Structure and Thermo-mechanical Response of Na₂O-TiO₂-SiO₂ Glasses to Temperature

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Abstract:

In-situ high temperature Raman spectroscopy, Brillouin light scattering (BLS), and dilatometry have been used to study the structure and properties of $x\text{Na}_2\text{O}-y\text{TiO}_2-(1-x-y)\text{SiO}_2$ glasses. Glasses with compositions $x=10, 15, 20$, and 25 , and $y=4, 7$, and 10 were prepared through a traditional melt-quench method. Addition of Na₂O decreases the temperature response of elastic moduli and increases the temperature response of the Poisson's ratio and the coefficient of thermal expansion (CTE). TiO₂ increases the magnitude of elastic moduli, but does not change their responses to temperature appreciably. TiO₂ has a much smaller effect in changing the CTE and the Poisson's ratio than Na₂O. Changes in the position and intensity of Raman peaks with temperature have been discussed. Changes in the temperature responses of mechanical and material properties have been correlated to the underlying structural changes reflected in the temperature responses of Raman peak positions and intensities.

1. Introduction

Studying the response of glasses to external stimuli, such as temperature or pressure, can provide valuable insights into understanding their behavior. Especially, the elastic and vibrational properties of glass are directly related to the interatomic forces and potentials, embodying the local structure and bonding information [1,2]. Therefore, perturbing the glass with thermal or mechanical agitation (e.g., temperature or pressure) and measuring changes in its elastic and vibrational properties, can be used as a probe to gain insights into the atomic level structure of glass. Vukceвич proposed a two-state model in 1972 for silica glass using changes in structure to explain the pressure and temperature dependence of compressibility, thermal expansion, and specific heat [3]. McMillan et al. and Kalampounias et al. studied how the structure of silica glass changed with temperature via *in-situ* Raman spectroscopy [4,5]. Deschamps et al. performed similar experiments with *in-situ* high pressure Raman spectroscopy [6]. However, our understanding of the behavior of glasses in response to external stimuli is still very limited outside of simple glass systems, such as silica, and building this understanding is critical towards developing glasses with improved properties [2,7].

Understanding the response of structure and properties to temperature is of particular interest for Ti containing glasses. Binary $\text{TiO}_2\text{-SiO}_2$ glasses are well known for their extremely low coefficients of thermal expansion [8,9]. These glasses also show an anomalous increase of elastic moduli with temperature [10,11]. Alkali-titania-silicate glasses and melts have also been shown to have unusual responses to temperature, particularly in regards to their compressibility [12,13], shear viscosity [14], partial molar volume and thermal expansivity [15], and heat capacity, viscosity, and configurational entropy [16]. The coordination state of Ti is highly dependent on the surrounding glass composition [15,17,18], which has been attributed to be the origin of some of the unusual properties of titania-containing glasses [15].

Most of the *in-situ* high temperature measurements of the structure and elastic properties of the $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ system has been focused on melts, with less attention given to the behavior of the glass between room temperature and the glass transition temperature. High temperature Raman studies have been limited to either a single composition [19] or a constant Na_2O content [20]. Studies on the high temperature elastic properties are even more limited [21]. In this work we examined the high temperature response of the structure, elastic moduli, and thermal expansion of $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ glasses. Structure was probed through *in-situ* high temperature Raman spectroscopy, elastic moduli through *in-situ* high temperature Brillouin light scattering (BLS), and thermal expansion through dilatometry. Glasses examined have compositions of $x\text{Na}_2\text{O-yTiO}_2\text{-(1-x-y)SiO}_2$, where $x=0.1, 0.15, 0.2$, and 0.25 and $y=0.04, 0.07$, and 0.10 . Room temperature study for this system has already been presented in a previous work [22]. Temperature responses of mechanical and material properties were correlated with the changes in the underlying structure reflected in the temperature responses of Raman peaks.

2. Methods

Sample preparation and general experimental details have already been presented elsewhere [22], so only a brief summary will be given here. Glasses were prepared in 80 g batches through a traditional melt-quench process using SiO_2 , TiO_2 , and NaHCO_3 powders of 99% purity or higher. Glasses were melted at $1500\text{ }^\circ\text{C}$ in a Pt-10Rh crucible, held at $1700\text{ }^\circ\text{C}$ for 20 minutes,

poured onto a preheated steel plate in air and then transferred to an annealing furnace and annealed at 600 °C for 1 hour. For thermal expansion measurements, glass bars with dimensions of 2" by 0.25" by 0.25" and finely ground ends and coarsely ground sides were prepared. For *in-situ* high temperature Raman and Brillouin experiments, samples were ground to a thickness of ~100 µm and polished to an optical finish using a CeO₂ slurry.

For high temperature light scattering experiments, Raman and Brillouin spectra were collected together. Further detail of the experimental setup can be found in our previous studies [22,23]. The sample was heated at 50 °C/min to the target temperature, held for five minutes to allow it to thermally equilibrate, the Brillouin spectrum was collected, followed by the Raman spectrum. *In-situ* high temperature Raman spectra were collected at 50, 200, 400, 600, and 800 °C. Brillouin spectra were collected every 50 °C, with measurements taken every 10 °C between 450 °C and 650 °C to better observe the behavior around the glass transition temperature. Raman spectra were corrected for frequency and temperature distortion [4], and then normalized to the maximum intensity of the main silica band (400-600 cm⁻¹).

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

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

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

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

$$\nu = (V_L^2 - 2V_T^2) / 2(V_L^2 - V_T^2) \quad (4)$$

where V_L and V_T are longitudinal and transverse sound velocities, ρ is sample density, E is Young's modulus, K is bulk modulus, μ is shear modulus, ν is Poisson's ratio.

Coefficient of thermal expansion (CTE) was measured using a dual pushrod differential dilatometer at Corning, Inc. Measurements were made from room temperature to 480 °C using a 4 °C/min heating rate and a 5 minute hold at the maximum temperature. Coefficients of thermal expansion were calculated every 25 °C from 50 °C to 475 °C. Sapphire was used as a reference material.

Where possible, error is presented as the standard deviation across multiple measurements. Only one sample was measured per composition for *in-situ* high temperature Raman and Brillouin light scattering experiments, for CTE and DTA measurements. Average standard deviations across five spots for Brillouin measurements at room temperature are 0.4 GPa in elastic moduli and 0.004 for the Poisson's ratio. Errors in the slopes of elastic moduli represent the standard deviations calculated through the linear least squares fit regression. T_g was estimated by the inflection point from DTA measurements, and error in T_g can be estimated as the range of glass transition, which is ± 12 °C or less from the inflection point.

3. Results

The change of CTE with temperature is shown in Fig. 1. The CTE is almost constant for samples with 10 Na₂O between 50 and 475 °C. As the Na₂O content is increased, the CTE shows an increased sensitivity to temperature, increasing as the temperature is increased.

Changes in the TiO_2 content have less effect on the CTE, and the small changes that are observed appear to shift from an increase in CTE at 10 Na_2O to a decrease at 25 Na_2O .

Fig. 1. CTE of Na_2O - TiO_2 - SiO_2 glasses versus temperature. 4, 7, and 10 mol% TiO_2 glasses are represented by black circles, red triangles, and blue squares, respectively.

