Designing glass with non-dispersive stress-optic response

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Abstract

The dispersion of the stress-optic response of a series of barium and lead phosphate glasses is measured using an ellipsometric method. It is found that the barium glasses display consistently positive dispersion with decreasing wavelength, while the lead glasses display consistently negative dispersion. It is found that the dispersion is roughly additive so that in mixed barium/lead phosphates, a composition may be found for which the dispersion is essentially zero across the optical range. The dispersion itself is shown to correlate with glass structure, giving an empirical relationship between stress-optic dispersion and composition. These results thus suggest a design rule for controlling stress-optic response in glass as a function of wavelength.

Keywords:

Stress-optic response, Photoelastic response

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1. Introduction

Glass is optically isotropic, but when a stress is applied, usually becomes birefringent. This effect is known as photoelasticity and has been extensively studied in oxides [1–15]. Early theories of photoelasticity relate birefringence to atomic structure and polarizability of ions [2], while a recent empirical model of photoelasticity uses bond length and cation coordination to predict new zero-stress optic oxide glasses [9]. In this model, structure is explicitly correlated with the stress-optic response through the parameter $\langle d/N_C \rangle$. This parameter represents the cation-oxygen bond length d divided by the first-neighbor cation-oxygen coordination number N_C, molar averaged over the glass constituents. Zero stress-optic glasses are key components in many products, including fiber optics, optical research instruments, and projection optics.

Formally, photoelasticity is the proportionality between stress and dielectric response, and can be expressed as

$$\Delta \epsilon_{ij}^{-1} = \pi_{ijkl}\sigma_{kl}. \tag{1}$$

Here ϵ is the dielectric response, σ the stress, and π the photoelasticity. Because all these quantities are tensors, the indices are necessary to specify directions. The situation simplifies in an isotropic material, such as glass, under a small uniaxial stress. One then finds

$$\Delta n = C\sigma, \tag{2}$$

where σ is a (compressive or tensile) stress, the direction of which defines the so-called "extraordinary" direction; $\Delta n = n_e - n_o$ is the difference in index

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of refraction in the extraordinary and perpendicular (ordinary) direction; and the coefficient of proportionality C is the stress-optic coefficient. The differential index of refraction Δn also leads to a phase shift, Δ, between components of polarization

$$\Delta = \frac{2\pi l}{\lambda}\Delta n = \frac{2\pi l}{\lambda}C\sigma, \tag{3}$$

where l is the sample thickness and λ the wavelength of light. In Eq. 3 there is an explicit wavelength dependence but note that the indices of refraction and C itself are wavelength-dependent. In fact for small stress (the elastic limit), the stress-optic coefficient can be related to the photoelastic tensor through [16]

$$C = -\frac{1}{2}n^3(\pi_{11} - \pi_{12}). \tag{4}$$

Here n is the unstressed, isotropic index of refraction, and the π are elements of the photoelastic tensor. When $\pi_{12} > \pi_{11}$ we have $C > 0$ and hence $\Delta n > 0$, in other words, positive response and positive induced birefringence; $\pi_{12} < \pi_{11}$ leads to negative birefringence, and $\pi_{12} = \pi_{11}$ to the interesting and useful case of zero induced birefringence under a stress load, that is, to zero stress optic glass. We note that C can also be expressed in terms of strain, rather than stress, whereby $C = -n^3 p_{44}/2G$, where G is the shear modulus and p_{44} the shear photoelastic tensor element for strain.

Because both the index of refraction and the photoelastic tensor exhibit dispersion, then so too does C. In other words, the stress-optic response of glass depends on the wavelength of light used for measurement. Therefore, it is of interest technologically to investigate where *dispersionless* stress-response glass can be designed. Such glass could be used for precise polarization optics over a broad bandwidth, rather than just on average or at a

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single wavelength and might find application in polarized light microscopes and fiber optics. While the physics of photoelastic dispersion are complex and not yet fully understood, we have made considerable progress in designing dispersionless stress-optic glass from an empirical approach, which we report here, focusing just on lead and barium containing phosphate glasses.

