Structure and Thermo-mechanical Response of TiO₂-SiO₂ Glasses to Temperature

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Abstract:

Structure and elastic moduli of xTiO₂ - (1-x) SiO₂ (x=0-10 mol%) glasses prepared via the sol-gel process have been investigated through *in-situ* high temperature Raman and Brillouin light scattering from room temperature to 1200 °C. Three other synthetic glasses prepared by the flame hydrolysis deposition (FHD) process, namely, synthetic silica glass (Corning 7980) and two titania silicate glasses (x=5.4 and 8.3), were also examined under the same conditions. The coefficients of thermal expansion of sol-gel glasses were measured up to 800 °C. Differences in properties of sol-gel glasses, FHD glasses, and literature values are presented and discussed. Changes in elastic moduli and Raman peak positions with composition and temperature are discussed. Young's modulus, bulk modulus, and shear modulus were found to decrease with increasing TiO₂ content and increase with temperature. A possible explanation for the anomalies in TiO₂-SiO₂ glasses is suggested based on the response of elastic moduli, Raman spectra, and coefficients of thermal expansion to temperature.

Introduction:

Titania is added to silica to produce ultra-low expansion (ULE) glasses, i.e., glasses that have zero or even negative coefficient of thermal expansion (CTE) at room temperature [1,2]. This unique characteristics has made them very useful in many applications, such as machine tool reference blocks, mirror blanks for telescopes and space satellites, and mask substrates for extreme ultra-violet lithography (EUVL) in the semiconductor industry [3]. However, the role titanium plays in the glass structure to give the ultra-low CTE is still under much speculation despite the extensive studies in the past few decades [1,2,4, and 5].

In addition, other properties of titania silicate glasses have been found to behave anomalously with increasing TiO₂ content. Shelby showed that the density is almost independent of the TiO₂ content below 10 wt% (7.7 mol%) TiO₂, while the sensitivity of density to fictive temperature increases with increasing TiO₂ [6,7]. An anomalous response of transverse sound velocity to temperature has been shown in several titania silicate glasses from 0 to 300 K, where a minimum occurs around 80 K, above which it increases with increasing temperature [8]. Young's modulus and Poisson's ratio were shown to increase with temperature from room temperature to 900 °C for Corning 7971 ULETM glass [9]. Young's modulus, bulk modulus and shear modulus of a TiO₂-SiO₂ glass with 8.4 wt% of TiO₂ were observed to decrease with pressure up to 2 GPa [10]. It has been suggested that the anomalous response of elastic moduli to temperature is connected to low thermal expansion of titania silicate glasses [8].

The structure of TiO₂-SiO₂ glasses has been studied frequently over the last several decades. Sandstrom et al. examined the glasses through extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge spectroscopy (XANES) to measure the coordination of Ti in the glass [11]. They showed that Ti⁴⁺ occupies primarily four-fold coordination, with a

small concentration of six-fold coordinated atoms. More recent XANES experiments by Henderson et al. [12] showed that Ti^{4+} actually occupies five-fold coordinated sites at concentrations below 3.6 wt% with further additions of Ti occupying primarily four-fold coordinated sites. Chandrasekhar et al. [13] examined $\text{TiO}_2\text{-SiO}_2$ glasses through infrared (IR) and Raman spectroscopy. Henderson and Fleet provided a more detailed Raman peak analysis [14] for a variety of TiO_2 containing glasses. The structure of $\text{TiO}_2\text{-SiO}_2$ glasses has also been studied through neutron diffraction by Pickup et al. [15], and through quantum-chemical calculations by Sokolov et al., who estimated their vibrational frequencies, IR and Raman spectra [16]. These structural studies have generally been in agreement about the behavior of Ti^{4+} cations in the glass at room temperature. They replace Si^{4+} cations in the glass structure, initially with a higher coordinated state, either five- or six-fold. After approximately 2 mol%, Ti^{4+} becomes primarily four-fold coordinated until it phase separates into six-fold coordinated crystals above 10 mol%. To date, the structure of $\text{TiO}_2\text{-SiO}_2$ glasses under conditions other than ambient has been much less well studied.

In order to understand the role of TiO_2 in silica glass, particularly, to gain a fundamental understanding of the anomalous thermal and elastic responses to temperature from the structure point of view, it is helpful to examine how the structure of the glass changes over a large composition and temperature range. In this study, we examined $\text{TiO}_2\text{-SiO}_2$ glasses from 0 - 10 mol% TiO_2 produced through the sol-gel process and three synthetic glasses with 0, 5.4, and 8.3 mol% TiO_2 prepared by the flame hydrolysis deposition (FHD) process by using *in-situ* high temperature Raman and Brillouin light scattering from room temperature to 1200 °C. Density and CTE up to 800°C of these glasses were also measured. Glasses produced through the sol-gel method are compared with other synthetic glasses by FHD in terms of density, thermal expansion, elastic moduli, and Raman spectra. Correlations are drawn between changes in Raman peak shifts with temperature, and changes in responses of elastic moduli and thermal expansion to temperature. A possible explanation for the anomalous responses of $\text{TiO}_2\text{-SiO}_2$ glasses to temperature is suggested.