Fig. 2. Temperature response of the elastic moduli for $\text{Na}_2\text{O}-\text{TiO}_2-\text{SiO}_2$ glasses with a) the Young's modulus, b) shear modulus, c) bulk modulus, and d) the Poisson's ratio. Glasses are offset into different panes by Na_2O content, with three TiO_2 contents in each pane. Black

circular symbols correspond to 4 mol% TiO_2 , red triangles to 7 mol% TiO_2 , and blue squares to 10 mol% TiO_2 .

Fig. 2a-d shows the response of elastic moduli to temperature for the $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ glasses examined in this study. Young's modulus changes from anomalous behavior at 10 Na_2O , becoming stiffer with increasing temperature, to intermediate behavior at 15 Na_2O , where it remains constant with respect to changes in temperature, and then normal behavior at 20 and 25 Na_2O , where it decreases with increasing temperature (Fig. 2a). The slope of Young's modulus with temperature decreases with increasing Na_2O content and does not show a consistent change with increasing TiO_2 content. Increasing Na_2O significantly lowers the magnitude of Young's modulus from 10 to 15 to 20, but the change from 20 to 25 shows a much smaller reduction. Increasing TiO_2 increases the magnitude of Young's modulus and increases the glass transition temperature.

The shear modulus behaves almost identically to Young's modulus, in that there is a decrease in magnitude, slope, and transition temperature with increasing Na_2O content, with the decrease in magnitude and slope only small between 20 and 25 Na_2O (Fig. 2b). Increasing the TiO_2 content increases the magnitude and the glass transition temperature without significantly changing the slope.

The bulk modulus increases in magnitude with both increasing TiO_2 and increasing Na_2O (Fig. 2c). The increase with Na_2O is large between 10 and 15, and between 20 and 25, but small between 15 and 20 mol%. Increasing the Na_2O content still decreases the slope, similar to the Young's modulus and shear modulus.

The Poisson's ratio shows a strong increase with increasing Na_2O and a weak increase with increasing TiO_2 (Fig. 2d). The increase in the Poisson's ratio with increasing Na_2O is reduced with each further addition of Na_2O , increasing by approximately 0.025, 0.02, and 0.015 when Na_2O content is increased from 10 to 15, from 15 to 20, and from 20 to 25, respectively. Additionally, the difference in slope from below to above the transition temperature increases significantly with increasing Na_2O , which is related to the increased fragility of the system [24]. Changing the TiO_2 content does not appear to affect the fragility much other than changing the glass transition temperature.

Fig. 3. Glass transition temperature versus number of bridging oxygen per network forming cation. Differential thermal analysis (DTA) data is from Scannell et al. [25]. T_g values from BLS are measured as the temperature at which the slope of the shear modulus changes.

Fig. 3 shows the glass transition temperature (T_g) for $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ glasses as fit from the temperature at which the slope of the shear modulus changes and from the differential thermal analysis (DTA) [25]. T_g of glasses with 10 Na_2O from DTA are extrapolated from samples with higher Na_2O content for comparison with Brillouin data. T_g from BLS experiments occurs at $\sim 0.9T_g$ of DTA measurements. Between 20 and 25 Na_2O , or from 3.6 to 3.4 bridging oxygens per network forming cation, T_g remains approximately constant. A more detailed explanation of how the number of bridging oxygens per network forming cation is calculated can be found in Scannell et al. [22].

The temperature responses of the elastic moduli including the Young's modulus, shear modulus, bulk modulus and the Poisson's ratio below and above T_g are shown in Fig. 4(a-d). The slopes below T_g are obtained through a least squares linear fit to the elastic moduli between 100 °C and 400 °C and the slopes above T_g through a least squares fit from where a visible slope change begins to occur or 500 °C if the slope does not noticeably change. Below T_g , slopes of the Young's modulus and shear modulus decrease as the number of bridging oxygen per network cation decreases, but between 3.6 and 3.4 the slope remains almost constant, similar to the behavior of T_g in this composition range. The bulk modulus exhibits a continuous decrease in slope with decreasing number of bridging oxygen. Slopes of the Poisson's ratio are extremely small and show significant scatter, but there is an overall trend of a decreasing slope with decreasing number of bridging oxygen.

Above T_g , the slopes of elastic moduli with temperature change in a similar way with changes in composition as below T_g . The slopes of the Young's modulus, shear modulus, and bulk modulus decrease with decreasing number of bridging oxygen. However, the slope of the Young's modulus decreases significantly more with decreasing number of bridging oxygen. Additionally, the sample with 3.47 bridging oxygen shows a steeper slope for the Young's modulus and the Poisson's ratio than the rest of the glasses examined in this study.

Fig. 4. Temperature response of elastic moduli versus the number of bridging oxygen per network forming cation below and above T_g for a) the Young's modulus, b) shear modulus, c) bulk modulus, and d) the Poisson's ratio.

Fig. 5. Raman spectra for (10, 15, 20, and 25) Na₂O - 7 TiO₂ - SiO₂ glasses at 50, 200, 400, 600, and 800 °C. Spectra intensities are normalized to the maximum intensity in the 400-600 cm⁻¹ region and offset vertically with increasing temperature for clarity.

Raman spectra for Na₂O - 7 TiO₂ - SiO₂ glasses at 50, 200, 400, 600, and 800 °C are shown in Fig. 5a-d. The spectra were fit with Gaussian peaks using Fityk [26]. An example of the peak deconvolution is shown in Fig. 6. Peaks were fit at 460, 490, 540, 600, 720, 800, 840, 900, 980, 1080, and 1100 cm⁻¹. Peak positions and intensities from the fits are given in Table 1. As in any spectrum deconvolution, peak positions and intensities are dependent on the initial parameters used for fitting. Errors in peak positions and intensities are difficult to determine precisely. For well defined peaks, such as the 900 cm⁻¹ peak, the position is accurate to ± 2 cm⁻¹, while for small peaks that are largely underneath other peaks, such as the 340 or 720 cm⁻¹ peaks, the error in peak position could be ± 5 cm⁻¹ or more. Error in the peak intensity is $\leq \pm 0.01$ for small peaks and

± 0.02 for larger peaks. Additional small peaks appear at ~ 340 and ~ 460 cm^{-1} in most, but not all samples. For clarity, the large peak that is located between 460 and 520 cm^{-1} will be referred to as the main band and the small peak that occurs at 460 cm^{-1} will be referred to as the 460 cm^{-1} peak. The position and intensity of these peaks are also reported in Table 1.

Fig. 2. Deconvoluted Raman spectrum of 15 Na_2O - 4 TiO_2 - 81 SiO_2 glass at room temperature. Individual peaks are given in red, the overall fitted spectrum in green, and the measured Raman spectrum in black.

The silica main band increases in frequency and decreases in intensity between 10 and 25 Na_2O . The response of the main band to temperature remains almost unchanged with changing Na_2O , shifting by to higher frequencies and changing by less than 0.07 in relative intensity from 50 to 800 $^\circ\text{C}$ in all samples.

The 540 cm^{-1} peak also shifts to higher frequencies and increases in intensity from 0.1 to 0.36 with increasing Na_2O . In response to temperature, the peak position remains constant at 10, 15, and 20 Na_2O , and shifts from 552 to 538 cm^{-1} at 25 Na_2O . The intensity decreases slightly between 50 and 800 $^\circ\text{C}$.

Peaks at 490 and 600 cm^{-1} are assigned to 4- and 3-membered Si-O ring breathing modes, respectively. Position of these peaks do not change with either Na_2O composition or temperature. The relative intensity of the 490 cm^{-1} peak remains constant with increasing Na_2O , while the intensity of the 600 cm^{-1} peak increases. Intensities of both peaks are insensitive to temperature.

