Structure and Properties of Na₂O-TiO₂-SiO₂ Glasses: Role of Na and Ti on Modifying the Silica Network

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Abstract:

Changes in the structure and properties of $x\text{Na}_2\text{O}-y\text{TiO}_2-(1-x-y)\text{SiO}_2$ glasses have been studied with regards to composition through Raman spectroscopy, Brillouin light scattering, and dilatometry. Twelve glasses with compositions $x=10, 15, 20$, and 25 , and $y=4, 7$, and 10 were prepared through a traditional melt quench method. Na_2O was found to increase the density, refractive index, coefficient of thermal expansion (CTE), bulk modulus, and Poisson's ratio of glasses, and to decrease Young's modulus and shear modulus. Density, refractive index, Young's modulus, shear modulus, bulk modulus and Poisson's ratio increase with the increase of TiO_2 content. CTE was found to increase with the initial addition of 4 mol% TiO_2 and to remain constant with further additions, regardless of the Na_2O content. Changes in the Raman spectra with composition have been discussed and related to the changes in resulting properties.

Introduction:

Titanium dioxide is a common minor additive in minerals and natural glasses, and it is used in commercial glasses for its optical and thermal expansion properties. It is of interest to both geologists and glass scientists because of the strong impact small quantities of TiO_2 can have on mechanical, optical, and thermodynamic properties [1-13]. Understanding the role TiO_2 plays in glass systems is complicated by the fact that Ti^{4+} can occupy four-, five-, and six-fold coordination states, in tetrahedral, square pyramidal, and octahedral geometries, respectively. The coordination state that Ti adopts is dependent on the chemistry of the surrounding glass, and a change of coordination can result in TiO_2 having a completely different effect on the resulting properties.

Alkali- TiO_2 - SiO_2 glasses provide a convenient composition space to observe the change in behavior of TiO_2 from the binary TiO_2 - SiO_2 [14]. Glasses of these compositions have been the subject of numerous studies designed to explore the structural environment around Ti. The coordination and local structure of TiO_2 containing glasses and minerals were extensively examined through XANES and XAFS by Farges et al. [15-19]. The structure of these glasses has also been examined through other means, including infrared spectroscopy [20-22], Raman spectroscopy [20,23-27], pulsed neutron scattering [28], and a variety of X-ray techniques [29-31]. A general agreement has emerged from these studies that many of the property changes caused by TiO_2 can be explained through an increase in the medium-range order.

Farges et al. proposed a percolation model for a $\text{Na}_2\text{O}-\text{TiO}_2-2\text{SiO}_2$ glass with pockets of 3-6 Å in size of high alkali concentration surrounded by a ^{51}Ti -rich region, which is then surrounded by areas with lower concentrations of network modifiers [16]. Henderson et al.'s later study of the same system, $x\text{TiO}_2-(1-x)\text{Na}_2\text{SiO}_3$ glasses, showed that ^{47}Ti occurs at low Ti contents and gradually transitions to ^{51}Ti as the Ti content is increased to ~14 wt% [31]. Inoue

et al.'s study included glasses with TiO_2 contents up to approximately 40% and found that Ti coordination increases from 4 to 5 to 6 as the concentration of Ti is increased [1].

As our understanding of how TiO_2 behaves in glasses has improved, there have been numerous studies on the connections between compositional, structural behavior and optical properties, such as index of refraction and dispersion [1,2], or thermodynamics properties, such as viscosity, heat capacity, and configurational entropy [3-5]. However, studies on the thermo-mechanical properties of these glasses, such as elastic moduli and thermal expansion, generally dated from before much of the structural studies were done [6-8], had a much more general focus [9,10], or focused primarily on glass melts [11-13].

In this work, we examined the structure through Raman spectroscopy, elastic moduli through Brillouin light scattering, and thermal expansion through dilatometry, of glasses with compositions of $x\text{Na}_2\text{O}-y\text{TiO}_2-(1-x-y)\text{SiO}_2$, where $x=0.1, 0.15, 0.2$, and 0.25 and $y=0.04, 0.07$, and 0.10 . These compositions were chosen to provide complementary structural information to existing literature, as most glasses studied have large Na_2O or TiO_2 contents (>30 mol%). This composition range also allows for a direct comparison to glasses from the binary systems, $\text{TiO}_2\text{-SiO}_2$ and $\text{Na}_2\text{O-SiO}_2$, as previously studied [2,9,10,32-36]. Structural information from Raman spectra was correlated to the observed thermo-mechanical properties of $\text{Na}_2\text{O-TiO}_2\text{-2SiO}_2$ glass and compared with those of $\text{TiO}_2\text{-SiO}_2$ and $\text{Na}_2\text{O-SiO}_2$ glasses when possible.