2. Experimental Methods

2.1. Glass preparation

Lead phosphate glasses were prepared by melt-quenching, starting from commercial PbO and $NH_4H_2PO_4$. Melts were held in air at 1000°C for 1–2 hrs, and quenched and annealed at 300°C. Barium phosphate glasses were prepared similarly, except from $BaCO_3$, melting at 1200°C for 12–36 hrs, quenching at ambient temperature, and annealing at 500°C. Finally, lead-barium phosphate glasses were melted at 1100°C for 2 hrs, and quenched and annealed at 400°C.

Once annealed, the glasses were cut and polished for optical measurements. The glasses were cut into rectangular cuboids of varying dimensions using a low-speed saw (Buehler IsoMet, with a Lapcraft diamond saw blade). Two sets of parallel faces were ground with 1200 grit silicon carbide to remove any imperfections that would affect the homogeneity of stress. The glasses were often affixed to a polishing screw so that the sides remained perfectly parallel when ground. One set of parallel sides was then polished to between 1 μm and 30 μm optical transparency using cotton polishing pads soaked with diamond paste of decreasing particle size (MetaDi polishing compounds, Buehler).

2.2. Measurement of the stress-optic coefficient

Under uniaxial stress, glass typically exhibits an index of refraction n_e in the stress direction (the extraordinary direction) that differs from the index of refraction in the perpendicular direction (n_o, the ordinary direction). The difference results in birefringence in the glass, $b = \Delta/l = n_e - n_o$, where Δ is the phase difference between ordinary and extraordinary rays and l is the thickness of the glass. For stress loads within the elastic region, the birefringence of a glass is proportional to the applied stress σ:

$$\Delta = Cl\sigma. \tag{5}$$

The constant of proportionality, called the stress-optic coefficient C, is used to characterize the glass. Its unit is Brewsters, where 1 B equals 10^{-12} Pa^{-1}.

In order to measure the stress-optic coefficient of a glass accurately and precisely, application of very homogeneous stress is necessary. A custom-built strain gauge was been developed in our laboratory, that consists of an optical rail system with two solid aluminum plates, a motorized screw, and a load cell. The glass sample sits between the two parallel plates, and the screw descends onto the top plate to stress the glass. Often, a compliant plastic layer is placed between the glass and the aluminum to ensure the stress is as uniform as possible. A load cell, located below the bottom plate, measures the force F acting on the glass sample. The stress σ can then be determined from $\sigma = F/A$, where A is the area of the face of the glass sample to which force is applied. The uniformity of the applied stressed is visually inspected using a polariscope (Strainoptics PS-100). The polariscope, or light table, is a Sénarmont compensator with a fluorescent bulb providing white light.

The strain gauge is placed between the tables two crossed polarizers, and the analyzer is rotated to determine the minimum intensity of light. If the stress is applied homogeneously, then phase shift of polarized light travelling through the glass will be equal at all spots and the intensity of light will be minimized uniformly across the sample.

2.3. Density and shear modulus

Densities ρ were measured by the Archimedes method using a Mettler Toledo density determination kit with $> 99\%$ ethanol as the immersion fluid. Transverse sound velocities v_T were measured by the ultrasonic method using a Panametric ultrasonic thickness gauge. The transverse sound velocity is related to the shear modulus G by $G = \rho v_T^2$.

2.4. Refractive index and stress-optic response

Refractive indices were measured between 200 nm and 1000 nm using a J. A. Woollam Co. M2000F spectroscopic ellipsometer in reflection mode. In this experiment the ratio of amplitudes of the reflected and incident s-polarized and p-polarized waves are reported, along with the phase shift between the reflected s and p waves. The phase shift and amplitude ratio are used to extract the index of refraction n from a fit to a Cauchy model:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}. \tag{6}$$

The angle of incidence of light on the glass surface was $\theta = 50°$. The parameters Ψ and Δ were measured at various locations on one polished side of the glass using a 20–30 s scan time. The data was analyzed using CompleteEASE and fit with a Cauchy model for glass substrates to find the real part of n.

The stress-optic coefficients were measured with the ellipsometer in transmission mode Here, Ψ and Δ are measured for s and p waves transmitted through the stressed glass. The wavelength-dependent phase shift was used to determine the stress-optic coefficient for glasses with known thickness d and stress according to Eq. 3. Stress was applied to the glasses as described above. For a glass sample, the phase shifts Δ were measured as a function of decreasing stress σ. At least five stresses were applied between maximum and minimum σ, and data collection times were 1–2 seconds for each applied stress. This process was repeated multiple times, and the location of the incident light on glass face was varied. The stress-optic coefficient was determined at each wavelength from the slope of Δ vs. σ for all measurements at all locations on the glass surface; the variation of the slope gives uncertainty in C.

