The structure and properties of xZnO–(67-x)SnO–33P$_2$O$_5$ glasses: (III) Photoelastic behavior

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ABSTRACT

The effects of composition and structure on stress-induced birefringence were studied for glasses with the nominal molar compositions xZnO–(67-x)SnO–33P$_2$O$_5$. The photoelastic constant (PEC) changes systematically from negative values to positive values when ZnO replaces SnO, and PEC $\approx$ 0 when $x = 18.5$ mol%. The zero PEC composition can be predicted from the observed coordination numbers and bond lengths of the Zn-, Sn-, and P-polyhedra using an empirical model from the literature.

1. Introduction

Typically, the isotropic refractive index in a well-annealed glass does not influence the propagation behavior of polarized light. However, a refractive index anisotropy can be induced in a glass subjected to an applied stress and this photoelastic effect can affect the performance of an optical system. For example, liquid crystal displays [1–3] and fiber current sensors [4] require rigorous control of the propagation angle of linearly polarized light for maintaining the color rendering property or sensing property based on the Faraday effect. For display applications, evaluations of wavelength dependence are significant because a difference of PEC causes image distortion [2]. However, the photoelastic effect caused by stress-induced birefringence leads to undesired rotation of the polarized light in glass, reducing the optical performance of the device. Therefore, glasses with a photoelastic constant (PEC) near zero are desired for the polarization-controlling fiber devices [5], and lead silicate compositions have long been used for such applications.

Glasses based on SnO are candidates to replace the PbO-silicate glasses for new optical devices that require zero PEC [1, 6]. Silica glass has a relatively large and positive PEC of $+3.5 \times 10^{-12}$ Pa^{-1} [7, 8], and this is reduced through zero to negative values with the systematic addition of SnO [1, 9]. Glasses with zero PEC have also been identified in the binary SnO–P$_2$O$_5$ [1] and ternary ZnO–SnO–P$_2$O$_5$ systems [6]. The latter ternary system includes pyrophosphate glasses with the nominal molar compositions xZnO–(67-x)SnO–33P$_2$O$_5$, with properties

[10] and structures [11] that have been described in the first two parts of the present study.

Zwanziger and co-workers developed an empirical parameter, d/N_c, to correlate PEC with the glass composition and structure [1, 12]. Here, the cation-anion bond-length, d, is related to the metallicity of the bond and the coordination number of oxygen around the cation, N_c, is related to cation polarizability. Zwanziger et al. revealed that the summation of d/N_c for the various sites in a glass structure gave a fair estimation of the compositions with zero PEC for several different types of glasses [1].

Sn^{2+} has a similar electronic configuration to that of Pb^{2+}, and is free from restrictions of use in optical device such as those defined by RoHS2 and REACH. The mechanisms of stress induced birefringence, the so-called photoelastic effect, with highly polarized cations in oxide glass have been described by Mueller [13], Tashiro [14], and Weyl and Marboe [15], with the latter relating the effect to the distortion of electrons associated with oxygen ions by uniaxial stress. For PbO-silicate glasses with zero or negative PEC, the 6s electrons of Pb^{2+} respond to the pressure-induced polarization of the oxygen 2p electrons. The sign of PEC depends on the polarization of the anion network in the absence of highly polarized cations, since most glasses contain some cations (Si^{4+}, P^{5+}, B^{3+}) with negligible polarizabilities [16].

In this paper, we apply the quantitative structural information obtained from a series of xZnO–(67-x)SnO–33P$_2$O$_5$ glasses [11] to the Zwanziger model to better understand the relationships between structure and photoelastic response, and identify a new PbO-free
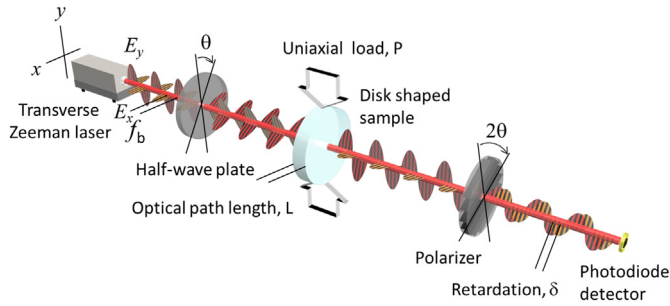
Fig. 1. An experimental setup for measuring the retardation of polarized light due to the uniaxial load for the determination of photoelastic constant (PEC).

composition with a zero PEC.

2. Experimental procedures

The preparation and properties of the xZnO–(67-x)SnO–33P$_2$O$_5$ glasses are described in Part I of this study [8]. In particular, the glass transition temperature increases from 270 to 370 °C when x increases from 0 to 50 [10]. Photoelastic constant measurements were usually made on polished glass disks ~10 mm or ~20 mm in diameter and ~10 mm tall [6, 17]; the disks with the larger diameters (~20 mm) were needed for glasses with low values of PEC ($< 0.5 \times 10^{-12}$ Pa^{-1}) in order to apply greater uniaxial loads (4–24 kg) without sample fracture, following the method described in [18]. Fig. 1 shows an experimental setup for the determination of the PEC. A frequency stabilized transverse Zeeman He–Ne laser (STZL) [18] operating at a wavelength of 632.8 nm was used as a light source. The STZL is composed of two linearly polarized light components (E$_x$ and E$_y$) crossing each other at right angles. The electric field displacements of the two components are written as Eqs. (1) and (2),

$$E_x = a_x \cos \omega t \tag{1}$$

$$E_y = a_y \cos(\omega t + 2\pi f_b t) \tag{2}$$

where a_x and a_y are the respective amplitudes of x and y components, ω is the optical frequency of x axis and f_b is the frequency difference between the x and y components. When the azimuth of fast axis is parallel to the x-axis, the phase of the y component is delayed by Δ. Then transmission intensity I can be written as Eq. (3),