Methods:

$\text{TiO}_2\text{-SiO}_2$ glasses were synthesized through the sol-gel process over the range of 0-10 mol% TiO_2 , based on the procedure used by Huang et al. [17]. TiO_2 content was limited in this range to avoid the tendency of glasses to crystallize [2,18]. Tetraethyl orthosilicate (TEOS) and titanium butanate were used as the silica source and the titania source, respectively. Methanol was used as the solvent, water and 0.1 M hydrochloric acid were used as catalysts for the hydrolysis process, and dimethyl formamide (DMF) was used as a drying control agent. Molar ratios of chemicals are 1: 12.8: 0.0025: 4.75: 0.85 for alkoxides: methanol: HCl: H_2O : DMF. Methanol and TEOS were mixed together, then the HCl and about half of the water were added to start the hydrolysis process. Titanium butanate was added dropwise with continuous stirring. Then the second portion of the water was added along with the DMF. The sol was stirred for approximately 30 minutes before being transferred to sample molds (plastic tubes with caps). The sols were gelled for one day at room temperature and then three days at 60°C. The gelled samples were removed from the molds and soaked in methanol for three days to remove any remaining water.

After soaking, the gels were dried under atmospheric conditions for one week. They were then heated at 60°C for three days to remove any remaining methanol/water. The dried

gels were sintered in a programmable tube furnace from room temperature to 1100 °C through the following steps (Fig. 1): ramp from room temperature to 70 °C at 1.5 °C/min; dwell at 70 °C for 60 minutes; ramp from 70 °C to 150 °C at 0.5 °C/min; dwell at 150 °C for 120 minutes; ramp from 150 °C to 200 °C at 0.2 °C/min; dwell at 200 °C for 120 minutes; ramp from 200 °C to 300 °C at 0.1 °C/min; dwell at 300 °C for 60 minutes; ramp from 300 °C to 350 °C at 0.2 °C/min; ramp from 350 °C to 400 °C at 0.5 °C/min; ramp from 400 °C to 700 °C at 1.0 °C/min; dwell at 700 °C for 240 minutes; ramp from 700 °C to 900 °C at 0.5 °C/min; ramp from 900 °C to 1100 °C at 6.0 °C/min; dwell at 1100 °C for 20 minutes; cool to room temperature in the furnace. Between 150 °C and 700 °C oxygen was flowed through the tube furnace at a rate of 60 ml/min to facilitate the decomposition of residual organics in the glass.

Fig. 1. Time-temperature profile for the sintering of sol-gel glasses. The area high-lighted in green represented time when oxygen flowed through the furnace.

Through this process cylindrical, bulk glass samples of up to 20 mm in length and 3 mm in diameter were prepared. As a reference, commercial synthetic silica glass (Corning 7980) and two $\text{TiO}_2\text{-SiO}_2$ glasses ($x=5.4$ and 8.3) prepared by FHD were used. The commercial synthetic silica glass was produced by the direct deposition of combusted silica precursor to transform into glass boule. On the other hand, $\text{TiO}_2\text{-SiO}_2$ glasses in this study were prepared through soot process. Fine soot particles of $\text{TiO}_2\text{-SiO}_2$ were produced by hydrolysis of gaseous silicon tetrachloride and titanium tetrachloride in oxygen-hydrogen flame. The porous soot preform was heat-treated at 1200°C for 3 h in air, at 1400°C for 4 h in vacuum, and at 1700°C for 4 h in vacuum. Then, the glasses were annealed at 1100°C for $x=5.4$ and 1040°C for $x=8.3$.

Density of samples was measured through the Archimedes method, using water as the liquid medium. Each sample was measured ten times, resulting in standard deviations between 0.005 and 0.01 g/cm³. Sintered sol-gel samples have densities between 2.15 and 2.18 g/cm³, very close to the values of $\text{TiO}_2\text{-SiO}_2$ glasses prepared through other methods [6-8], but lower

than the 2.20 g/cm³ of other synthetic glasses produced by FHD that were measured using the same method. Shelby [6] summarized densities of TiO₂-SiO₂ glasses from eight studies, where the majority of measured values are between 2.19-2.21 g/cm³ with the rest between 2.15 and 2.28 g/cm³. Densities of TiO₂-SiO₂ glasses prepared through the sol-gel process have been reported in the range of 2.10 to 2.36 g/cm³ [15], so the densities of our sol-gel samples seem reasonable, if generally slightly low.

Electron microprobe analysis (EMPA) was used to determine the composition and the homogeneity of four sol-gel TiO₂-SiO₂ glasses. Quartz and rutile were used as the Si and Ti references, respectively. Compositions were measured at 40 points across the surface for each sample. Nominal compositions, measured compositions, and standard deviations are shown in Table 1. Compositions are within 0.3 mol% of the nominal values, and have standard deviations of 0.04 mol% or less.

Table 1. Compositions and standard deviations (in mol%) of TiO₂-SiO₂ sol-gel glasses.

Sample	SiO ₂	SiO ₂ Std	TiO ₂	TiO ₂ Std
4 TiO ₂ - 96 SiO ₂	96.28	0.026	3.72	0.026
5.4 TiO ₂ - 94.6 SiO ₂	94.51	0.039	5.49	0.039
8.3 TiO ₂ - 91.7 SiO ₂	91.68	0.034	8.32	0.034
10 TiO ₂ - 90 SiO ₂	90.23	0.043	9.77	0.043

Fourier transform infrared spectroscopy (FTIR) was used to measure the water content in the glasses produced through the sol-gel process (Table 2). Hydroxyl concentrations were determined using the Beer-Lambert law, following procedures used in literature [19-21]. The water content in our sol-gel glasses is more than 2000 ppm, higher than that in Corning 7980 (800 ppm) and much higher than that in TiO₂-SiO₂ glasses (50 ppm) by FHD.

