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.

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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 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 is 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

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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 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 h, and quenched and annealed at 300 °C. Barium phosphate glasses were prepared similarly, except from $BaCO_3$, melting at 1200 °C for 12–36 h, quenching at ambient temperature, and annealing at 500 °C. Finally, lead–barium phosphate glasses were melted at 1100 °C for 2 h, 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 table's 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 traveling 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 s 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.

Table 1
Density d in g cm^{-3}, transverse sound velocity v_T in km s^{-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)