$$I = a_x^2 + a_y^2 + 2a_x a_y \cos(2\pi f_b t + \Delta) \tag{3}$$

Fig. 1 shows an experimental setup for measuring the intensity of the light passing through the glass disk, to which a uniaxial load is applied by the load cell. The laser light that goes through both the half-wave plate and the linear polarizer has variations of the phase of intra-mode beat signal with the rotation angle of the half-wave plate [18] shown in Fig. 1. Here the rotation angle of the half-wave plate and that of the linear polarizer were synchronized to each other with a ratio of 1 to 2 by each driving system under control by the software (LabVIEW). The phase difference between the x and y components was maximized when the direction of a linearly polarized light in the STZL was parallel to the fast axis (x axis) and the difference was minimized in the direction perpendicular to the fast axis. The phase difference Δ, namely the amplitude of the waveform, was normalized by the wavelength of the light source (632.8 nm) and was transformed to the retardation δ by the equation of δ [nm] = Δ [degree] × 632.8/360 [nm/degree]. The plus or minus signs of PEC were determined by the direction of the detected fast axis for that of the external stress (y axis in Fig. 1). The measured PEC of silica glass was compared to reported value, 3.52×10^{-12} Pa^{-1} for fused silica [7]. The reproducibility of PEC measurements for each glass was $\pm 0.02 \times 10^{-12}$ Pa^{-1} due to variations in sample quality and composition. In detail, the error ($\pm 0.02 \times 10^{-12}$ Pa^{-1}) is the maximum variation of measured values
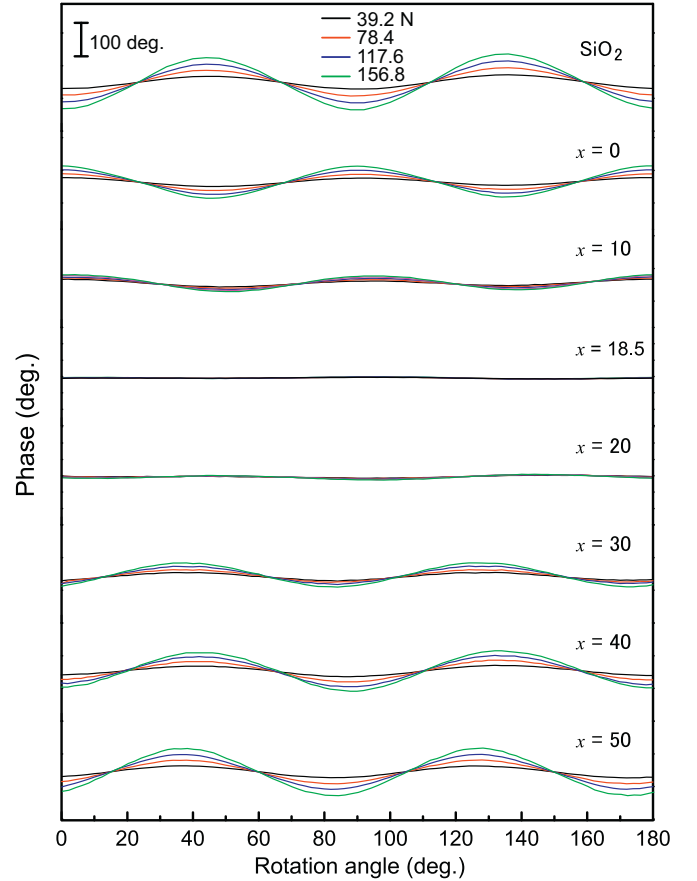

Fig. 2. Variations of phase changes with the rotation angle of the half-wave plate in the applied load range of ~40–157 N (~4–16 kg) for a fused SiO$_2$ glass (Corning 7940), and for the xZnO–(67-x)SnO–33P$_2$O$_5$ glasses, for x = 0, 10, 18.5, 20, 30, 40, and 50.

of one sample composition of this study found for the x = 40 and 45 samples; other compositions were reproducible to $\pm$ 0.005–0.01 $\times 10^{-12}$ Pa^{-1}.

3. Results

Fig. 2 shows variations of phase change (amplitude of wave) of a commercial fused SiO$_2$ glass (Corning 7940), and the xZnO–(67-x)SnO–33P$_2$O$_5$ glasses (x = 0, 10, 18.5, 20, 30, 40, and 50) as a function of the rotation angle of the half-wave plate from 0 to 180°. For glasses with $20 \leq x \leq 50$, the observed phase starts from the negative region (opposite behavior of the SiO$_2$), and the phase shifts to the positive region with an increase of the rotation angle of half-wave plate. For the x = 0 and x = 10 samples, the observed phase starts from the positive region, then shifts towards the negative region with increasing rotation angle, and so the sign of PEC is defined as minus (Figs. 3 and 4). For the x = 18.5 sample, the fast and the slow axes cannot be distinguished under the condition of uniaxial loading.

Fig. 3 shows the relationships between the retardation (δ) and the uniaxial load (P) for various compositions and commercial fused SiO$_2$ glass (Corning 7940) as a standard material. The PEC (C) was calculated from the measured slope (δ/P), using.

$$C = \frac{\pi D \delta}{8P} \tag{4}$$

where D is the diameter of a disk sample. The positive or negative sign of PEC was determined by the direction of the detected fast axis for that of the external stress (Fig. 2). The reported PEC of SiO$_2$ is $+3.53 \times 10^{-12}$ Pa^{-1} [7], which is in accordance with our result shown