Table 2. OH content in two sol-gel glasses and three FHD synthetic glasses. Values for FHD synthetic glasses are the published values.

Glass	OH content (ppm)
5.4 TiO ₂ - 94.6 SiO ₂ by sol-gel	2250
8.3 TiO ₂ - 91.7 SiO ₂ by sol-gel	2965
Synthetic silica, FHD	800
5.4 TiO ₂ - 94.6 SiO ₂ , FHD	50
8.3 TiO ₂ - 91.7 SiO ₂ , FHD	50

In-situ high temperature Raman spectra and Brillouin spectra were collected using the procedure described by Guerette and Huang [22]. A 532.18 nm Verdi V2 DPSS green laser was used as the probing light source. Brillouin measurements were collected every 100 °C from room temperature to 1200 °C. Spectra were collected until the longitudinal peak from the emulated platelet geometry reached a minimum of 600 counts to ensure a good peak fit. Raman spectra were collected every 100 °C from room temperature up to 800 °C. Raman spectra were averaged over six 50 second collections. Above 800 °C, the thermal background becomes more and more significant with increasing temperature, and peaks become increasingly more difficult to be determined. The spectral resolution for the Raman spectra is $\sim 1 \text{ cm}^{-1}$.

Elastic moduli and Poisson's ratio were calculated from the sound velocities measured through Brillouin light scattering and the density of the glasses using equations 1-4.

$$E = \rho V_T^2 (3V_L^2 - 4V_T^2) / (V_L^2 - V_T^2) \quad (1)$$

$$\mu = \rho V_T^2 \quad (2)$$

$$\nu = (V_L^2 - 2V_T^2) / 2(V_L^2 - V_T^2) \quad (3)$$

$$K = E / (3(1 - 2\nu)) \quad (4)$$

where V_L and V_T are longitudinal and transverse sound velocities, ρ is sample density, E is Young's modulus, μ is shear modulus, ν is Poisson's ratio, K is bulk modulus. Standard deviations for Brillouin light scattering experiments at room temperature have been reported at 0.2 to 0.5 GPa for glasses of different compositions [22-24]. No error bars are presented for high temperature experiments as only one sample was measured for each composition.

The thermal expansion of several sol-gel samples were measured using a dilatometer between room temperature and 800 °C at a rate of 4 °C/min.

Results:

Elastic moduli of TiO_2 - SiO_2 glasses at room temperature are shown in Fig. 2. In FHD synthetic glasses, Young's modulus, bulk modulus, and shear modulus decrease with increasing TiO_2 content. Sol-gel glasses follow this trend, but tend to have slightly lower values than those of FHD synthetic glasses, with the difference being larger at low content of TiO_2 .

Fig. 2. Elastic moduli of TiO₂-SiO₂ glasses with respect to the TiO₂ content. Solid symbols represent values of sol-gel glasses, while open symbols are for FHD synthetic glasses.

Fig. 3. Change of a) Young's modulus, b) bulk modulus, c) shear modulus, and d) Poisson's ratio with temperature for TiO_2 - SiO_2 glasses produced through the sol-gel process.

Response of elastic moduli to temperature for sol-gel glasses and TiO_2 - SiO_2 glasses by FHD are presented in Figs. 3 and 4. For sol-gel glasses, the Young's modulus changes from 66 GPa to 78 GPa for SiO_2 glass and from 64 GPa to 74 GPa for 10 TiO_2 - 90 SiO_2 when heated from room temperature to 800 °C. Values for bulk modulus are much closer, with SiO_2 and 10 TiO_2 - 90 SiO_2 differing by less than 1 GPa at room temperature, and by 2 GPa at 800 °C. Shear modulus differs by 2 GPa at both room temperature and at 800 °C. Change in elastic modulus with temperature is calculated from a least-squares linear fit to curves in Fig. 3 and 4(a)-(c) from room temperature to 800 °C and summarized in Table 3. The temperature dependence of Young's modulus generally decreases with increasing TiO_2 . Temperature dependence of the bulk modulus shows a decrease between 1.6 TiO_2 and 5.4 TiO_2 , but not between SiO_2 and 1.6 TiO_2 or between 5.4 TiO_2 and 10 TiO_2 . Change in the temperature dependence of the shear

modulus is less than the noise between samples. Overall, elastic moduli appear to have a slightly reduced anomalous response to temperature with increasing TiO₂ content.

Table 3. Change of elastic modulus with respect to temperature between 23 °C and 800 °C.

Composition	$d(\Delta E)/dT$ (GPa/100 °C)	$d(\Delta K)/dT$ (GPa/100 °C)	$d(\Delta \mu)/dT$ (GPa/100 °C)
SiO ₂	1.35	1.03	0.47
1.6 TiO ₂ - 98.4 SiO ₂ , sol-gel	1.47	1.04	0.54
5.4 TiO ₂ - 94.6 SiO ₂ , sol-gel	1.21	0.89	0.46
8.3 TiO ₂ - 91.7 SiO ₂ , sol-gel	1.29	0.92	0.51
10 TiO ₂ - 90 SiO ₂ , sol-gel	1.09	0.88	0.39
Synthetic silica, FHD	1.05	0.86	0.38
5.4 TiO ₂ - 94.6 SiO ₂ , FHD	1.08	0.98	0.37
8.3 TiO ₂ - 94.6 SiO ₂ , FHD	0.81	0.79	0.27

Poisson's ratio increases by approximately 0.01 with the addition of 10 mol% TiO₂. The change in Poisson's ratio with temperature appears constant across all compositions (increase by 0.025 from room temperature to 1200 °C). An interesting feature is that in the range of 400 - 800 °C Poisson's ratio appears to remain constant with increasing temperature for sol-gel TiO₂-SiO₂ glasses (Fig. 3(d)). This is unexpected and does not appear in the FHD synthetic glasses (Fig. 4(d)).

