of the near linear additivity of the absorption spectra of glass formers and glass modifiers. Further, we show that glass classifications based on the Abbe number are directly related to the glass's optical excitation spectrum.

2. Background

The IR and UV absorptions of vitreous silica [12], a typical glass-forming wide-gap insulator, are shown in figure 1. The index of refraction, shown by the dashed curve, exhibits strong dispersion at energies approaching the absorptions at the low- and high-energy limits of the transparent region. However, for visible light, dispersion amounts to only a few percent. Since the optical response of a charge is inversely proportional to its mass, the total oscillator strength of the IR absorption, which involves ionic motion, is of the order of 10^{-4} times smaller than that of the electronic transitions in the UV. Moreover, ionic dispersion lies well below the low-energy cut off of visible light. Thus to a first approximation, the refractive index at visible wavelengths is determined by electronic transitions. However, a full discussion of dispersion requires that both IR and UV transitions be considered.

Optical glasses generally consist of a glass former such as SiO_2, B_2O_3, etc., and glass-modifying metallic oxides such as Na_2O, CaO, PbO, BaO, etc. In silicate glasses the modifiers originally served as fluxes, that is, as agents to lower the melting point of silica by interrupting the strong Si–O bonds,
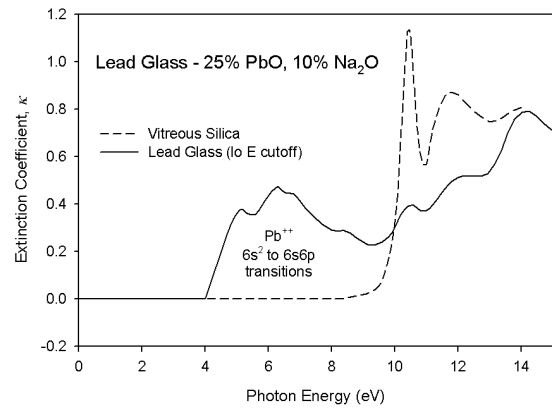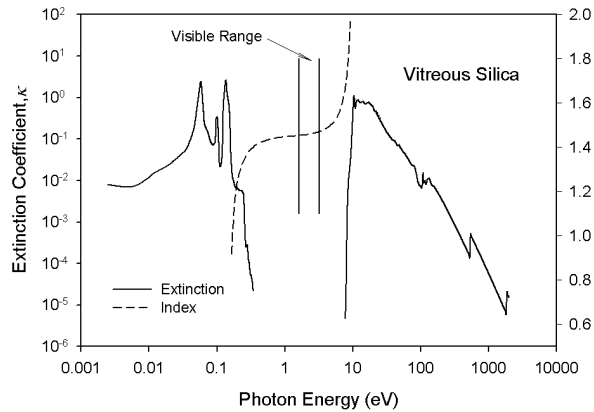
Figure 1. Absorption & dispersion in vitreous SiO$_2$. **Figure 2.** Absorption of lead glass [13].

but secondarily they alter other properties. In particular, the optical properties of glass-forming materials may be tailored to a limited extent by adding ions that introduce electronic absorptions in the UV. An example for PbO in silica [13] is shown in figure 2. Not only are new Pb^{2+} bands added, but the absorption of the silica host is altered by both dilution and perturbations caused by replacing Si–O bonds by Pb–O bonds. Changes in the net absorption in the IR are less pronounced (see [14]).
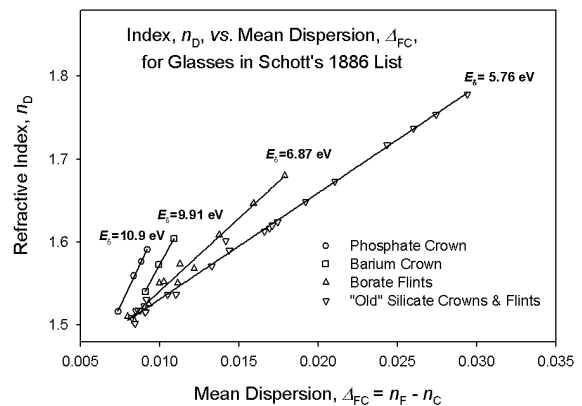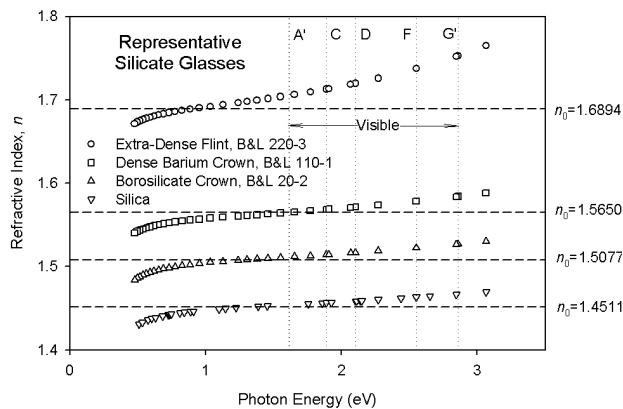