The position of the 720 cm^{-1} peak generally remains between 720 and 730 cm^{-1} for 10, 15, and Na_2O contents and the position appears relatively insensitive to temperature. The 25 Na_2O glasses show more variation, which could be due to the low intensity of this peak in the spectra. The intensity of the 720 cm^{-1} peak decreases significantly with increasing Na_2O . Additionally, the temperature response of the intensity decreases with increasing Na_2O , changing from positive to negative between 15 and 20 Na_2O .

The 800 cm^{-1} peak position is relatively insensitive to composition and temperature for 10, 15, and 20 Na_2O contents. At 25 Na_2O it decreases and shifts to lower frequencies with increasing temperature. The intensity of the 800 cm^{-1} peak remains fairly constant from 10 to 20 Na_2O , and the 10, 15, and 20 Na_2O compositions see an intensity increase with temperature. At 25 Na_2O the intensity decreases slightly with temperature.

The 840 cm^{-1} peak shifts slightly to lower frequencies with both increasing Na_2O and increasing temperature. The sensitivity to temperature increases with increasing Na_2O content, from a shift of -3 cm^{-1} at 10 Na_2O to -10 cm^{-1} at 25 Na_2O . The intensity of the 840 cm^{-1} peak generally decreases with increasing Na_2O content, with the temperature response changing from slightly negative to slightly positive.

The 900 cm^{-1} peak exhibits a weak, negative frequency response to temperature which remains constant at all Na_2O contents. Increasing Na_2O causes a small shift to lower frequencies. The intensity of the 900 cm^{-1} peak increases with increasing temperature and roughly with increasing Na_2O .

Position of the 980 cm^{-1} is relatively insensitive to Na_2O content, but the response to temperature becomes increasingly negative with increasing Na_2O . The intensity has a weak, negative response to temperature and is fairly insensitive to Na_2O content.

The peak at 1080 cm^{-1} decomposes into two peaks, a large peak at 1080 and a smaller peak at 1100 cm^{-1} . At 10 and 15 Na_2O , the peak position is relatively insensitive to temperature and the intensity increases slightly. At 20 and 25 Na_2O , the peak position decreases with temperature, while the intensity increases slowly between 50 and 400 $^{\circ}\text{C}$ and then much faster between 400 and 800 $^{\circ}\text{C}$.

The peak at 1100 cm^{-1} peak also shows a change in behavior. At 10 and 15 Na_2O , the position is relatively constant with increasing temperature. The position increases at 20 and 25 Na_2O and decreases with temperature. The intensity increases significantly between 20 and 25 Na_2O . With the large increase in intensity between 20 and 25 Na_2O , there is also a significant change in the response to temperature.

To summarize the effects of Na_2O on the peak positions, intensities, and their responses to temperature, increasing the Na_2O content from 10 to 25 mol% causes the main band, 540, 1080, and 1100 cm^{-1} peaks to shift to higher frequency and the 900 cm^{-1} peak to shift to lower frequencies. Changes in composition have only small effects on the positions of the 490, 600, 720, 800, 840, and 980 cm^{-1} peaks. For the temperature responses of these peaks, increasing the Na_2O content causes the 540, 980, and 1100 cm^{-1} peaks to have an increased negative dependence of peak position to temperature, with the temperature responses of the other peaks remaining unchanged.

In regard to intensity, increasing the Na_2O content decreases the intensities of the main band and the 720 cm^{-1} peaks, increases the intensities of the 540, 600, 1080, and 1100 cm^{-1} peaks, and either has no effect or an inconsistent effect on the intensities of the 490, 800, 840, 900, and 980 cm^{-1} peaks. The temperature response of the 540 and 720 cm^{-1} peaks become more negative with increasing Na_2O , and all the other peaks remain largely unaffected by changing Na_2O content. An exception to this is the 800 and 840 cm^{-1} peaks, which see little change between 10 and 20 Na_2O but a large change between 20 and 25 Na_2O . The response of the 800 cm^{-1} peak becomes more negative and the response of the 840 cm^{-1} peak becomes more positive. The 1100 cm^{-1} peak shows a large change between 15 and 20 Na_2O .

Fig. 7. High temperature Raman spectra for 10 Na₂O - TiO₂ - SiO₂ and 25 Na₂O - TiO₂ - SiO₂ glasses. Spectra are normalized to the maximum in the 400-600 cm⁻¹ region and offset vertically with increasing temperature for clarity.

Changes in high temperature Raman spectra with changing TiO₂ content is shown in Fig. 7a-d for 10 and 25 Na₂O glasses, respectively. Peak positions and intensities from Fityk peak fitting are given in Table 1. The main band shifts slightly to higher frequencies when TiO₂ is increased, increasing more at higher Na₂O contents. It shifts to higher frequencies linearly with temperature. The intensity of the main band increases with increasing TiO₂, and the temperature response is constant with increasing TiO₂ contents.

The 540 cm⁻¹ peak shows little response to TiO₂ at 10 Na₂O. However, at 25 Na₂O it has a large change between 4 and 10 TiO₂, shifting to higher frequencies and decreasing in intensity. The temperature response of the peak position does not appear to change with TiO₂ content. The intensity temperature response increases with TiO₂ content at 10 Na₂O, but decreases slightly or remains constant at 25 Na₂O.

The position of the 490 and 600 cm^{-1} peaks are both insensitive to changes in temperature or TiO_2 content at 10 Na_2O , although the 600 cm^{-1} peak is not visible in the 10 Na_2O - 10 TiO_2 spectra until 800 $^\circ\text{C}$. At 25 Na_2O , the 490 cm^{-1} peak shows a slight shift to lower frequencies with increasing TiO_2 content, and the shift with temperature changes from slightly positive to almost zero at 10 TiO_2 . The 600 cm^{-1} peak is still insensitive to temperature and TiO_2 content at 25 Na_2O . The intensities of the two breathing-mode peaks decrease in intensity and have a more negative temperature response as TiO_2 content increases.

The 720 cm^{-1} peak shifts to lower frequencies with increasing TiO_2 content. Increasing TiO_2 also causes the temperature response to increase from slightly negative to slightly positive. The intensity of the 720 cm^{-1} peak increases with TiO_2 content, and the temperature response of the intensity changes slightly with increasing TiO_2 , but not in a consistent way.

The 800 cm^{-1} peak shifts slightly to higher frequencies with increasing TiO_2 . At 10 Na_2O , the 800 cm^{-1} peak position is insensitive to temperature, while at 25 Na_2O it shifts to lower frequencies with increasing temperature, and this shift is greater at higher TiO_2 contents. The intensity of the 800 cm^{-1} peak increases with increasing TiO_2 . The temperature response of the intensity is slightly positive at 10 Na_2O and almost constant at 25 Na_2O .

The 840 cm^{-1} peak position shifts to higher frequencies slightly with increasing TiO_2 . The temperature response decreases slightly with increasing TiO_2 at 10 Na_2O and decreases slightly more at 25 Na_2O . The intensity does not change significantly with increasing TiO_2 for 10 Na_2O glasses and increases for 25 Na_2O glasses. The temperature response changes from negative to positive with increasing TiO_2 .

The 900 cm^{-1} peak does not change significantly in position with changing TiO_2 content. The temperature dependence does not change with TiO_2 except for 25 Na_2O glasses whose temperature dependence becomes more negative with increasing TiO_2 . The intensity of the 900 cm^{-1} peak increases with increasing TiO_2 , but the temperature dependence is independent of TiO_2 content.

