Photoelastic response of permanently densified oxide glasses

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ABSTRACT

The stress-induced birefringence (photoelastic response) in oxide glasses has important consequences for several applications, including glass for flat panel displays, chemically strengthened cover glass, and advanced optical glasses. While the effect of composition on the photoelastic response is relatively well documented, the effect of pressure has not been systematically studied. In this work, we evaluate the effect of hot isostatic compression on the photoelastic response of ten oxide glasses within two commonly used industrial glass families: aluminosilicates and boroaluminosilicates. Hot isostatic compression generally results in decreasing modifier-oxygen bond lengths and increasing network-former coordination numbers. These structural changes should lead to an increase in the stress optic coefficient (C) according to the model of Zwanziger et al., which can successfully predict the composition and structure dependence of C. However, in compressed glasses, we observe the opposite trend, viz., a decrease in the stress optic coefficient as a result of pressurization. We discuss this result based on measured changes in refractive index and elastic moduli within the context of atomic and lattice effects, building on the pioneering work of Mueller. We propose that the pressure-induced decrease in C is a result of changes in the shear modulus due to underlying topological changes in the glass network.

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1. Introduction

Glasses are inherently isotropic due to their lack of long-range order. However, under a deviatoric stress the glass can exhibit an anisotropic response, including optical birefringence. The magnitude of this stress-induced birefringence can be quantified by the stress optic coefficient (C), which is the proportionality constant between birefringence and applied stress:

$$\delta = C\sigma l, \tag{1}$$

where δ is the difference in the optical path length for light polarization along the stress axis and the orthogonal direction, σ is the applied uniaxial stress, and l is the sample thickness. When the uniaxial stress is applied to the glass, it changes its dielectric response in both the stress direction and in the orthogonal direction. The resulting birefringence is proportional to this difference.

For advanced optical applications, small amounts of birefringence can be a serious problem [1–4]. Typically standard network formers (e.g., SiO_2, B_2O_3, and P_2O_5) lead to a large positive birefringence (thus large positive C value), while traditional network modifiers (e.g., Na_2O and CaO) act to decrease the birefringence only slightly, leading to positive birefringence for standard oxide glass compositions. To obtain zero-stress optic glasses, the positive birefringence originating from the typical glass formers has traditionally been counterbalanced by the addition of PbO, which affects the birefringence negatively [5–7]. However, recent health and environmental regulations that aim at reducing the usage of lead due to its toxicity have necessitated research in the compositional and structural origins of the photoelastic response [2,8,9]. This research has led to the development of new lead-free glass compositions, exhibiting zero-stress optic response when strained anisotropically [2,7,9–13].

In the 1930s, Mueller proposed that the stress optic response of a material arises from lattice distortions and atomic polarizability [14,15]. Building on Mueller's concepts, Zwanziger and co-workers [2] proposed an empirical model to predict the birefringence in oxide glasses from the ratio between the cation-anion bond length (d) and the cation coordination number (N_c) of the glass

components. Based on the available literature data, they discovered that a d/N_c ratio of approximately 0.5 Å leads to a zero-stress glass, while negative and positive birefringence occurs when the ratio is above and below 0.5 Å, respectively. Mathematically, the empirical condition for $C = 0$ is

$$\sum_i x_i \left(\frac{d}{N_c} \right) \approx 0.5 \mathring{A}, \tag{2}$$

where the sum is over all the components i in the glass, and x_i is their respective mole fraction.

In their initial work, Zwanziger and co-workers used bond lengths and coordination numbers from crystallographic data, resulting in good qualitative agreement between model and data [2]. Later studies have supported their original findings by using more accurate bond lengths and coordination numbers in the actual glasses based on simulations [16,17] and experimental structural probes such as Mössbauer spectroscopy [17], nuclear magnetic resonance spectroscopy [7,8,17], Raman spectroscopy [9,18], extended X-ray absorption fine structure [18], and X-ray diffraction [7]. These findings support the original approach for estimating the stress optic response of oxide glasses, but they also show that detailed structural information is required to enable accurate predictions of the composition dependence of C.

The importance of d and N_c in controlling the stress optic response originates from their effect on the elastic response of a glass subjected to anisotropic stress. The bond length correlates positively with bond metallicity [19]. A more metallic bond is less directional and is thus free to be distorted in both the direction of the anisotropic stress and in the orthogonal direction. The coordination number also affects the deformation mechanism. Structural units with high coordination numbers tend to be distorted isotropically, whereas structural units with low coordination numbers are more susceptible to anisotropic distortion. Accordingly, glasses with tailored stress response can be produced by balancing the distortion mechanisms through glass composition design.