Figure 3. Refractive indices of silicate glasses. **Figure 4.** Index vs. dispersion in early glasses.

Concentrating on the transparent region, we give examples of the index at visible wavelengths for a range of commercial silicate glasses [12, 15] in figure 3. Here, pure vitreous SiO$_2$ has the lowest index and dispersion. As modifiers are added, the refractive index increases; the dispersion increases even more markedly, especially toward the blue. It is notable that the low-energy dispersion from ionic vibration is not as strongly dependent on doping.

3. Linear-response treatment of refraction

For insulators, the Kramers-Kronig dispersion expression for the refractive index, $n(E)$, may be divided into contributions from IR vibrational and UV electronic absorptions [9, 10],

$$n(E) - 1 = \frac{2}{\pi} P \int_{IR} \frac{E'}{E'^2 - E^2} \kappa(E')dE' + \frac{2}{\pi} P \int_{UV} \frac{E'}{E'^2 - E^2} \kappa(E')dE', \qquad (1)$$

where $\kappa(E)$ is the extinction coefficient. For energies, E, in the transparent region between the IR and UV, the integrands may be expanded in power series, the first in the variable $(E'/E)^2$, the second in $(E/E')^2$. The index then takes the form of a Laurent series,

$$n(E) \;\approx\; 1 \;+\; \frac{2}{\pi}\,(\cdots - \mu_1 E^{-2} + \mu_{-1} + \mu_{-3}E^2 + \mu_{-5}E^4 \cdots)\,, \tag{2}$$

where $\mu_1 = \int_{IR} E'\,\kappa(E')\,dE'$ is the 1st moment of the IR absorption, and $\mu_{-n} = \int_{UV} \dfrac{\kappa(E')}{E'^{\,n}}\,dE'$ is the inverse n^{th} moment of the UV electronic absorption. Similarly, the mean dispersion between the F and C lines is

$$\Delta_{FC} \;\equiv\; n_F - n_C \;\approx\; \frac{2}{\pi}(E_F^2 - E_C^2)\,\Big[\,\frac{\mu_1}{E_F^2 E_C^2} \;+\; \mu_{-3} \;+\; \mu_{-5}(E_F^2 + E_C^2)\,\Big]. \tag{3}$$

Electronic absorption typically accounts for 97% or more of $n-1$ at visible wavelengths, with the bulk of the contribution arising from the μ_{-1} term [10, 16]. Infrared contributions from the μ_1 term are commonly less than 0.3%. Though relatively unimportant for the index, the μ_{-3} term dominates the dispersion. The μ_1 and μ_{-5} terms are retained because of their contribution to partial dispersion. Higher-order terms can always be added for greater accuracy, but are not needed for the present semi-quantitative considerations. (Herzberger finds that the E^4 term must be retained for designing infrared lenses [17]).

4. First-order formulation: Index and mean dispersion
To a first approximation, the index, n_D, at the Fraunhofer D line (which is near the centre of the visible) and the mean dispersion, Δ_{FC}, between the C and F lines (which span the red and the blue) are

$$n_D - 1 \;\approx\; \frac{2}{\pi}\,\mu_{-1}\,, \tag{4} \qquad \text{and} \qquad \Delta_{FC} \;\approx\; \frac{2}{\pi}(E_F^2 - E_C^2)\,\mu_{-3}. \tag{5}$$

It should be noted that the index and dispersion are not entirely independent quantities since both depend on the shape of the UV absorption. However, this shape may be varied by changing the composition of the glass, which allows a limited degree of independence of n_D and Δ_{FC}.