The 980 cm^{-1} peak position shifts slightly to lower frequencies with increasing TiO_2 and there is no apparent change in the temperature response with TiO_2 content. The intensity of the 980 cm^{-1} peak increases with increasing TiO_2 , and generally has a negative temperature dependence. The temperature dependence becomes larger with increasing TiO_2 for 10 Na_2O glasses and remains constant for 25 Na_2O glasses.

The 1080 cm^{-1} peak shifts to lower frequencies with increasing TiO_2 and increasing temperature. For 10 Na_2O glasses, the intensity also decreases with increasing TiO_2 content. For 25 Na_2O glasses, the intensity is roughly constant for all TiO_2 contents and the temperature dependence is positive.

The 1100 cm^{-1} peak shifts significantly to lower frequencies with increasing TiO_2 content for 10 Na_2O glasses, but not for 25 Na_2O glasses. The temperature response in the 10 Na_2O glasses shifts from negative to zero with increasing TiO_2 , while in the 25 Na_2O glasses it has a constant, negative response for all TiO_2 contents. The intensity of the 1100 cm^{-1} peak decreases with increasing TiO_2 , while the change in temperature response is independent of TiO_2 .

To summarize the effects of changing TiO_2 content at 10 Na_2O , increasing the TiO_2 content causes the main band and the 800 cm^{-1} peak to shift to higher frequencies and the 1080 and 1100 cm^{-1} peaks to shift to lower frequencies. It also makes the response to temperature more positive for the main band, less negative for the 1100 cm^{-1} peak, and more negative for the 1080 cm^{-1} peak. At 25 Na_2O , increasing the TiO_2 content causes the main band and the 540 cm^{-1} peak to shift to higher frequencies and the 1080 cm^{-1} peak to shift to lower frequencies. The responses to

temperature become more positive for the main band and change from positive to neutral for the 490 cm^{-1} peak.

For 10 Na_2O glasses, the intensity of the main band, 720, 800, 900, and 980 cm^{-1} peaks increase and the intensity of the 1080 and 1100 cm^{-1} peaks decrease with increasing TiO_2 . The temperature response of intensities becomes less negative for the main band, changes from negative to positive for the 840 cm^{-1} peak, and becomes more negative for the 490, 540, and 980 cm^{-1} peaks. For the 25 Na_2O glasses, increasing the TiO_2 content causes the main band, 720, 800, 840, 900, and 980 cm^{-1} peaks to increase in intensity and the 490, 540, 600, and 1100 cm^{-1} peaks to decrease in intensity. This also causes the temperature response of the 490 cm^{-1} peak to become slightly negative, the 600 and 1100 cm^{-1} peaks to change from positive to neutral, and the 840 cm^{-1} peak to change from neutral to negative.

Table 1

Peak positions and intensities of high temperature Raman spectra for Na_2O - TiO_2 - SiO_2 glasses.

10 Na_2O - 4 TiO_2 - 86 SiO_2												
Peak Positions												
Position (cm^{-1})	Main band	460	490	540	600	720	800	840	900	980	1080	1100
50 °C	446	458	491	537	603	732	795	847	909	977	1077	1088
200 °C	449	458	491	534	599	730	796	844	907	976	1076	1087
400 °C	450	454	490	534	604	725	792	844	906	973	1074	1086
600 °C	453	459	490	531	605	717	796	844	904	974	1074	1084
800 °C	458	467	494	530	603	706	796	844	907	978	1079	1083
Peak Intensity												
Intensity (a.u.)	Main band	460	490	540	600	720	800	840	900	980	1080	1100
50 °C	0.88	0.09	0.12	0.05	0.02	0.21	0.37	0.34	1.50	0.64	0.83	0.30
200 °C	0.87	0.09	0.12	0.05	0.02	0.23	0.41	0.29	1.53	0.58	0.85	0.29
400 °C	0.86	0.09	0.13	0.06	0.03	0.23	0.43	0.36	1.58	0.56	0.88	0.30
600 °C	0.86	0.10	0.11	0.05	0.04	0.22	0.51	0.22	1.67	0.45	0.90	0.28
800 °C	0.83	0.10	0.13	0.05	0.06	0.18	0.54	0.16	1.70	0.40	0.98	0.23

10 Na ₂ O - 7 TiO ₂ - 83 SiO ₂													
Peak Positions													
Position (cm ⁻¹)	340	Main band	460	490	540	600	720	800	840	900	980	1080	1100
50 °C		432	458	488	532		724	798	847	906	973	1072	1081
200 °C		468	461	488	545	602	726	796	844	908	976	1069	1078
400 °C	334	466	468	491	539		728	800	847	910	978	1066	1083
600 °C	340	467	470	491	541	602	726	797	841	907	978	1058	1083
800 °C	331	471	469	490	534	605	722	798	844	908	979	1069	1081
Peak Intensity													
Intensity (a.u.)	340	Main band	460	490	540	600	720	800	840	900	980	1080	1100
50 °C		0.89	0.08	0.14	0.10		0.30	0.56	0.39	2.22	1.26	0.74	0.18
200 °C		0.84	0.06	0.16	0.04	0.10	0.31	0.43	0.38	1.92	0.88	0.64	0.17
400 °C	0.10	0.92	0.04	0.08	0.05		0.40	0.52	0.41	2.28	0.86	0.82	0.16

600 °C	0.10	0.93	0.04	0.07	0.04	0.05	0.44	0.51	0.32	2.23	0.56	0.86	0.15
800 °C	0.07	0.92	0.04	0.08	0.03	0.06	0.41	0.58	0.31	2.42	0.56	0.88	0.18

10 Na₂O - 10 TiO₂ - 80 SiO₂													
Peak Positions													
Position (cm ⁻¹)	340	Main band	460	490	540	600	720	800	840	900	980	1080	1100
50 °C	330	451	457	491	535		725	807	853	910	973	1062	1077
200 °C	330	458	455	490	536		723	807	855	909	971	1068	1075
400 °C	324	462	457	490	535		725	806	844	907	972	1054	1075
600 °C	320	465	460	490	532		724	806	845	905	969	1055	1070
800 °C	314	468	462	492	532	605	744	806	849	908	970	1051	1076
Peak Intensity													
Intensity (a.u.)	340	Main band	460	490	540	600	720	800	840	900	980	1080	1100
50 °C	0.05	0.92	0.05	0.11	0.08		0.54	0.85	0.43	2.36	1.40	0.67	0.11
200 °C	0.06	0.91	0.06	0.12	0.09		0.54	0.91	0.45	2.51	1.52	0.72	0.12
400 °C	0.07	0.91	0.05	0.10	0.06		0.53	0.86	0.29	2.32	1.07	0.72	0.14
600 °C	0.05	0.91	0.04	0.09	0.05		0.52	0.88	0.32	2.35	1.00	0.74	0.12
800 °C	0.04	0.90	0.06	0.09	0.03	0.04	0.58	0.68	0.49	2.5	0.71	0.93	0.07