To further clarify the structural and topological origins of the photoelastic response of oxide glasses, here we investigate the effect of hot compression at 1 GPa on C in two families of industrial oxide glasses, covering a range of aluminosilicate and boroaluminosilicate compositions. Compression is performed at high pressure-high temperature conditions (typically near the ambient T_g), enabling permanent and isostatic densification at modest pressure (~1 GPa) of bulk samples (cm^3). Due to the high viscosity of the glass at ambient conditions, the glass structure is captured permanently in the densified state as a result of the pressure-quench [20]. This, in turn, enables *ex situ* measurements of

pressure-induced changes in mechanical and optical properties [21]. Although the dependence of the photoelastic effect on density and pressure has previously been discussed to some extent [22,23], this study will clarify the role of permanent network densification and pressure-induced structural transformations on photoelasticity. This is because the hot compression method is known to induce permanent changes in oxide glass structures, including modifier-oxygen bond lengths and cation coordination numbers [24]. As such, this approach enables us to test the underlying assumptions of the Zwanziger model (Eq. (2)), i.e., whether the effects of bond length and coordination number on C are indeed causal relations. Furthermore, we compare the pressure-induced changes in C with the changes in elastic moduli, since a recent study showed that the resistance of a material to elastic shear deformation is related to birefringence [25]. For this work, we choose ten different glass compositions with significantly different initial C values (from 1.86 to 6.22 nm MPa^{-1} cm^{-1}, see Table 1) in the borosilicate and aluminosilicate families, as these glasses are known to exhibit different but well-understood structural responses to hot isostatic compression [21,26–29]. For example, hot compression at 1 GPa can result in pronounced structural changes in borosilicate glasses (e.g., B^{III} → B^{IV}) [28], while the structural changes in aluminosilicate glasses (e.g., Al^{IV} → Al^{V}) are more modest at this pressure range [26].

2. Experimental section

The total of 10 different silicate glasses (Table 1) were prepared by mixing the appropriate amounts of raw materials, then melting the mixtures overnight in a covered Pt crucible in air at 1650 °C, and finally quenching the melts on metal plates. The glass transition temperatures (T_g) of the glasses were determined by beam bending viscometry, and the glasses were annealed for 30 min at their respective T_g. After thermal annealing, all glasses were subjected to hot isostatic compression (see Ref. [21] for details) at 1 GPa for 30 min at the ambient pressure T_g value, which was well above the structural relaxation time at this temperature. The samples were compressed in a nitrogen gas pressure chamber, which contains a multizone cylindrical furnace. Following the 30-min compression at T_g, the system was first cooled and then decompressed at around 60 K min^{-1} and 30 MPa min^{-1}, respectively.

The Archimedes buoyancy principle was used for determination of glass density ρ of both annealed and compressed samples. Ethanol was used as the immersion liquid and each sample was weighed ten times in both air and ethanol. From the density data, we calculated the plastic compressibility (β) and the molar volume (V_M) as

Table 1
Sample code and oxide components, glass transition temperature (T_g), plastic compressibility (β), density (ρ), stress optic coefficient (C), refractive index (n), shear modulus (G), and Young's modulus (E) of the glasses in this study. The errors associated with the measured values are ± 0.003 GPa for β, ± 0.002 g cm^{-3} for ρ, <1% for C, ± 0.0001 for n, and <1% for G and E.

Glass ID	Oxide components	T_g (K)	β (GPa^{-1})	ρ (g cm^{-3})		C (nm MPa^{-1} cm^{-1})		n (−)		G (GPa)		E (GPa)	
				ambient	1 GPa	ambient	1 GPa	ambient	1 GPa	ambient	1 GPa	ambient	1 GPa
SAP1	SiO$_2$, Al$_2$O$_3$, P$_2$O$_5$, Na$_2$O, ZnO	935	0.023	2.519	2.578	3.22	3.07	1.505	1.517	27.4	29.6	66.8	72.8
SAP2	SiO$_2$, Al$_2$O$_3$, P$_2$O$_5$, Na$_2$O, ZnO	858	0.020	2.571	2.623	3.17	3.03	1.514	1.526	28.2	29.6	68.9	72.8
SAB1	SiO$_2$, Al$_2$O$_3$, B$_2$O$_3$, CaO	827	0.064	2.190	2.340	4.88	3.90	1.480	1.512	20.9	26.0	51.6	64.4
SAB2	SiO$_2$, Al$_2$O$_3$, B$_2$O$_3$, CaO	891	0.066	2.223	2.381	4.66	3.73	1.490	1.522	22.1	27.6	54.6	68.2
SAB3	SiO$_2$, Al$_2$O$_3$, B$_2$O$_3$, CaO	921	0.070	2.218	2.386	4.45	3.78	1.490	1.520	22.5	27.2	54.7	65.8
SABP1	SiO$_2$, Al$_2$O$_3$, B$_2$O$_3$, P$_2$O$_5$	903	0.057	2.203	2.337	4.43	3.82	1.473	1.500	23.0	27.6	55.4	66.7
SAB4	SiO$_2$, Al$_2$O$_3$, B$_2$O$_3$	746	0.070	2.119	2.280	5.28	4.14	1.477	1.511	19.1	24.9	47.4	61.4
SABP2	SiO$_2$, Al$_2$O$_3$, B$_2$O$_3$, P$_2$O$_5$	703	0.066	2.073	2.219	6.22	4.90	1.462	1.494	15.3	19.7	37.1	47.8
SA1	SiO$_2$, Al$_2$O$_3$, MgO, CaO	1088	0.008	2.918	2.941	1.86	1.81	1.664	1.670	42.1	42.7	107.1	109.1
SA2	SiO$_2$, Al$_2$O$_3$, MgO, CaO	1097	0.012	2.907	2.941	1.86	1.80	1.653	1.659	41.2	42.0	105.4	107.5