Methods:

Glasses were prepared in 80 g batches in a Pt or 10%Rh - 90%Pt crucible through a traditional melt-quench method. Compositions prepared include $(x)\text{Na}_2\text{O}-(y)\text{TiO}_2-(1-x-y)\text{SiO}_2$, where $x=10, 15, 20$, and 25 and $y=4, 7$, and 10 mol%. Powders were mixed for 30 minutes and then melted at $1400\text{-}1500$ °C for three hours. The mixed powder was added in three to four stages during the first hour, and the glass melt was stirred five to six times during the last two hours to improve homogeneity. The glass melt was held at $1600\text{-}1700$ °C for 10 minutes immediately prior to pouring. The poured glasses were then annealed at $550\text{-}600$ °C, slightly above their glass transition temperatures, for 1 hour before furnace cooling overnight. Glasses were checked for residual stresses using a polarizer, and crushed and re-melted if significant residual stresses were observed.

Samples were cut from the prepared bulk glasses using an abrasive cutting wheel. Samples were ground using 240, 400, and 600 grit Al_2O_3 papers and then polished to an optical finish using a CeO_2 slurry. For Raman light scattering and Brillouin light scattering (BLS) experiments, sample dimensions were approximately $2\text{ mm} \times 1\text{ mm} \times 100\text{ }\mu\text{m}$, with both surfaces parallel and polished to an optical finish.

Light scattering experiments were conducted by using a 532.18 nm Verdi V2 DPSS green laser as the probing light source. The experimental setup used for BLS and Raman light scattering experiments is similar to that described by Guerette and Huang [37], which allows a simultaneous measurement of longitudinal peak from the backscattering geometry, longitudinal and shear peak from the emulated platelet geometry. BLS spectra were collected until the longitudinal peak from the emulated platelet geometry reached a minimum of 600 counts to ensure a good peak fit.

Elastic moduli, including Poisson's ratio, were calculated from the sound velocities measured through BLS and the density of the glasses 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.

Densities of samples were measured through the Archimedes method using water as the liquid medium. Sample weight was measured ten times each in air and water and the density was calculated from average weight values in each medium. Standard deviations were calculated through error propagation of standard deviations of weight in air and in water. Average standard deviation across the 12 compositions examined was 0.0026 g/cm³, and the maximum standard deviation of compositions measured was 0.0047 g/cm³.

The index of refraction was measured for each composition using a thin sample, around 0.5-1 mm thick, with two optically polished, parallel surfaces. Index of refraction measurements were performed using a Metricon Model 2010/M Prism Coupler. Five measurements were made for each sample. Average standard deviation for the twelve compositions was 0.000381, and the maximum standard deviation was 0.000646. Error bars plotted on figures for index of refraction are smaller than the symbols.

Thermal expansion of samples was measured with a dual pushrod differential dilatometer at Corning, Inc. Glass bars with dimensions of 2" by 0.25" by 0.25" and finely ground ends and coarsely ground sides were prepared. Measurements were done using a 4 °C/min heating and cooling rate from room temperature to 480 °C, and 5 minutes hold at the top temperature. Sapphire was used as a reference material.

Electron microprobe analysis (EMPA) was used to determine the composition and the homogeneity of Na₂O-TiO₂-SiO₂ glasses. Albite and jadeite were used as Na references; titanite, Ti metal, and rutile were used as Ti references; and quartz was used as the Si reference. Compositions were measured at 7 points across the surface of each sample. Nominal compositions, measured compositions, and standard deviations are shown in Table 1 for the 12 glasses examined here. The 10 Na₂O - 10 TiO₂ - 80 SiO₂ and 25 Na₂O - 4 TiO₂ - 71 SiO₂ glasses were measured at 40 points across the sample to provide a measure of homogeneity.

Table 1. Compositions and standard deviations (in mol%) of Na₂O-TiO₂-SiO₂ glasses.