15 Na₂O - 7 TiO₂ - 78 SiO₂												
Peak Positions												
Position (cm ⁻¹)	Main band	460	490	540	600	720	800	840	900	980	1080	1100
50 °C	453	460	491	530	604	725	795	842	906	975	1068	1083
200 °C	457	456	489	530	601	726	800	846	905	973	1069	1079
400 °C	466	455	491	527	605	725	800	846	903	972	1066	1077
600 °C	467	451	489	523	605	724	800	842	901	968	1065	1074
800 °C	488		489	530	599	732	796	834	902	969	1066	1086
Peak Intensity												
Intensity (a.u.)	Main band	460	490	540	600	720	800	840	900	980	1080	1100
50 °C	0.80	0.10	0.19	0.06	0.04	0.26	0.48	0.37	1.78	0.81	0.70	0.15
200 °C	0.81	0.16	0.20	0.06	0.04	0.29	0.50	0.32	1.78	0.84	0.74	0.15
400 °C	0.82	0.11	0.18	0.06	0.04	0.31	0.55	0.28	1.89	0.75	0.81	0.18
600 °C	0.82	0.09	0.18	0.06	0.04	0.30	0.59	0.31	2.01	0.70	0.85	0.17
800 °C	0.86		0.12	0.07	0.03	0.33	0.66	0.40	3.28	0.75	1.45	0.22

20 Na₂O - 7 TiO₂ - 73 SiO₂													
Peak Positions													
Position (cm ⁻¹)	340	Main band	460	490	540	600	720	800	840	900	980	1080	1100
50 °C	351	508	458	495	541	584	732	796	849	909	978	1082	1096
200 °C	344	514	458	496	541	582	728	798	850	908	977	1081	1094
400 °C	342	521	455	497	543	585	724	795	846	906	975	1076	1095

600 °C	336	526	456	495	541	585	731	797	846	905	974	1077	1092
800 °C	340	532	458	498	541	592	730	798	845	916	973	1077	1091
Peak Intensity													
Intensity (a.u.)	340	Main band	460	490	540	600	720	800	840	900	980	1080	1100
50 °C	0.04	0.70	0.05	0.16	0.30	0.08	0.24	0.44	0.47	2.71	1.27	1.32	0.24
200 °C	0.04	0.71	0.04	0.15	0.27	0.08	0.24	0.49	0.43	2.72	1.20	1.30	0.26
400 °C	0.04	0.72	0.04	0.16	0.27	0.07	0.20	0.51	0.38	2.82	1.10	1.33	0.31
600 °C	0.03	0.76	0.03	0.14	0.23	0.07	0.23	0.55	0.47	3.14	1.00	1.44	0.31
800 °C	0.03	0.77	0.04	0.15	0.21	0.12	0.18	0.63	0.72	2.92	0.97	1.74	0.28

25 Na₂O - 4 TiO₂ - 71 SiO₂													
Peak Positions													
Position (cm ⁻¹)	340	Main band	490	540	600	720	800	840	900	980	1080	1100	
50 °C	337	498	498	551	597	736	790	837	901	978	1086	1100	
200 °C	346	480	497	550	598	736	789	846	900	978	1091	1097	
400 °C	338	504	504	549	595	735	789	841	898	971	1083	1095	
600 °C	351	501	504	547	595	728	789	837	898	972	1081	1093	
800 °C	333	516	510	545	595	742	787	831	898	974	1077	1092	
Peak Intensity													
Intensity (a.u.)	340	Main band	490	540	600	720	800	840	900	980	1080	1100	
50 °C	0.04	0.63	0.14	0.36	0.16	0.06	0.26	0.14	1.55	0.57	1.22	0.68	
200 °C	0.03	0.58	0.17	0.40	0.20	0.03	0.22	0.07	1.65	0.66	1.60	0.45	
400 °C	0.03	0.65	0.15	0.30	0.17	0.06	0.28	0.20	1.70	0.58	1.40	0.75	
600 °C	0.03	0.66	0.18	0.25	0.20	0.05	0.30	0.17	1.93	0.50	1.40	0.90	
800 °C	0.02	0.62	0.17	0.25	0.28	0.07	0.23	0.16	2.11	0.36	1.60	0.98	

25 Na₂O - 7 TiO₂ - 68 SiO₂													
Peak Positions													
Position (cm ⁻¹)	340	Main band	460	490	540	600	720	800	840	900	980	1080	1100
50 °C	342	509	447	491	551	597	712	791	840	897	973	1083	1098
200 °C	340	502	452	491	550	597	728	789	841	897	973	1080	1096
400 °C	340	516	445	489	549	597	722	788	837	895	967	1074	1094
600 °C	330	528	448	491	546	594	732	787	836	895	967	1072	1092
800 °C	331	539	454	491	538	591	742	789	830	893	961	1067	1091
Peak Intensity													
Intensity (a.u.)	340	Main band	460	490	540	600	720	800	840	900	980	1080	1100
50 °C	0.04	0.66	0.03	0.14	0.36	0.13	0.06	0.36	0.16	2.34	0.84	1.45	0.52
200 °C	0.05	0.65	0.02	0.12	0.35	0.13	0.10	0.35	0.25	2.51	0.80	1.45	0.67
400 °C	0.05	0.68	0.03	0.12	0.33	0.11	0.06	0.35	0.24	2.46	0.72	1.38	0.76
600 °C	0.03	0.68	0.03	0.13	0.30	0.15	0.10	0.34	0.29	2.68	0.61	1.55	0.72
800 °C	0.02	0.63	0.04	0.12	0.33	0.26	0.08	0.30	0.28	2.99	0.55	1.70	0.88

25 Na ₂ O - 10 TiO ₂ - 65 SiO ₂													
Peak Positions													
Position (cm ⁻¹)	340	Main band	460	490	540	600	720	800	840	900	980	1080	1100
50 °C	342	520	528	499	560	598	726	795	847	902	974	1072	1102
200 °C	346	522	528	497	559	597	734	794	841	900	975	1072	1102
400 °C	340	534	527	499	560	599	738	799	839	897	972	1071	1098
600 °C	345	538	527	497	557	597	727	791	834	896	971	1068	1095
800 °C	340	546	529	498	556	599	738	790	831	894	968	1062	1091
Peak Intensity													
Intensity (a.u.)	340	Main band	460	490	540	600	720	800	840	900	980	1080	1100
50 °C	0.08	0.78	0.02	0.09	0.23	0.09	0.27	0.54	0.48	3.72	1.00	1.24	0.55
200 °C	0.07	0.80	0.03	0.09	0.21	0.10	0.28	0.47	0.40	3.69	1.00	1.30	0.48
400 °C	0.08	0.81	0.03	0.07	0.19	0.07	0.33	0.50	0.37	3.74	0.96	1.45	0.43
600 °C	0.06	0.82	0.03	0.07	0.18	0.11	0.26	0.62	0.37	4.12	0.86	1.64	0.42
800 °C	0.06	0.81	0.04	0.06	0.18	0.13	0.30	0.56	0.53	4.21	0.66	1.70	0.56

4. Discussions

A thorough discussion of changes in Raman spectra, elastic moduli and CTE with composition at room temperature has been done previously [22]. The discussion here will build off of the previous discussion. Since changes in the Raman spectra, both in position and intensity, will be the main focus in attempting to explain changes in the structure, elastic moduli and CTE with temperature, it is convenient to briefly summarize the Raman peak assignments.