Fig. 4. Change of a) Young's modulus, b) bulk modulus, c) shear modulus, and d) Poisson's ratio with temperature for sol-gel and FHD synthetic $\text{TiO}_2\text{-SiO}_2$ glasses.

Raman spectra of sol-gel and FHD synthetic glasses at room temperature are shown in Fig. 5. Intensities were normalized to the maximum of the 450 cm^{-1} peak. Peak positions are reported in Table 4 with those of synthetic silica glass, and 5.4 TiO_2 and 8.3 TiO_2 FHD synthetic glasses included as references. Peak positions of the sol-gel glasses agree quite well with FHD synthetic samples. The 450 cm^{-1} peak and peaks in the $900\text{-}1200\text{ cm}^{-1}$ range have been shown to be sensitive to sintering temperature, with the 450 cm^{-1} , 1060 cm^{-1} , 1100 cm^{-1} , and 1200 cm^{-1} peaks shifting to higher frequencies with increasing sintering temperature (thus, increasing density) and the 950 cm^{-1} peak shifting to lower frequencies with increasing sintering temperature [25].

Fig. 5. Room temperature Raman spectra of a) sol-gel and b) FHD synthetic glasses. Spectra intensity was frequency corrected and normalized to the intensity of the 450 cm^{-1} peak. Spectra are offset vertically for clarity.

Changes in intensity of Raman peaks in sol-gel $\text{TiO}_2\text{-SiO}_2$ glasses at room temperature in Fig. 5(a) are similar to those observed in FHD synthetic glasses in Fig. 5(b) and in literature [14,25]. With the addition of TiO_2 , two new peaks appear at $\sim 950 \text{ cm}^{-1}$ and at $\sim 1100 \text{ cm}^{-1}$. The intensity of these peaks increases with TiO_2 content. Peaks at $\sim 1060 \text{ cm}^{-1}$ and 1200 cm^{-1} remain visible with 1.6 mol% TiO_2 , but become indiscernible above 3 mol% TiO_2 as the $\sim 1100 \text{ cm}^{-1}$ peak grows in intensity. A peak at $\sim 650\text{-}700 \text{ cm}^{-1}$ appears in 6.1, 8.3, and 10 mol% TiO_2 sol-gel glasses and in both FHD synthetic glass. Most of the peak positions in the 8.3 mol% TiO_2 sol-gel sample are lower than those in the FHD synthetic sample of the same composition, suggesting that the sol-gel sample did not densify fully during the sintering process. The 10 TiO_2 sol-gel sample shows several small peaks in the $400\text{-}700 \text{ cm}^{-1}$ range. This sample is uniformly clear and transparent, so these peaks are likely due to slight crystallization of both rutile and anatase phases [14].

Table 4. Positions of Raman peaks at room temperature for sol-gel and FHD synthetic glasses.

Peak Position (cm^{-1})	SiO_2	1.6 TiO_2 98.4 SiO_2	3 TiO_2 97 SiO_2	4 TiO_2 96 SiO_2	6.1 TiO_2 93.9 SiO_2	8.3 TiO_2 91.7 SiO_2	10 TiO_2 90 SiO_2	FHD silica	FHD 5.4 TiO_2	FHD 8.3 TiO_2
450	450	456	450	443	449	436	437	449	443	442
490	490	485	485	481	492	486	484	491	490	488
600	605	601	599	600	609	-	-	604	601	602
665	-	-	-	-	-	683	656	-	695	702
800	801	802	798	796	810	803	804	794	806	809
950	-	953	944	938	942	936	936	-	939	936

1060	1062	-	-	-	-	-	-	1061	-	-
1100	-	1110	1108	1106	1112	1106	1105	-	1108	1107
1200	1203	-	-	-	-	-	-	1200	-	-

In-situ high temperature Raman spectra from room temperature to 800 °C are shown in Fig. 6 for sol-gel glasses. All Raman spectra are for temperatures below T_g , which is indicated by the slope change in elastic moduli between 900 and 1000 °C. For sol-gel SiO_2 in Fig. 6(a), peak shifts are quite small with increasing temperature, in good agreement with previous studies in literature [22, 26]. The 450 cm^{-1} peak shifts slightly toward higher frequencies, while the 490, 605, 1060, and 1200 cm^{-1} peaks shift toward lower frequencies. The 800 cm^{-1} peak does not appear to move with increasing temperature. With the addition of TiO_2 , the change in peak position with temperature increases for the majority of peaks. The shift in the 450 cm^{-1} peak increases with increasing TiO_2 content. The 490 cm^{-1} and 605 cm^{-1} peaks show little change in their temperature response with the addition of TiO_2 . The 800 cm^{-1} peak initially remains insensitive to temperature with the addition of up to 4 mol% TiO_2 , but at higher TiO_2 contents shows a significant shift to lower frequencies. The two new high frequency peaks that appear at 950 and 1100 cm^{-1} with the addition of TiO_2 show a much stronger temperature dependence than the 1060 and 1200 cm^{-1} SiO_2 peaks, shifting by $\sim 30\text{ cm}^{-1}$ and $\sim 20\text{ cm}^{-1}$ to lower frequency, respectively.