Nominal Composition (Na ₂ O-TiO ₂ -SiO ₂)	Na ₂ O	Na ₂ O Std	TiO ₂	TiO ₂ Std	SiO ₂	SiO ₂ Std
	Mol%					
10-4-86	10.26	0.33	3.90	0.12	85.84	0.28
10-7-83	10.35	0.35	6.52	0.14	83.13	0.46
10-10-80	8.59	0.44	10.29	0.30	81.12	0.65
15-4-81	15.32	0.26	3.93	0.12	80.75	0.22
15-7-78	15.69	0.42	6.77	0.14	77.54	0.45
15-10-75	15.71	0.23	9.59	0.13	74.70	0.26
20-4-76	20.61	0.28	3.92	0.10	75.46	0.23
20-7-73	20.42	0.27	6.70	0.09	72.89	0.28
20-10-70	20.60	0.43	9.46	0.17	69.94	0.39
25-4-71	24.99	0.70	3.79	0.12	71.22	0.74
25-7-68	26.60	0.25	6.87	0.14	66.53	0.24
25-10-65	25.74	0.30	9.27	0.29	64.99	0.46

Fourier transform infrared spectroscopy (FTIR) was used to measure the water content in Na₂O-TiO₂-SiO₂ glasses (Table 2). Hydroxyl concentrations were determined using the Beer-Lambert law, following procedures used in literature [38-40]. The water content in most of our glasses is ≤ 50 ppm, except the 15 Na₂O - 10 TiO₂ - 75 SiO₂ sample, having an OH concentration of 92.8 ppm.

Table 2. OH content in Na₂O-TiO₂-SiO₂ glasses.

Nominal Composition (Na ₂ O-TiO ₂ -SiO ₂)	OH Concentration (ppm)
10-7-83	50.2
10-10-80	38.8
15-4-81	46.8
15-7-78	46.8
15-10-75	92.8
20-4-76	34.8
20-7-73	30.9
20-10-70	24.9
25-4-71	23.5
25-7-68	27.5
25-10-65	29.8

Results:

Fig.1 shows the density of glasses versus the number of bridging oxygen per network forming cation. Calculation for the number of bridging oxygen is given in Eqn. 5, more detail can be found elsewhere [41]. Eqn. 5 assumes that Ti has a 50-50 mixture of four- and five-fold

coordination state. In this case, a $^{[4]}\text{Ti}$ forms four bridging bonds, acting to remove one sodium from the network, effectively restoring one Si bridging oxygen, and a $^{[5]}\text{Ti}$ forms four bridging bonds and one non-bridging bond, with the non-bridging oxygen being charge-balanced by two sodium atoms.

$$n_{BO} = (4([Si] + [Ti]) - ([Na] - [Ti])) / ([Si] + [Ti]) \quad (5)$$

The density generally increases with increasing TiO_2 and increasing Na_2O , in good agreement with Hamilton's study of similar compositions [34]. The 10 Na_2O - 10 TiO_2 - 80 SiO_2 sample has a slightly lower density than would be expected from other compositions. This corresponds to the slightly lower than nominal TiO_2 content, 8.59 mol% instead of 10 mol%.

Fig. 1. Density of Na_2O - TiO_2 - SiO_2 glasses versus the number of bridging oxygen per network forming cation. For each Na_2O composition, TiO_2 increases from left to right (4, 7, and 10%). Density of TiO_2 - SiO_2 glasses [33], Na_2O - SiO_2 [32], and SiO_2 glasses are also shown for comparison. TiO_2 - SiO_2 glasses shown are for 5.4 and 8.3 mol% TiO_2 .

Refractive index versus the number of bridging oxygen per network forming cation is presented in Fig. 2. Refractive index increases with both increasing Na_2O and TiO_2 concentrations, although significantly more with the addition of TiO_2 than with Na_2O . Values measured are in good agreement with Hamilton's study of similar compositions [34].

Fig. 2. Index of refraction versus the number of bridging oxygen per network forming cation for Na₂O-TiO₂-SiO₂ glasses. For each Na₂O composition, TiO₂ increases from left to right (4, 7, and 10%). Values for TiO₂-SiO₂ [42], Na₂O-SiO₂ [32], and SiO₂ glasses are also shown for comparison. TiO₂-SiO₂ glasses shown are for 3, 5.5, and 8 mol% TiO₂.

Coefficients of thermal expansion (CTE) are plotted against the number of bridging oxygen per network forming cation in Fig. 3. CTE increases linearly with increasing Na₂O. With the initial addition of 4 TiO₂ the CTE increases by around $1 \times 10^{-6} \text{ C}^{-1}$. Further additions of TiO₂ from 4 to 10 mol% only change the CTE very slightly.