3. Results

Table 1 lists the density, transverse sound velocity, and shear modulus derived for each glass. All glasses show the expected smooth increase in density and index of refraction with lead or barium addition; however, the barium system seems to show a small anomaly in G at the 40% BaO level. This is almost within the experimental uncertainty so it may not be a symptom of unusual physical behavior but only of a sample flaw in this one composition.

Fig. 1 shows the stress optic coefficient C and the shear photoelastic tensor element p_{44} for a series of binary lead phosphate glasses. The stress-optic response in these glasses shows uniformly negative-trending dispersion as the wavelength of the light decreases. For low lead content the average

Table 1: Density d in g cm^{-3}, transverse sound velocity v_T in km sec^{-1}, shear modulus G in GPa, and index of refraction at 589 nm for glass compositions studied here.

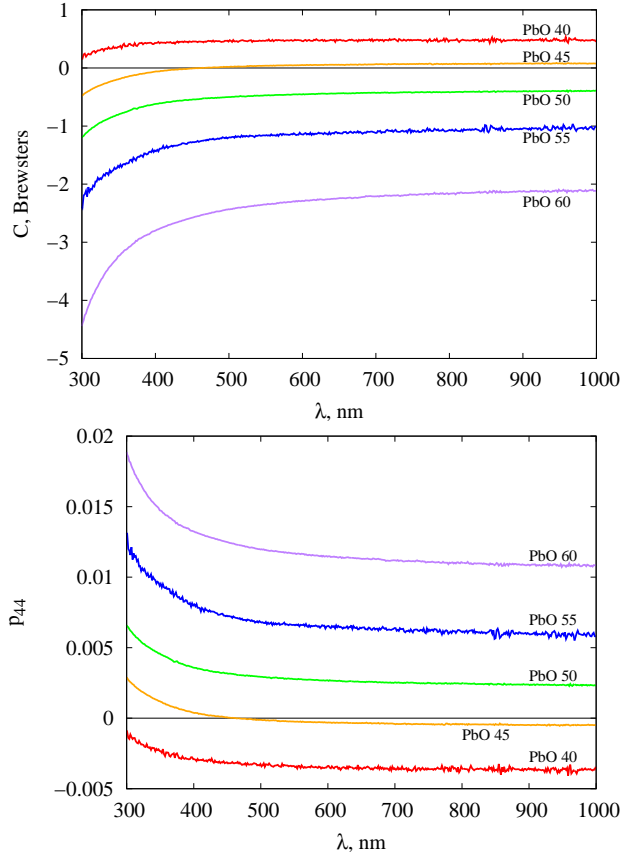| Composition	d	v_T	G	n
$(PbO)_{40}(P_2O_5)_{60}$	4.04	1.895	14.5(6)	1.46(1)
$(PbO)_{45}(P_2O_5)_{55}$	4.34	1.846	14.8(6)	1.68(1)
$(PbO)_{50}(P_2O_5)_{50}$	4.65	1.774	14.6(6)	1.70(1)
$(PbO)_{55}(P_2O_5)_{45}$	5.02	1.735	15.1(6)	1.75(1)
$(PbO)_{60}(P_2O_5)_{40}$	5.42	1.680	15.3(7)	1.78(1)
$(BaO)_{35}(P_2O_5)_{65}$	3.26	2.287	17.1(6)	1.55(1)
$(BaO)_{40}(P_2O_5)_{60}$	3.35	2.491	20.8(7)	1.54(1)
$(BaO)_{45}(P_2O_5)_{55}$	3.48	2.387	19.8(7)	1.58(1)
$(BaO)_{50}(P_2O_5)_{50}$	3.65	2.309	19.5(7)	1.59(1)
$(BaO)_{55}(P_2O_5)_{45}$	3.84	2.287	20.1(7)	1.60(1)
$(PbO)_{10}(BaO)_{40}(P_2O_5)_{50}$	3.80	2.300	19.3(8)	1.62(1)
$(PbO)_{20}(BaO)_{30}(P_2O_5)_{50}$	4.00	2.257	19.4(8)	1.65(1)
$(PbO)_{30}(BaO)_{20}(P_2O_5)_{50}$	4.19	2.185	19.6(8)	1.67(1)
$(PbO)_{40}(BaO)_{10}(P_2O_5)_{50}$	4.39	2.127	19.6(8)	1.69(1)