Fig. 6. Raman spectra of a) SiO₂, b) 3 TiO₂ - 97 SiO₂, c) 6.1 TiO₂ - 93.9 SiO₂, and d) 8.3 TiO₂ - 91.7 SiO₂ sol-gel glasses from room temperature to 800 °C. The intensity of Raman spectra was corrected for frequency and temperature, and then normalized to the intensity of the 450 cm⁻¹ peak. Spectra are offset vertically for clarity.

Fig. 7. Raman spectra of a) 5.4 TiO₂ and b) 8.3 TiO₂ FHD synthetic glasses from room temperature to 800 °C. The intensity of Raman spectra was corrected for frequency and temperature, and then normalized to the intensity of the 450 cm⁻¹ peak. Spectra are offset vertically for clarity.

In-situ high temperature Raman spectra for the two FHD synthetic TiO₂-SiO₂ glasses are presented in Fig. 7. Compared to Raman spectra of sol-gel glasses, the 450 cm⁻¹ peak tends to be higher in intensity in the FHD synthetic glasses, and the 490 cm⁻¹ and 600 cm⁻¹ peaks tend to be better defined, particularly at high temperatures. The 800, 950, and 1100 cm⁻¹ peaks are basically identical to the sol-gel glasses in terms of relative intensity, shape, and how the shape changes with temperature. The positions of peaks and the shift in position in response to temperature shows similarity between the FHD synthetic glasses and the sol-gel glasses.

The shift in peak positions from room temperature to 800 °C are summarized in Table 5. For the FHD synthetic samples, from room temperature to 800 °C, the 450 cm⁻¹ appears to shift further to higher frequencies with increasing TiO₂ content. The 490, 605, 800, 950, and 1100 cm⁻¹ peaks all appear to shift by the same amount in response to temperature regardless of the TiO₂ concentration. At room temperature, the peak positions of the FHD synthetic silica glass are similar to those of the sol-gel silica glass. However, the peak shifts are drastically different, particularly those of the 800, 1050, and 1200 cm⁻¹ peaks. Frequency shift from room temperature to 800 °C differs in magnitude by 14, 17, and 19 cm⁻¹ for these peaks, respectively. The smaller shift to lower frequency with increasing temperature in the sol-gel silica glass may indicate additional densification during high temperature Raman measurements.

Table 5. Raman peak shifts for TiO₂-SiO₂ glasses from room temperature to 800 °C. Blanks indicate that the peak is not expected or not distinguishable for that composition.

Peak Position (cm ⁻¹)	SiO ₂	3 TiO ₂ 97 SiO ₂	4 TiO ₂ 96 SiO ₂	6.1 TiO ₂ 93.9 SiO ₂	7.8 TiO ₂ 92.2 SiO ₂	8.3 TiO ₂ 91.7 SiO ₂	FHD silica	FHD TiO ₂	FHD TiO ₂
450	3	10	19	19	8	-4	1	12	17
490	-3	-3			-2		-2	-5	-5

600	-4	-3	-3	-7	-1		2	-2	-3
800	-1	-3	0	-13	-9	-13	-15	-12	-13
950		-35	-27	-24	-39	-28		-30	-28
1060	-6						-23		
1100		-23	-24	-19	-24	-21		-22	-22
1200	-9						-28

Fig. 8. a) CTE versus TiO_2 content for FHD synthetic glasses and sol-gel glasses from our and from Kamiya and Sakka's study [2], and b) CTE versus temperature for sol-gel glasses from our study. CTE values in part a) are average values from room temperature to 300°C for our sol-gel glasses and FHD synthetic glasses, and from room temperature to 700°C for Kamiya and Sakka's values [2].

CTE of our sol-gel glasses as a function of TiO_2 content is shown in Fig. 8(a), in comparison with those of FHD synthetic glasses and sol-gel glasses from Kamiya and Sakka's study [2]. Values of our sol-gel glasses are higher than FHD synthetic glasses and literature values for these glasses, which is likely caused by the lower density of sol-gel glasses and the higher water content in them compared to those produced through other methods [6-8]. However, the change in thermal expansion with composition matches literature quite well. By adding 10 mol% TiO_2 , the CTE decreases by $7 \times 10^{-7}/^\circ\text{C}$, while in literature the change by adding ~ 8 mol% TiO_2 is $8 \times 10^{-7}/^\circ\text{C}$ [2]. Change of the CTE for sol-gel glasses with temperature is shown in Fig. 8(b) for 0, 5.4, and 10 mol% TiO_2 . The change in CTE with temperature also matches well with literature. Schultz and Smyth [1] reported CTE values for TiO_2 - SiO_2 glasses with 0 - 9.45 wt% TiO_2 in the temperature range from 0 to 750°C . For these glasses the CTE decreases with increasing TiO_2 , and shows a reduced response to temperature with increasing TiO_2 up to 7.4 wt%; i.e., the CTE changes less with temperature, similar to the trend seen in Fig. 8(b).