Notwithstanding this, a remarkably strong correlation between index and dispersion holds for glasses within families of the same glass former. This is apparent in figure 4 that shows that index-dispersion pairs with the same glass former, such as SiO_2, B_2O_3, etc., fall on nearly straight lines. This linear dependence may be understood by considering a two-component glass. Designating the atomic fractions of the glass former and modifier by c_f and c_m, respectively, we require that (a) $c_f + c_m = 1$, and (b) assume the electronic absorption is additive so that the total electronic absorption becomes $\kappa(\omega) = c_f \kappa_f(\omega) + c_m \kappa_m(\omega)$. Additivity of host and dopant absorption is seen at low dopant concentration in colour centres [18], and appears to hold approximately at higher concentrations in glasses provided the dopant's effect on the electronic structure of the host glass former is taken into account. Then the index and dispersion of the composite glass becomes

$$n_D - 1 \;\approx\; \frac{2}{\pi}[c_f\,\mu_{-1,f} + c_m\,\mu_{-1,m}] \tag{6} \qquad \text{and} \qquad \Delta_{FC} \;\approx\; \frac{2}{\pi}(E_F^2 - E_C^2)[c_f\,\mu_{-3,f} + c_m\,\mu_{-3,m}], \tag{7}$$

where $\mu_{-i,f}$ and $\mu_{-i,m}$ are the inverse i^{th} moments of glass former and glass modifier, respectively.

Eliminating the concentrations between these equations and solving for the index as a function of the dispersion yields

$$n_D - n_{D,\,f} = \frac{1}{E_F^2 - E_C^2}\left(\frac{\mu_{-1,m} - \mu_{-1,f}}{\mu_{-3,m} - \mu_{-3,f}}\right)[\Delta_{FC} - \Delta_{FC,f}]\,, \tag{8}$$

where we have abbreviated the index and dispersion of the glass former by

$$n_{\mathrm{D,f}} - 1 = \frac{2}{\pi}\mu_{-1,\mathrm{f}} \qquad (9) \qquad \text{and} \qquad \Delta_{\mathrm{FC,f}} = \frac{2}{\pi}(\omega_{\mathrm{F}}^2 - \omega_{\mathrm{C}}^2)\mu_{-3,\mathrm{f}}. \qquad (10)$$

Equation (8) shows that the index of the composite glass is linear in dispersion, starts at the index-dispersion point of the glass former, and has slope

$$\frac{1}{E_{\mathrm{F}}^2 - E_{\mathrm{C}}^2}\left(\frac{\mu_{-1,\mathrm{m}} - \mu_{-1,\mathrm{f}}}{\mu_{-3,\mathrm{m}} - \mu_{-3,\mathrm{f}}}\right) = \frac{<E_{\delta\kappa}^2>}{E_{\mathrm{F}}^2 - E_{\mathrm{C}}^2}. \qquad (11)$$

In writing the right-hand side of equation (11), we have interpreted the moments ratio as the change in average (square) excitation energy caused by the modifier,

$$<E_{\delta\kappa}^2> = \frac{\mu_{-1,\mathrm{m}} - \mu_{-1,\mathrm{f}}}{\mu_{-3,\mathrm{m}} - \mu_{-3,\mathrm{f}}} = \frac{\displaystyle\int_{\mathrm{UV}} E'^{-1}\delta\kappa(E')\ dE'}{\displaystyle\int_{\mathrm{UV}} E'^{-3}\delta\kappa(E')\ dE'}. \qquad (12)$$

This reasoning is based on the observation that the differences in spectral moments can be written as moments of the difference spectra, $\delta\kappa(\omega) = \kappa_{\mathrm{m}}(\omega) - \kappa_{\mathrm{f}}(\omega)$, that is, the absorption introduced by the glass-modifier and the accompanying decrease in glass-former absorption. An example of this difference is given in figure 5 for data derived [13] from reflectivity data currently available for a lead-silicate glass. In light of the limited reflectivity data available, details of this figure are provisional.
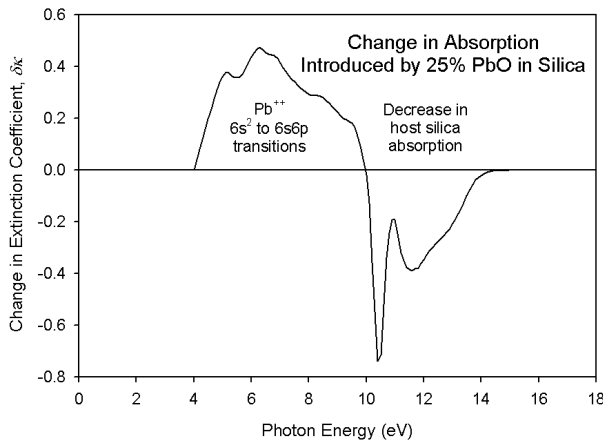