The low frequency peaks at 490, 540, and 600 cm⁻¹ and the main silica band are generally agreed upon in their assignments. The main silica band corresponds to Si-O-Si symmetric vibrations, and tends to broaden and shift to higher frequencies with the increase of Na₂O content, as the structure becomes less organized and more densely packed. The small peaks at 490 and 600 cm⁻¹ correspond to 4- and 3-membered Si-O ring breathing mode vibrations [3]. These rings tend to be stiff and resistant to changes, so their position does not change significantly with composition. The 540 cm⁻¹ peak is assigned to Si-O delocalized vibrational modes caused by the presence of non-bridging oxygens (nBOs) in the silica network [27]. This peak appears with the addition of Na₂O, and its position and intensity is strongly tied to the glass composition.

The high frequency peaks at 900, 980, 1080, and 1100 cm⁻¹ are slightly more difficult to assign, as they either do not appear exactly in the Na₂O-SiO₂ and TiO₂-SiO₂ binary systems or they appear in both binary systems. The 900 cm⁻¹ peak has been assigned to the Ti=O titanyl bond of ^[5]Ti in a square pyramidal coordination [17,19,20]. The 980 cm⁻¹ peak intensity is strongly dependent on the TiO₂ content of the glass, and is assigned to the Ti-O bond of ^[5]Ti. In the binary system the Ti-O peak appears at 950 cm⁻¹ for ^[4]Ti, so a shift to higher frequencies corresponds to the increased packing density in the ternary system. A peak at 1100 cm⁻¹ appears in both binary systems and has been generally assigned to anti-symmetric oxygen vibrations of Q³ species. In our ternary system, there can be both Si Q³ and Ti Q³ species. We assign the 1080 cm⁻¹ peak to the Ti Q³ and the 1100 cm⁻¹ peak to the Si Q³ species for two reasons. The

longer and weaker Ti-O bond should produce a lower frequency than the Si-O bond and the polarizability of Ti bonds is greater than that of the Si-O bond, which corresponds to the greater intensity of the 1080 cm^{-1} peak.

The 720, 800, and 840 cm^{-1} peaks are assigned to cation oxygen vibrations, primarily caused by cation motion. Peaks at 800 and 840 cm^{-1} are observed in pure silica glasses and are assigned to Si Q^4 silicon vibrations [4]. The 720 cm^{-1} peak appears with the addition of TiO_2 , and thus can be assigned to Ti Q^4 titanium vibrations. Shift of the 720 cm^{-1} peak to higher frequencies with increasing TiO_2 corresponds to the transition from a combination of $^{[4]}\text{Ti}$ and $^{[5]}\text{Ti}$ to almost completely $^{[5]}\text{Ti}$ and the increased packing density [22]. This peak has been reported at $\sim 750 \text{ cm}^{-1}$ in $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ glasses with 25 mol% TiO_2 and is compared to the 767 cm^{-1} band in Ba_2TiO_4 [17].

Additional small peaks appear at 340 cm^{-1} and 460 cm^{-1} , the assignments of which are uncertain. The 340 cm^{-1} peak has been tentatively assigned to the presence $^{[6]}\text{Ti}$ [28]. The small peak observed at 460 cm^{-1} is tentatively assigned to a rocking mode vibration between two 3- or 4-membered rings, based on its frequency and the resistance to changes in frequencies or intensity to composition and temperature. This peak could also be caused by breathing mode vibrations of 7- or 8- membered Si-O rings, but these rings tend to be quite flexible and thus it is unlikely that they would remain symmetric enough to produce a breathing vibration mode [22].

Assuming these assignments are valid, it should be possible to observe a correlation with the variations in peak intensities and positions with temperature to the changes in structure, elastic moduli and CTE. The temperature response of the elastic moduli, seen in Figs. 2a-d, show a general trend of decreasing slope with increasing Na_2O , and a greater change in slope at the glass transition for higher Na_2O contents. CTE likewise increases in slope with increasing Na_2O . The temperature responses of both are largely unaffected by changes in the TiO_2 content.

Examining how the temperature responses of the intensities of Raman peaks change when Na_2O content is increased, we can see that there are changes in the 540, 720, 800, 840, 980, 1080, and 1100 cm^{-1} peaks. The responses of main band (Fig. 8a), 490, 600, and 900 cm^{-1} peaks to temperature is almost unchanged by varying the Na_2O content, even if their room temperature positions and intensities are. The 490 and 600 cm^{-1} peaks are associated with Si-O vibrations of rigid ring structures, thus less sensitive to temperature or local environment. The fact that the 900 cm^{-1} peak is not affected suggests that the titanyl oxygen vibrations are not sensitive to changes in the Na_2O concentration, either.

Fig. 8. Change in peak intensities with temperature for (10, 15, 20, and 25) Na₂O - 7 TiO₂ - SiO₂ glasses are shown for a) the main band Si-O vibrations, b) 540 cm⁻¹ delocalized oxygen vibrations, c) 720 cm⁻¹ Ti cation vibrations, d) 800 cm⁻¹ Si cation vibrations, e) 1080 cm⁻¹ Ti-nBO vibrations, f) 1100 cm⁻¹ Si-nBO vibrations.

The 540 cm⁻¹ peak both decreases in intensity more (Fig. 8b) and shifts further to lower frequencies with increasing temperature at high Na₂O contents (Table 1). The frequency change would suggest that the free volume of the glass increases with temperature more quickly at higher Na₂O contents. The intensity change possibly suggests that the delocalized vibrations caused by nBOs are weaker; that the difference between a BO and a nBO is less at higher temperatures.

The 720 cm⁻¹ peak increases in intensity with temperature at 10 Na₂O, and this response decreases until it is slightly negative at 20 Na₂O (Fig. 8c). As this peak is assigned to cation vibrations of Ti with four bridging oxygens, this suggests that the population of Q⁴ Ti decreases with temperature at an increased rate at higher Na₂O. The 800 cm⁻¹ peak sees a similar change in behavior to a decreasing intensity with increasing temperature (Fig. 8d), but only at 25 Na₂O, where the population of the Ti Q⁴ species is extremely low. It is possible that that Ti Q⁴ change bonding to form nBO more easily than Si Q⁴, which would explain why there is little change in the Si-O symmetric vibrational peaks: 460, 490, and 600 cm⁻¹. Interestingly, the 840 cm⁻¹ peak, while reduced in intensity overall with increasing Na₂O, actually has a greater positive temperature response at higher Na₂O contents. The change in the 800 cm⁻¹ peak matches an increased temperature response in the 1100 cm⁻¹ peak (Fig. 8f), suggesting a decrease in the Si Q⁴ population and an increase in the Si Q³ population with temperature. It might be expected that similar changes would occur in the Ti Q⁴ and Q³ populations. However, that appears not to be the case. Rather, the 980 and 1080 cm⁻¹ peaks both show an increased shift to lower frequencies (Table 1), but unchanged intensity responses to temperature. Intensity of the 1080 cm⁻¹ peak does show an increased temperature response at and above 600 °C for the 20 and 25 Na₂O glasses (Fig. 8e). A lower frequency could correspond to an increased local free volume, a change in bond angle, or a reduced bond strength.