Discussion:

Sol-gel $\text{TiO}_2\text{-SiO}_2$ glasses have comparable structure and properties to those of glasses of similar composition synthesized through other methods [1, 8, 9], as seen from results presented above, although it is not trivial to control the sol-gel process to get fully densified and/or homogenous glasses. Hirao et al. [8] measured the acoustic velocities of $\text{TiO}_2\text{-SiO}_2$ glasses in the low temperature region. Their samples were prepared by sintering powders at 1400 °C and acoustic velocities were measured by using the cube resonance method (a type of ultrasonic measurement). Hirao et al.'s measurements are plotted together with our measurements of sol-gel and FHD synthetic samples in Fig. 9(a). Values for 8.3 TiO_2 FHD synthetic glass line up with those of the 8 TiO_2 glass by Hirao et al., better than sol-gel values, while this is reversed for the 5.4 TiO_2 samples. The explanation for this is that the 5 TiO_2 sample prepared by Hirao has a density of 2.157 g/cm^3 , which is much closer to that of our sol-gel sample (2.16 g/cm^3) than FHD synthetic sample (2.2 g/cm^3). While the 8 TiO_2 sample prepared by Hirao has a density of 2.193 g/cm^3 , so it matches the FHD synthetic sample (2.2 g/cm^3) more closely than our sol-gel sample (~2.18 g/cm^3). The same trend is seen in Fig. 9(b), where the Young's modulus of our sol-gel sample is lower than FHD synthetic sample and Gulati's sample (2.2 g/cm^3) due to the lower density. Fig. 9(b) also shows the elastic response of $\text{TiO}_2\text{-SiO}_2$ glass to temperature is very sensitive to the subtle difference in sample preparation even using the same synthesis technique. Gulati's sample has TiO_2 content (5.7 mol%) close to that of the 5.4 TiO_2 FHD synthetic sample, the difference in Young's modulus and its variation with temperature seem beyond what can be explained by the small composition difference. On the other hand, it cannot be completely ruled out that different techniques for measuring elastic moduli may contribute to the discrepancy, especially at high temperatures.

Fig. 9. a) Transverse acoustic velocity and b) Young's modulus versus temperature in $\text{TiO}_2\text{-SiO}_2$ glasses prepared by different methods. Hirao's data in a) were taken from [8] and Gulati's data in b) were taken from [9].

This sensitivity of elastic properties to density in $\text{TiO}_2\text{-SiO}_2$ glasses is also apparent in their Raman spectra. Raman peak positions of sol-gel glasses at room temperature and the shifts from room temperature to 800 °C, presented in Tables 4 and 5 respectively, generally match

those of FHD synthetic glasses, but show significantly more scatter with changes in composition. A shift to lower frequencies would be expected with decreasing density; however, the observed shifts are a mix of lower and higher frequencies, indicating some level of non-uniformity of sol-gel glasses. It is highly likely that the fictive temperatures of the sol-gel glasses vary significantly, which would also contribute to the significant scatter observed. While the general trend in response to both composition and temperature are the same as FHD synthetic glasses, the scatter in sol-gel glasses makes discussion of structure-property relations difficult. Thus, the focus of the rest of the discussion will be mostly on the results of the FHD synthetic glasses and available data from literature.

To further discuss the changes in properties with structure in titania silicate glasses, it is necessary to briefly review the Raman peak assignments in silicate glass. McMillan et al. [27,28] summarized numerous Raman studies for silica and the effects of many different additives to the silica spectra. The high frequency bands at 1060 cm^{-1} and 1200 cm^{-1} are assigned to non-symmetric Si-O-Si stretching vibrations within the three dimensional network of cornering sharing tetrahedra. The mid-range peak at 800 cm^{-1} is associated with motion of Si within its tetrahedral cage. The peaks in the low frequency range are generally associated with bridging oxygens or the Si-O-Si bonds. The 450 cm^{-1} peak is assigned to symmetric stretching of bridging oxygens and the 490 cm^{-1} and 600 cm^{-1} peaks are attributed to breathing vibrations of 3- and 4-member ring defects within the glass. These assignments are rather simplistic, as many of the peaks in the Raman spectra are not symmetric, suggesting that they are a combination of multiple peaks. Kalampounias et al. provided a more thorough analysis of the SiO_2 Raman peaks, including weaker peaks and deconvoluting the non-symmetric peaks [26].

Raman peaks in the TiO_2 - SiO_2 system have been discussed by Chandrasekhar et al. [13], Perry et al. [25], and Henderson and Fleet [14], among others. The 450 , 490 , 600 , and 800 cm^{-1} peaks remain largely unchanged in shape and intensity with the addition of TiO_2 , indicating that TiO_2 does not significantly disrupt the silica network. The two new bands that appear at 950 and 1100 cm^{-1} with the addition of TiO_2 are difficult to assign with certainty. Their positions match those of Q^2 and Q^3 species of non-bridging oxygen present in sodium silicate glasses, respectively [24]. However, in sodium silicate glasses the Q^2 peak does not become significant relative to the SiO_2 main band until the Na_2O content is more than 30 mol%. Additionally, the disruption in the 450 , 490 , and 600 cm^{-1} silica bands observed in sodium silicate glasses is not present in TiO_2 - SiO_2 system. Henderson and Fleet [14] noted that these bands could be due to Ti-O vibrations if the motion is mainly caused by the oxygen atom. Sokolov et al. [16] found through quantum-chemical calculations that the band near 1050 cm^{-1} is due to single ^{47}Ti atoms (Ti-O-Si) and that the band near 940 cm^{-1} is from both single (Ti-O-Si) and double ^{47}Ti (Ti-O-Ti). In TiO_2 - SiO_2 system with low TiO_2 content, the population of Ti-O-Ti linkages is negligibly small [29], so these bands are assigned to anti-symmetric Ti-O and Si-O stretches in the Ti-O-Si bridges. This corresponds to the low disruption of the silica network with the addition of TiO_2 .