Figure 1: (Top) Stress-optic coefficients (in Brewsters) as a function of wavelength for binary lead phosphate glasses; (bottom) shear element of photoelastic tensor as a function of wavelength. The lead phosphate glasses are of composition $(\mathrm{PbO})_x(\mathrm{P_2O_5})_{100-x}$, where x is indicated on the label for each trace. The data points were recorded in 1.5 nm steps and are connected by lines to guide the eye. The uncertainty on each point of C is about 0.03 Brewsters, and about 0.0003 for p_{44}.

stress optic response is positive but trends negative, while at high lead content it is negative at all wavelengths, but the dispersion is still towards even more negative values. Note that the $(PbO)_{45}(P_2O_5)_{55}$ composition is nearly zero stress-optic, but exactly so at only one wavelength, about 467 nm. Shown in the lower panel of the figure is the shear element of the photoelastic tensor, p_{44}, for each glass, extracted from the data for C and n (not shown) and the shear modulus. Because of the sign change, p_{44} shows positive dispersion where C showed negative dispersion. Of importance though is that p_{44} does strongly show dispersion, in other words, the dispersion of C is not simply due to the dispersion in n.

Fig. 2 shows the same information for binary barium phosphate glasses. Here the opposite trend is observed, namely C shows positive dispersion while p_{44} shows negative dispersion. In this case there is no zero stress optic composition (as expected on the basis of our empirical model [9]).

In Fig. 3 the data for ternary glasses of formula xPbO-$(50 - x)$BaO-$50P_2O_5$ are shown. Note here the trend from positive-going dispersion, for high barium/low lead content glass, to negative dispersion, for low barium/high lead content. Of most importance is the intermediate composition with a PbO to BaO ratio of 20/30, for which the dispersion in C is nearly cancelled up to close to the band edge. This glass, with stress-optic coefficient of about 0.9 B, is also nearly free from dispersion in p_{44}.

4. Discussion

It is remarkable that barium and lead as additives give the opposite dispersion to the stress-optic response, and equally remarkable that the disper-
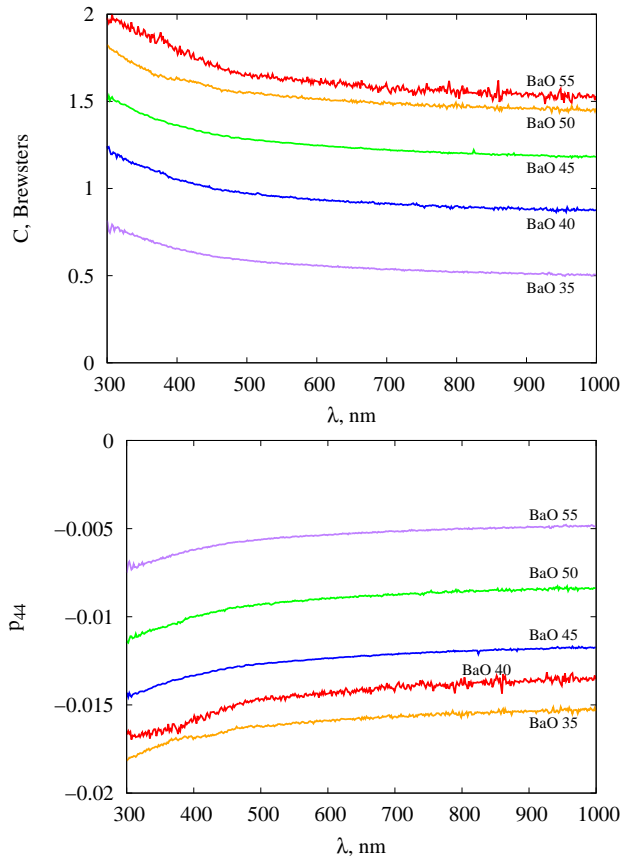
Figure 2: As in Fig. 1, but for binary glasses of composition $(\mathrm{BaO})_x(\mathrm{P_2O_5})_{100-x}$.