To seek an explanation for this, let's start from the percolation model proposed by Farges et al. [29]. In this model, clusters with relatively high concentrations of Ti and Na form. Titanyl oxygens would initially act to balance the Na^+ charge. As the Na^+ concentration increases, further charge balancing requires the formation of non-bridging oxygens. This is seen in a decrease in intensity of the 720 cm^{-1} peak and an increase in the intensities of the 1080 and 1100 cm^{-1} peaks with increasing Na_2O (Fig. 8c, e, f). As the temperature is increased, mobility and the amplitude of vibrations of Na^+ cations is going to increase significantly faster than that of Si or Ti cations, due to the lower mass and weaker bonding. Since the Na^+ concentration is higher in these clusters, there should be a higher packing density in the clusters than in the surrounding glass. The 800 and 840 cm^{-1} Si cation vibrational peaks are dependent on symmetry of bonds surrounding the cation [4], and this would logically extend to the 720 cm^{-1} Ti cation peak as well. The difference in Na^+ concentration outside and inside of these clusters could decrease this symmetry as the temperature is increased and Na^+ vibrations increase. The change in the temperature response of the intensity of the 720 cm^{-1} peak from positive to negative with increasing Na_2O could then be caused by either a change in Na_2O concentrations in these clusters or a greater fraction of the Ti participating in the clusters at higher Na_2O contents. The fact that there appears to be a saturation limit, where between 20 and 25 mol% Na_2O the intensity of the 720 cm^{-1} peak decreases drastically and the intensity of the 800 cm^{-1} peak also begins to decrease, suggesting that the increased participation of TiO_2 in these clusters at higher Na_2O concentrations is more likely, and that once enough Na_2O is present in the glass, further Na additions primarily form Si-O-Na nBOs.

The temperature response of elastic moduli and CTE can be related to changes in peak positions with temperature. The anomalous increase of elastic moduli with temperature in silica glass has been associated with the transition from soft puckered α -like to stiff puffed β -like 6-membered rings, similar to those in cristobalite polymorphs [30-33]. The stiffening of the silica ring network with temperature due to this transition corresponds to the increase in frequency of the silica Raman main band at $\sim 450\text{ cm}^{-1}$ by $\sim 8\text{ cm}^{-1}$ from room temperature to 800°C , overcoming the softening effect due to the anharmonicity. This is reflected in the consistent shift of high frequency peaks associated with Si-O anti-symmetric bridging oxygen vibrations at 1050 and 1200 cm^{-1} to lower frequencies with temperature (by -19 and -28 cm^{-1} in the same temperature range) [23]. In Na_2O - SiO_2 glasses [34], this anomalous response of elastic moduli to temperature was observed to decrease with increasing Na_2O content. The frequency change of the silica main band in response to temperature was also observed to decrease to -2 cm^{-1} in 25 Na_2O - 75 SiO_2 glass and to -6 in 40 Na_2O - 60 SiO_2 glass from room temperature to 500°C . In TiO_2 - SiO_2 glasses, the temperature response of the elastic moduli remains unchanged, and the shift in peak position of the main band with temperature actually increases slightly with increasing TiO_2 , by $+12$ and $+17\text{ cm}^{-1}$ from room temperature to 800°C in 5.4 TiO_2 - 94.6 SiO_2 and 8.3 TiO_2 - 91.7 SiO_2 glasses, respectively. This is due to the increase flexibility of the network to promote the α -like to β -like ring transitions after the incorporation of Ti atoms in the silica network. This counter-balances a stronger softening effect due to longer and weaker Ti-O bonds reflected in larger shift of the 950 and 1100 cm^{-1} peaks associated with Ti-O anti-symmetric bridging oxygen vibrations (by -30 and -20 cm^{-1} in the same temperature range) [35]. In Na_2O - TiO_2 - SiO_2 glasses, we observed the transition from anomalous to normal behavior in terms of the response of elastic moduli to temperature with the increasing Na_2O content from 10 to 25 mol%, similar to Na_2O - SiO_2 glasses; however, the shift in peak position of the silica main band remains strongly positive for all compositions, similar to TiO_2 - SiO_2 glasses. The lower

sensitivity to composition of the shift in the main band peak position with temperature in the ternary system suggests that Na₂O in the glass has limited interaction with the 6-membered Si-O rings. A preferential interaction of Na₂O with TiO₂ agrees with the percolation model suggested by Farges et al. [29], where Na₂O and TiO₂ form clusters with relatively high concentrations of Na₂O within the clusters and high concentrations of TiO₂ in the boundaries of the clusters. In other words, TiO₂ removes Na₂O from silica rich regions of the glass and forms the higher bond density within the clusters. As the Na₂O content increases, the volume fraction of relatively intact Si-O rings decreases, causing the reduced intensity of the silica main band seen in Fig. 8a, and causes the stiffening of the glass network with increasing temperature to decrease. Meanwhile, TiO₂ does not promote the anomalous temperature response of the elastic moduli in the ternary system as it does in the TiO₂-SiO₂ binary system, as Ti atoms are not uniformly dispersed in the silica network. Therefore, the peak position of the silica main band in the ternary system increases with temperature, similar to the behavior in pure silica or in the TiO₂-SiO₂ binary system. However, the response of the elastic moduli to temperature changes from anomalous to normal with the increase of Na₂O content in the ternary system, similar to the trend in the Na₂O-SiO₂ binary system, due to the diminishing stiffening effect of the intact silica network and the increasing softening effect of the Na₂O rich clusters with temperature.

The temperature response of CTE matches the increasing shift of the 540, 980, 1080, and 1100 cm⁻¹ peaks to lower frequencies with increasing temperature. This corresponds to an increase in the Ti-O and Si-O bond length with temperature within the glass regions with lower connectivity due to the addition of Na₂O. As the Na₂O content is increased and these regions occupy a greater volume fraction of the glass, they are less constrained by the silica network and are able to expand more freely. Or equivalently, as the silica network is more disrupted, free volume is decreased and the increase in bond length is accommodated by volume expansion instead of bond rotation of tetrahedra. It is interesting that that CTE does not change as the TiO₂ content is increased, as it is expected that Ti⁴⁺ transitions from a mixture of ^[4]Ti and ^[5]Ti at 4 mol% TiO₂ to primarily ^[5]Ti at 10 mol% TiO₂ [17,29]. An increase in the TiO₂ content has a significant impact on the intensities and positions of peaks, but has only a slight influence on their CTE responses to temperature. Farges et al. suggested that Ti-rich domains formed were quite rigid and resistant to thermal expansion [36]. So it is possible that the increase in stiffness and increase in density that accompany the increase in TiO₂ offset each other somewhat, resulting in only a small change in CTE.

5. Conclusions

Changes in structure, elastic moduli, and CTE of Na₂O-TiO₂-SiO₂ glasses with temperature have been investigated through *in-situ* high temperature Raman spectroscopy, Brillouin light scattering, and dilatometry. Increasing the Na₂O content decreases the Young's modulus and shear modulus, while it increases bulk modulus and the Poisson's ratio. It also changes the elastic response to temperature, shifting from an anomalously increase in elastic moduli with temperature at 10 Na₂O to a normal decrease at 20 and 25 Na₂O, with 15 Na₂O having an intermediate response. Increasing the TiO₂ content increases the magnitude of elastic moduli, but does not change the temperature response appreciably. The CTE increases both magnitude and slope with increasing Na₂O content, but showing almost no change with variation in TiO₂ content.

Changes in the Raman spectra with temperature and Na₂O content have been discussed to understand the underlying structural changes, which were correlated to the changes in the temperatures responses of CTE and elastic moduli. The change in the slope of elastic moduli with temperature matches an explanation based on the percolation model proposed by Farges et al. [29].