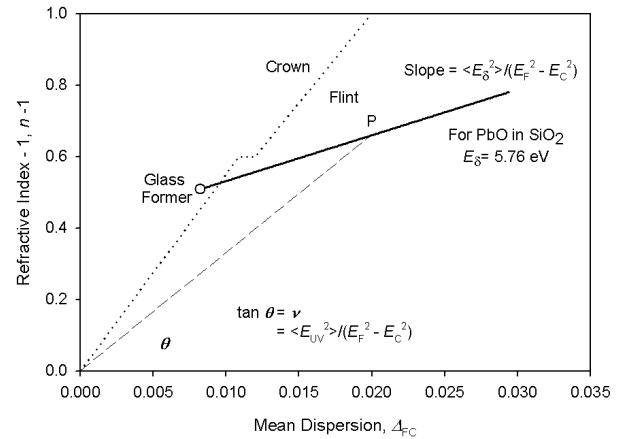**Figure 5.** Change in absorption with Pb doping.

Figure 6. Schematic index *vs.* dispersion plot.

Thus, it seems reasonable to interpret the ratio of moments of the difference spectrum as the net change in excitation energy introduced by the glass former, a view that is in line with the intuitive picture of dopant atoms replacing host atoms. This formulation may be summarized in a schematic index-*vs.*-dispersion diagram, figure 6. For this example, measured values of index and dispersion for lead silicate glasses have been used. The modifier, PbO, introduces absorption bands in the region of transparency of the host, and lowers the average excitation energy. Starting from the pure glass former shown by the open circle, addition of PbO yields glasses with (n, Δ) pairs lying along the solid line, with greater distances from the glass-former origin correspond to greater modifier concentration. According to equation (11), the slope of the glass-family line is determined by the *net change* in excitation energy caused by the modifier, $<E_{\delta\kappa}^2>^{1/2}$. A fit to experimental data for lead-silica glass gives $<E_{\delta\kappa}^2>^{1/2} = 5.76$ eV, which is consistent with the change in the extinction coefficient derived from reflectivity measurements shown in figure 5.

5. Classification in terms of the Abbe number

Traditionally, glasses are classified by index and "reciprocal dispersion" or Abbe number, v, a quantity that arises in lens-design. This corresponds to specifying the glass at point P in figure 6 by its index and the tangent of the angle θ.

$$v_D = \frac{n_D - 1}{n_F - n_C} = \tan\theta \approx \frac{1}{E_F^2 - E_C^2}\left(\frac{\mu_{-1}}{\mu_{-3}}\right) = \frac{<E_{UV}^2>}{E_F^2 - E_C^2}. \tag{13}$$

Here, in analogy with the treatment of the slopes of the glass-family lines, we have observed that the moments ratio on the right-hand side of equation (13), μ_{-1}/μ_{-3}, has units of energy squared, and that, by the mean-value theorem, it may be interpreted as the square of an average energy for electronic excitations of the *glass as a whole*, $<E_{UV}^2>$. Typical values of $<E_{UV}^2>^{1/2}$ range from 7.4 to 15.1 eV.

The historical division of optical glass into low-dispersion crown (soda-lime silicate) and high-dispersion flint (lead-alkali silicate) glasses has been formalized by defining crowns as having Abbe numbers of ~50 or more [4]. From equation (13) and the energies of the C and F Fraunhofer lines, this limit corresponds to $<E_{UV}^2>^{1/2} \approx 12.4\,eV$. Thus, crown glasses are "wide-gap" materials with excitation energies greater than ~12.4 eV, while flint glasses are their "narrow-gap" counterpart.

6. Second-order formulation: Partial dispersion

The primary chromatic aberration of a single lens can be eliminated by using a crown-flint doublet with the appropriate index-dispersion combinations for the two lenses (for details see [1, 3]). The geometric-optics requirement is that two colours, here C and F, focus at the same point. However, higher-order aberrations remain since all other colours remain out of focus to some extent. The reason is that the slope of index *vs.* photon energy curve is not constant, but differs slightly from that associated with the mean dispersion, especially in the far-red and violet. Mitigation of the remaining aberration in second-order is achieved [1, 3] by requiring that three colours are confocal. In the thin-lens approximation this is achieved in a doublet if the relative partial dispersions of the two lenses,