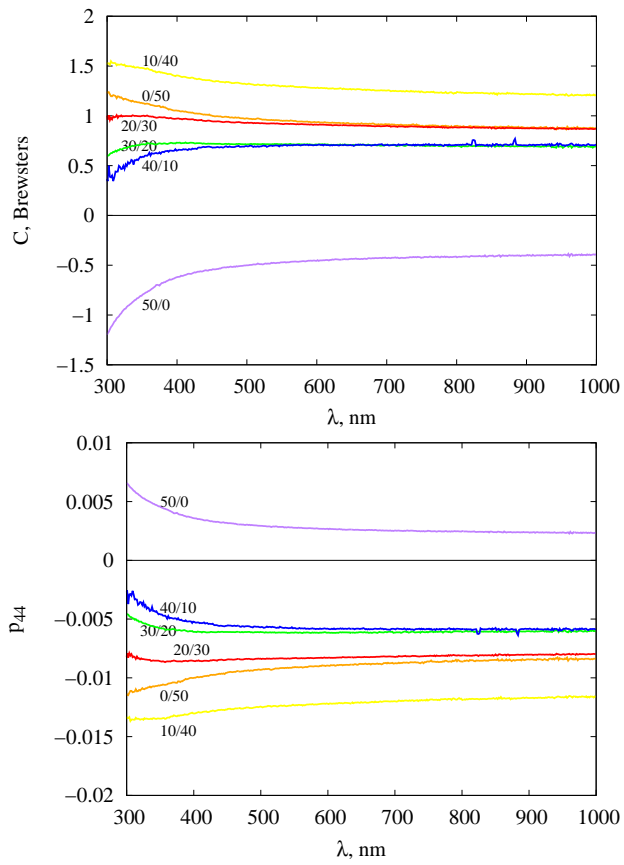Figure 3: As in Fig. 1 but for the ternary glasses $(PbO)_x(BaO)_{50-x}(P_2O_5)_{50}$. Traces are labelled as "$x/50-x$" for PbO/BaO content.

sion in either case is not simply inherited from the dispersion in the index of refraction but rather is inherent in the photoelastic tensor element p_{44} itself. Furthermore as Fig. 3 shows, the dispersive effect is broadly additive when both barium and lead are present, leading to the significant finding that the dispersion from both sources can cancel, as in $(\text{PbO})_{20}(\text{BaO})_{30}(\text{P}_2\text{O}_5)_{50}$, leading to glass the stress-optic response of which is virtually free from dispersion.

The reason that the effect is additive is likely due to the long wavelength nature of linear optical response: the length scale of the light waves, 400– 700 nm, is very large compared to the chemical bond length scale and hence the details of the electron distribution (and distortion). Therefore, the effects are averaged over and additivity results.

Naturally, given that it is possible to cancel the effects of positive and negative dispersion, it is interesting to consider under what circumstances the cancellation is possible and whether it can be constructed to yield, in addition, zero stress-optic glass with zero dispersion. A first-principles understanding of the dispersion of photoelasticity is at this point not available, so we adopted an empirical approach. We fit the dispersion curves for C with a pseudo-Cauchy model of the form

$$C(\lambda; \lambda_0, \alpha, \beta, \gamma) = \alpha + \frac{\beta}{\lambda/\lambda_0} + \frac{\gamma}{(\lambda/\lambda_0)^2}, \tag{7}$$

where λ is the wavelength of light, λ_0 is the absorption edge, and α, β, and γ are fit parameters. Physically, α represents the long wavelength limit of the stress optic response, γ its curvature, and β the slope. The sign of γ is the qualitative indication of positive-going or negative-going dispersion. This form was chosen as a simple functional form that reasonably described
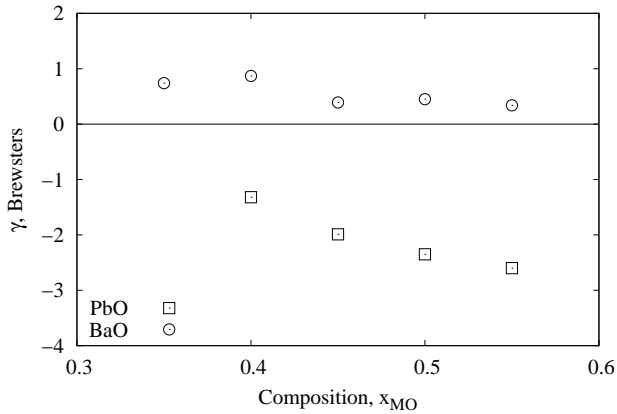
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Figure 4: Dependence of the pseudo-Cauchy fit parameter γ on composition in binary barium phosphate and lead phosphate glasses. The plot shows γ (see Eq. 7) as a function of barium oxide or lead oxide fraction in phosphate glass.