The addition of TiO_2 to SiO_2 causes a shift in position of the 450 cm^{-1} and 800 cm^{-1} peaks as seen in Raman spectra of the three FHD synthetic glasses in Fig. 5(b). The main band at 450 cm^{-1} shifts to lower frequencies with increasing TiO_2 content, which is expected with substitution of heavier Ti for Si within the glass network. This shift may also be partially attributed to an opening up and increased flexibility of the glass structure. Sandstrom et al. [11], measured bond length of the Ti-O bond as $1.81 \pm 0.02\text{ \AA}$ through EXAFS. This matches the bond lengths measured by Pickup et al. [15] through neutron diffraction, where the Ti-O is $1.84 \pm 0.01\text{ \AA}$ and the Si-O is $1.61 \pm 0.01\text{ \AA}$ for 8 TiO_2 - 92 SiO_2 glass. Farges et al. [30] reported the Ti-O bond as

1.84 Å with a bond valence 0.95 v.u. and the Si-O bond as 1.62 Å with a bond valence of 1.00 v.u. The increased bond length and related entropy with addition of TiO₂ to SiO₂ network are also manifested in the systematic decrease in strain and annealing points up to ~10wt% TiO₂ content [18] and the smearing of silica's scattering features [29].

The 800 cm⁻¹ peak shifts to higher frequencies with increasing TiO₂. Kalampounias et al. [26] deconvoluted this peak in silica to two bands at 790 and 830 cm⁻¹, which were assigned to apex-bridged tetrahedra and four membered supertetrahedra substructures, respectively. As the TiO₂ content increases the peak appears to become more symmetric, resulting in a shift of the peak to higher frequencies. So the addition of TiO₂ may promote more organized substructures within the glass network.

The addition of TiO₂ to SiO₂ reduces the elastic moduli of the glass as seen in Fig. 3 and in Gulati's study [9]. This can be attributed to the longer length and the weaker strength of Ti-O bonds compared to Si-O bonds. Response of silica glass to temperature is characterized by an anomalous increase in elastic moduli and an unusually low CTE. The addition of TiO₂ has a minor effect, if any, on the thermal response of the elastic moduli, but reduces the CTE. This change in thermal expansion due to the addition of TiO₂ is relatively small, compared to the difference between silica glass and quartz [26], but is technologically important as it causes the CTE to pass through zero [2,9].

The anomalous response of elastic moduli to temperature in silica glass has been attributed to transitions between α - and β -like six member rings [31-33], similar to ring structure in α - and β' -cristobalite [34], respectively. This transition is accompanied by a slight increase in the intra-ring Si-O-Si angles [35] as the bonds rotate into a more symmetric and stiffer conformation. However, the main 450 cm⁻¹ Raman band shifts to higher frequencies with increasing temperature. This suggests that O moves further from the Si-Si line as the Si-O bond length increases with temperature, in order to have a smaller average Si-O-Si angles [28]. This can occur through cooperative rotation of adjacent tetrahedra, which allows for conformational changes to occur below the glass transition temperature (T_g) due to the small energy barrier between different ring conformations [34]. It should be reminded that Raman spectra reported were collected at temperatures below T_g .

Adding TiO₂ to silica glass appears to preserve the transition between α -like and β -like rings with increasing temperature, based on the response of elastic moduli to temperature in Figs. 3 and 4. Raman spectra show that while the 450 cm⁻¹ band shifts to lower frequencies with increasing TiO₂ at room temperature, the peak shift to higher frequencies in response to temperature increases faster with TiO₂ content (Table 5). The shift in the 490 and 600 cm⁻¹ peaks with temperature remains at approximately -3 and -5 cm⁻¹, respectively, after the addition of TiO₂, suggesting that there is little change in the response of the breathing mode vibrations of 3- and 4-member rings with temperature. This makes sense given that the peak shifts in this temperature range are due primarily to conformation changes. 3- and 4-member rings are much tighter than the 6-member rings that undergo the transition between α - and β -ring conformations. It is reasonable that these small rings would only expand slightly with temperature and be resistant to significant rearrangement below the glass transition temperature.

The 800 cm⁻¹ peak shifts by 15 cm⁻¹ to lower frequency from room temperature to 800 °C in silica and by 12-13 cm⁻¹ in the FHD synthetic glasses. As these peaks occur from the motion of Si or Ti in Si-O or Ti-O stretching modes, the shift in these peaks corresponds to either an increase in the motion of Si and Ti with temperature or a change in the local structure to more open arrangements. As Ti is significantly more massive than Si, it is more likely to promote

smaller cation motions, which corresponds to the observed change in peak shift with temperature. It is also possible that the glass experiences a change in population from more organized structures (such as supertetrahedra suggested by Kalampounias) to more open apex-bridged tetrahedra, which requires only small angular changes [26] and is possible at temperatures below T_g .

The high frequency bands at 950 and 1100 cm^{-1} in TiO_2 - SiO_2 glasses shift to lower frequencies quickly with increasing temperature. The total shift of these peaks is approximately equal to those for the 1050 and 1200 cm^{-1} bands in pure silica (Table 5). If these peaks correspond to the anti-symmetric vibrations of oxygen in Si-O-Ti triplets, this suggests that the oxygen atom is moving further off the Si-Ti line, resulting in a decrease in the average inter-tetrahedral angles with temperature. This agrees with the change in symmetric vibrations of the oxygen atoms; the shift of the 450 cm^{-1} peak to higher frequencies with temperature. The addition of TiO_2 increases the free volume of the glass and reduces the stiffness of the network, which results in a significantly larger shift in the 450 cm^{-1} peak than in pure silica, due to a larger reduction in the average inter-tetrahedral angles with temperature.