$$P_{XY} \equiv \frac{n_X - n_Y}{n_F - n_C} \approx \frac{E_X^2 - E_Y^2}{E_F^2 - E_C^2}\left\{1 - \frac{\mu_1}{\mu_{-3}}\left(\frac{1}{E_X^2 E_Y^2} - \frac{1}{E_C^2 E_F^2}\right) + \frac{\mu_{-5}}{\mu_{-3}}\left(E_X^2 + E_Y^2 - E_F^2 - E_C^2\right)\right\}, \tag{14}$$

are equal. The right-hand side of equation (14) has been obtained by substituting equation (2) for the index in the definition of P_{XY} and by using $1/(1 + a) \sim 1 - a$, $a \ll 1$, to simplify the small terms involving μ_1 and μ_{-1}. Had these small terms been neglected (as in our first-order treatment), the relative partial dispersion would be constants for all glasses, $P_{XY} = (E_X^2 - E_Y^2)/(E_F^2 - E_C^2)$.

Equation (14) can be further transformed to reflect the relationship of the moments to the Abbe number by introducing ratios of moments in which the powers of energy within the various integrals sum to zero. For a distributed absorption, these factors are of the order of unity and vary slowly with compositions. Then,

$$P_{XY} = \frac{E_X^2 - E_Y^2}{E_F^2 - E_C^2}(1 - \alpha_{ionic}v^2 + \beta_{electronic}v^{-1}), \tag{15}$$

where the coefficients α and β are nearly constant. The IR term is quadratic in v; the electronic term is hyperbolic. At small Abbe numbers (large dispersion) where electronic effects dominate, the magnitude of the partial dispersion decreases rapidly with v. In contrast, at large Abbe numbers (small dispersion) where electronic effects are small, the magnitude of the partial dispersion increases quadratically. For practical values of v, the effective dependence is nearly linear as found by Abbe [1, 3, 5, 6, 19]. Fits of equation (15) to the observed P_{XY} are shown in figures 7 and 8. The curves for silicate and borate glasses are distinct since the ratio of IR and UV absorption strengths enters α_{ionic}.
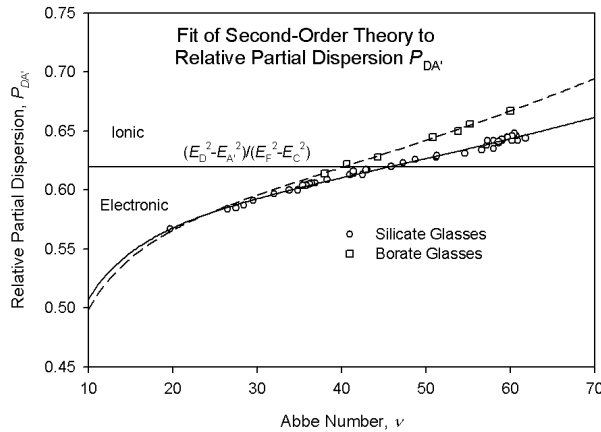
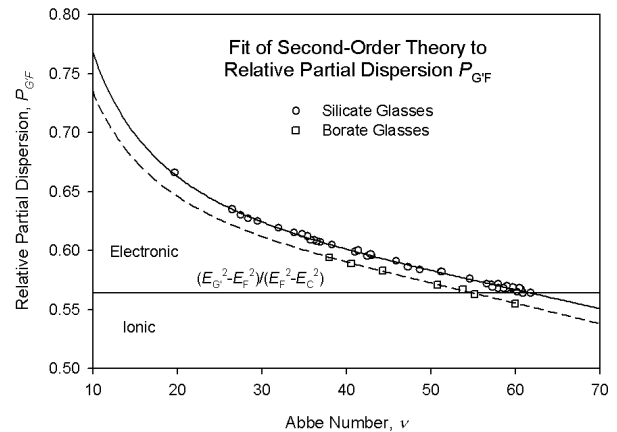**Figure 7.** Relative partial dispersion in the far red.

Figure 8. Relative partial dispersion in the violet.

7. Summary

A Laurent-series expansion of the refractive index over the region of transparency of optical materials provides a systematic means of treating dispersive phenomena in terms of moments of the material's absorption spectra. In first order the empirical linear relation between index and dispersion within glass families follows from the approximate additivity of the electronic absorptions of glass former and glass modifier. Partial dispersion requires a second-order treatment in which both vibrational absorption in the IR and higher-order electronic terms in the UV are considered.

Acknowledgments

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