the dispersion curves, and is a generalization of the form sometimes used in the literature, namely $C = C_0/(1 - \lambda_0/\lambda)$ [17]. In this simpler form, the parameter λ_0 is the only fit parameter (and not equated to the absorption band edge); its sign determines the curvature of the dispersion.

When a glass is made from a mixture of additives, the dispersion in the stress optic coefficient is roughly the sum of two equations of the form in Eq. 7. Ideally, for cancellation, one would like the band edges λ_0 for the two glass additives to be equal, and the pairs of fit parameters to be equal and opposite in sign. At least in the present case, however, the parameters have rather different qualitative behavior. For example, Fig. 4 shows the composition dependence of the fit parameter γ in barium phosphate and lead phosphate glasses. While the dependence in the lead glasses is strong, with the dispersion becoming more pronounced (larger magnitude γ) as lead is added, in the barium case the dependence is quite weak. This type of
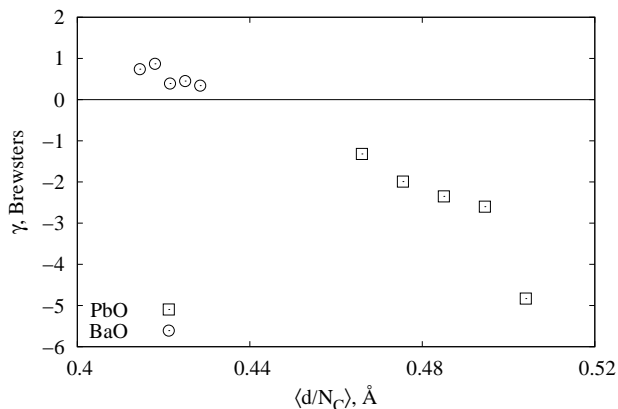
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Figure 5: Dependence of the pseudo-Cauchy fit parameter γ on structure as represented by $\langle d/N_C \rangle$ in lead phosphate and barium phosphate glasses.

difference makes it difficult to cancel the dispersion behavior in arbitrarily chosen additive pairs.

Nevertheless, there is some correlation of the curvature parameters α, β, and γ with structure, as in the stress optic coefficient C itself. Fig. 5 shows the correlation of γ, the parameter most closely linked with the curvature of C, as a function of $\langle d/N_C \rangle$ in the lead phosphate and barium phosphate glasses. While the data clearly correlate with $\langle d/N_C \rangle$, one can see that the zero crossing occurs about about 0.44–0.45 Å. This value is significantly less than that 0.5 Å value observed empirically for zero (average) stress-optic behavior, and glasses with $\langle d/N_C \rangle < 0.5$ Å are observed to have positive stress optic response. Thus at this point it would seem that, while dispersive behavior in the stress-optic response is correlated with structure similarly to the correlation observed in C itself, non-dispersive stress-optic glass can be designed only for positive average stress optic response, not zero or negative.

5. Conclusions

It was shown that the dispersion in the stress-optic response of glass is broadly additive in the dispersion of its constituents, and that non-dispersive photoelasticity could be designed into the glass by choosing constituents in the proper ratio to cancel their two responses. Other recent examples of glass design by this approach are discussed in reference [18]. Furthermore it was shown that the dispersion itself correlated reasonably with structure through the parameter d/N_C, used previously for the average stress-optic response, but that the dispersion can be expected to be zero only in cases that also have positive average stress-optic response. Current interesting challenges in this field include developing a first-principles understanding of the dispersion of photoelasticity and its dependence on bonding, and to try to overcome the apparent limitation of the above approach to glasses with only positive average stress-optic response.

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