Both anomalous responses of elastic moduli and thermal expansion in TiO_2 - SiO_2 glasses to temperature can be explained through this enhanced conformational and angular changes. It is important to remember that actual changes that occur with the addition of TiO_2 are relatively small compared to the differences that already exist between amorphous and crystalline silica. The CTE changes from $35 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ to $0.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ between quartz and silica glass [35]. It changes from $0.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ to $-0.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ with the addition of 8 mol% TiO_2 [2]. Thus, the addition of 8 mol% TiO_2 increases the difference in CTE between silica glass and quartz by slightly less than 3%. Based on the observed responses of elastic moduli, Raman spectra, and CTE to temperature, we propose the following explanation for the anomalous behaviors in TiO_2 - SiO_2 glasses.

It has been shown that Ti enters the silica network in primarily a five-fold coordination for the first 2.7 mol%, above which it primarily adopts a four-fold coordination [12]. Henderson et al. proposed that it is necessary to increase the flexibility and the open nature of the network in order to incorporate Ti in the tetrahedral network [12]. The lack of a change in density with the addition of heavier Ti agrees with the opening up of the network and increasing the free volume in the glass. This increase in free volume, lower Ti-O bond strength, and the heavier mass of the Ti atom all contribute to reduction of the stiffness of the glasses seen in room temperature elastic moduli (Fig. 2) and the shift of 450, 490, and 600 cm^{-1} Raman peaks to lower frequencies with addition of TiO_2 to SiO_2 (Table 4). The resulting opening up and increased flexibility of the glass structure promotes the conformational transitions between softer α -like and stiffer β -like rings, to compensate the sensitivity of weaker bonds to temperature, which explains the almost constant increase in the stiffness of the network with increasing temperature, regardless of TiO_2 content, as observed in *in-situ* high temperature Brillouin light scattering study. β -like rings occupy larger volumes than the α -like rings, so it would be expected that these conformational transitions would cause an increase in expansion. However, these conformational expansions occur in the relatively open tetrahedral network and can take advantage of the large free volume in the glass. While the inter-tetrahedral angles increase slightly within these rings, the cooperative rotation of adjacent tetrahedra results in a net decrease in the average inter-tetrahedral angle throughout the network, which explains the increased shift in the 450 cm^{-1} peak to higher frequencies in response to temperature in glasses with increasing TiO_2 content. These

rotations effectively allow the glass to counter balance the normal thermal expansion by rearranging the tetrahedron packing to reduce the free volume when temperature is increased.

Conclusions:

Structure and elastic moduli of $\text{TiO}_2\text{-SiO}_2$ glasses have been studied with regards to compositions and in their response to temperature through *in-situ* high temperature Raman and Brillouin light scattering. Glasses produced through both the sol-gel process and the FHD process were examined. Glasses produced through the sol-gel process were found to be clear, transparent, and homogeneous. Sol-gel glasses have lower elastic moduli than the FHD synthetic glasses, which can be attributed to the slightly lower densities, in the range of 2.15-2.18 g/cm^3 as opposed to 2.20 g/cm^3 for the FHD synthetic glasses. Sol-gel glasses are also characterized by a shift in Raman peaks to lower frequencies and an increased coefficient of thermal expansion, both of which match a lower density glass.

In the composition range where $^{[4]}\text{Ti}$ atoms are four-fold coordinated in silica network, the addition of TiO_2 reduces the elastic moduli and shifts Raman peaks at room temperature to low frequencies due to the heavier mass of Ti atoms, more importantly, resulting from a more open and flexible network given by the longer and weaker Ti-O bonds. The balance between increased mass and free volume from the addition of TiO_2 results in an almost constant density of $\text{TiO}_2\text{-SiO}_2$ glasses, independent of TiO_2 content.

Our *in-situ* high temperature studies show that the anomalies in $\text{TiO}_2\text{-SiO}_2$ glasses are similar to those in pure SiO_2 glass, which can be explained by the conformational and angular changes with temperature. The incorporation of TiO_2 into silica increases the network flexibility and the free volume of the glass while preserving the tetrahedral network structure, and thus facilitates the ring conformational transitions given enough thermal energy to overcome the energy barrier. The increased conformational transitions between softer α -like and stiffer β -like rings compensate the sensitivity of weaker bonds to temperature, so the amount of stiffening of the network with increasing temperature does not change obviously with TiO_2 content. The resulting opening up and increased flexibility of the glass structure promotes the cooperative rotation of adjacent tetrahedra, resulting in a net decrease in the average inter-tetrahedral angles. The larger change (reduction) of the average inter-tetrahedral angles with temperature is the underlying mechanism for the Raman band at 450 cm^{-1} to shift further to higher frequencies with increasing TiO_2 . The normal thermal expansion due to bond elongation with temperature is counter balanced by the free volume reduction facilitated by the cooperative rotation of adjacent tetrahedra assisted by thermal energy. As the network flexibility increases with the amount of TiO_2 addition to silica, the coefficient of thermal expansion decreases with TiO_2 content, as long as the silica tetrahedral network is preserved, i.e., in the composition range where $^{[4]}\text{Ti}$ atoms adopt four-fold coordinated sites.

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