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References

- [1] W.H. Wang, The Elastic Properties, Elastic Models and Elastic Perspectives of Metallic Glasses, *Prog. Mater. Sci.* 57 (2012) 487–656.
- [2] T. Rouxel, Elastic Properties and Short-to Medium-Range Order in Glasses, *J. Am. Ceram. Soc.* 90 (2007) 3019–3039.
- [3] R. Vukceovich, A new interpretation of the anomalous properties of vitreous silica, *J. Non-Cryst. Solids.* 11 (1972) 25–63.
- [4] P. McMillan, B. Poe, P.H. Gillet, B. Reynard, A study of SiO₂ glass and supercooled liquid to 1950 K via high-temperature Raman spectroscopy, *Geochim. Cosmochim. Acta.* 58 (1994) 3653–3664.
- [5] A. Kalampounias, S. Yannopoulos, G. Papatheodorou, Temperature-induced structural changes in glassy, supercooled molten silica from 77 to 2150 K, *J. Chem. Phys.* 124 (2006) 014504.
- [6] T. Deschamps, C. Martinet, D. de Ligny, B. Champagnon, Elastic anomalous behavior of silica glass under high-pressure: In-situ Raman study, *J. Non-Cryst. Solids.* 355 (2009) 1095–1098.
- [7] L. Wondraczek, J. Mauro, J. Eckert, U. Kuhn, J. Horbach, J. Deubener, et al., Towards Ultrastong Glasses, *Adv. Mater.* 23 (2011) 4578–4586.
- [8] K. Kamiya, S. Sakka, Thermal Expansion of TiO₂-SiO₂ and TiO₂-GeO₂ glasses, *J. Non-Cryst. Solids.* 52 (1982) 357–363.
- [9] V. Pukh, L. Baikova, M. Kireenko, L. Tikhonova, Properties of silica glass doped with titanium oxide, in: *Glass - The Challenge for the 21st Century*, Trans Tech Publications, 2008: pp. 153–158.
- [10] S. Gulati, Mechanical Properties of SiO₂ vs. SiO₂-TiO₂ Bulk Glasses and Fibers, *Mat. Res. Soc. Symp. Proc.* 244 (1992) 67–83.
- [11] K. Hirao, K. Tanaka, S. Furukawa, N. Soga, Anomalous temperature dependence of the sound velocities of SiO₂-TiO₂ glasses, *J. Mater. Sci. Lett.* 14 (1995) 697–699.
- [12] S. Webb, D. Dingwell, Compressibility of titanosilicate melts, *Contrib. Mineral. Petrol.* 118 (1994) 157–168.

- [13] Q. Liu, R. Lange, Y. Ai, Acoustic velocity measurements on $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ liquids: Evidence for a highly compressible TiO_2 component related to five-coordinated Ti, *Geochim. Cosmochim. Acta.* 71 (2007) 4314–4326.
- [14] D. Dingwell, Shear Viscosity of alkali and alkaline earth titanium silicate liquids, *Am. Mineral.* 77 (1992) 270–274.
- [15] Q. Liu, R. Lange, The partial molar volume and thermal expansivity of TiO_2 in alkali silicate melts: systematic variation with Ti coordination, *Geochim. Cosmochim. Acta.* 65 (2001) 2379–2393.
- [16] M. Bouhifd, A. Sipp, P. Richet, Heat Capacity, viscosity, and configurational entropy of alkali titanosilicate melts, *Geochim. Cosmochim. Acta.* 63 (1999) 2429–2437.
- [17] G. Henderson, X. Liu, M. Fleet, A Ti L-edge X-ray absorption of Ti-silicate glasses, *Phys. Chem. Miner.* 29 (2002) 32–42.
- [18] H. Hidaka, N. Iwamoto, N. Umesaki, T. Fukunaga, K. Suzuki, Structural analysis of sodium silicate glasses containing TiO_2 by pulsed neutron scattering, *J. Mater. Sci.* 20 (1985) 2497–2502.
- [19] B. Reynard, S. Webb, High-temperature Raman spectroscopy of $\text{Na}_2\text{TiSi}_2\text{O}_7$ glass and melt: coordination of Ti^{4+} and nature of the configurational changes in the liquid, *Eur. J. Mineral.* 10 (1998) 49–58.
- [20] B. Mysen, D. Neuville, Effect of temperature and TiO_2 content on the structure of $\text{Na}_2\text{Si}_2\text{O}_5\text{-Na}_2\text{Ti}_2\text{O}_5$ melts and glasses, *Geochimica et Cosmochimica Acta.* 59 (1995) 325–342.
- [21] M. Manghnani, Pressure and Temperature dependence of the elastic moduli of $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ glasses, *J. Am. Ceram. Soc.* 55 (1972) 360–365.
- [22] G. Scannell, S. Barra, L. Huang, Structure and Properties of $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ Glasses: Role of Na and Ti on Modifying the Silica Network, *J. Non-Cryst. Solids.* 448 (2016) 52–61.
- [23] M. Guerette, L. Huang, A simple and convenient set-up for high-temperature Brillouin light scattering, *J. Phys. D: Appl. Phys.* 45 (2012) 275302.
- [24] T. Rouxel, Thermodynamics of viscous flow and elasticity of glass forming liquids in the glass transition range, *J. Chem. Phys.* 135 (2011) 184501.
- [25] G. Scannell, L. Huang, T. Rouxel, Elastic properties and indentation cracking behavior of $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ glasses, *J. Non-Cryst. Solids.* 429 (2015) 129–142.
- [26] M. Wojdyr, Fityk: a general-purpose peak fitting program, *J. Appl. Crystallogr.* 43 (2010) 1126–1128.
- [27] P. McMillan, Structural studies of silicate glasses and melts--applications and limitations of Raman spectroscopy, *Am. Mineral.* 69 (1984) 622–644.
- [28] K. Kusabiraki, Infrared and Raman spectra of vitreous silica and sodium silicates containing titanium, *J. Non-Cryst. Solids.* 95-96 (1987) 411–417.
- [29] F. Farges, G.E.J. Brown, A. Navrotsky, H. Gan, J.J. Rehr, Coordination Chemistry of Ti(IV) in Silicate Glasses and Melts: II. Glasses at Ambient Temperature and Pressure, *Geochim. Cosmochim. Acta.* 60 (1996) 3039–3053.
- [30] L. Huang, J. Kieffer, Molecular dynamics study of cristobalite silica using a charge transfer three-body potential: Phase transformation and structural disorder, *J. Chem. Phys.* 118 (2003) 1487–1498.
- [31] L. Huang, J. Kieffer, Amorphous-amorphous transitions in silica glass. I. Reversible transitions and thermomechanical anomalies, *Phys. Rev. B.* 69 (2004) 224203.
- [32] L. Huang, J. Kieffer, Amorphous-amorphous transitions in silica glass. II. Irreversible transitions and densification limit, *Phys. Rev. B.* 69 (2004) 224204.

- [33] F. Yuan, L. Huang, α - β transformation and disorder in β -cristobalite silica, Phys. Rev. B. 85 (2012) 134114.
- [34] Q. Zhao, M. Guerette, G. Scannell, L. Huang, In-situ high temperature Raman and Brillouin light scattering studies of sodium silicate glasses, Journal of Non-Crystalline Solids. 358 (2012) 3418–3426.
- [35] G. Scannell, A. Koike, L. Huang, Structure and Thermo-mechanical response of TiO_2 - SiO_2 glasses to temperature, J. Non-Cryst. Solids. 447 (2016) 238–247.
- [36] F. Farges, A Ti K-edge EXAFS Study of the Medium Range Environment around Ti in Oxide Glasses, J. Non-Cryst. Solids. 244 (1999) 25–33.