Fig. 3. Coefficient of thermal expansion versus number of bridging oxygen per network forming cation. For each Na₂O composition, TiO₂ increases from left to right (4, 7, and 10%). TiO₂-SiO₂ glasses shown are for 5.4 and 8.3 mol% TiO₂. CTE of Na₂O-TiO₂-SiO₂ samples represent the values at 50 °C. TiO₂-SiO₂ values are the average between room temperature and 300 °C, and Na₂O-SiO₂ values are the CTE between room temperature and 100 °C [43].

Fig. 4. a) Young's modulus, bulk modulus, and shear modulus, and b) Poisson's ratio versus the number of bridging oxygen per network forming cation. For each Na₂O composition, TiO₂ increases from left to right (4, 7, and 10%). Na₂O-SiO₂ values are taken from previous research by Zhao et al. [32] and TiO₂-SiO₂ data by Scannell et al. [33]. Elastic moduli of TiO₂-SiO₂

glasses shown are for 5.4 and 8.3 mol% TiO_2 , decreasing with increasing TiO_2 for a) and increasing with increasing TiO_2 for b). Error bars are reported for all Na_2O - TiO_2 - SiO_2 glasses and represent the standard deviation across five measurements.

Elastic moduli versus the number of bridging oxygen are presented in Fig. 4. Fig. 4a shows changes in Young's modulus, bulk modulus, and shear modulus with changes in composition and Fig. 4b shows the corresponding changes of Poisson's ratio. Relative to pure silica, Young's modulus decreases with the addition of either Na_2O or TiO_2 . These changes are discussed in more detail for both the Na_2O - SiO_2 [32] and the TiO_2 - SiO_2 [33] systems elsewhere. With the addition of both Na_2O and TiO_2 , the observed change is quite different. In the presence of Na_2O , the effect of TiO_2 is directly opposite to the behavior observed in the binary system. With no Na_2O , adding 8.3 mol% TiO_2 decreases Young's modulus by 5.3 GPa from 72.7 to 67.4 GPa. With 10 Na_2O , adding 10 mol% TiO_2 increases Young's modulus by 6.3 GPa, from 69.0 to 75.3 GPa. And at 25 Na_2O , the same amount of TiO_2 increases Young's modulus from 61.8 GPa to 67.4 GPa, an increase of 5.6 GPa. A similar change in behavior can be observed with changes in Na_2O composition when TiO_2 is present. With no TiO_2 , Young's modulus decreases by 5.1 GPa between 10 and 25 Na_2O . At 4 mol% TiO_2 this decrease is 7.2 GPa and at 10 mol% TiO_2 it is 7.9 GPa.

The shear modulus shows a similar behavior to Young's modulus. Holding the amount of Na_2O constant and changing TiO_2 from 0 to 10 (or 8.3 for the binary case), with no Na_2O it decreases by 2.6 GPa, at 10 Na_2O it increases by 2.4 GPa, and at 25 Na_2O it increases by 2.4 GPa. In the reverse case, holding TiO_2 constant and changing Na_2O from 10 to 25, with no TiO_2 the shear modulus decreases by 3.2 GPa, at 4 TiO_2 it decreases by 4.4 GPa, and at 10 TiO_2 it decreases by 4.4 GPa. Thus, for both Young's modulus and shear modulus, in the presence of Na_2O , TiO_2 appears to stiffen the glass structure to both longitudinal and transverse vibrations while also making the integrity of the network more resistant to further increases in Na_2O .

Bulk modulus behaves differently with changes in Na_2O and TiO_2 . In the Na_2O - SiO_2 system, there is a slight decrease from 0 to 10 Na_2O , but then the bulk modulus increases with further additions of Na_2O . In the TiO_2 - SiO_2 system, it decreases in a similar fashion to Young's modulus and shear modulus but the change is much smaller, going from 36.4 to 35 GPa with the addition of 8.3 TiO_2 . Increasing the TiO_2 from 0 to 10 mol% increases the bulk modulus in the presence of Na_2O , from 36.2 to 40.6 GPa at 10 Na_2O , from 40.3 to 43.5 GPa at 25 Na_2O . The minimum in bulk modulus that occurs in the Na_2O - SiO_2 system between 0 and 10 Na_2O diminishes at 4 TiO_2 and disappears completely at 7 and 10 TiO_2 , where the bulk modulus increases with increasing Na_2O .

A similar behavior also appears in the response of Poisson's ratio to composition changes (Fig. 4b). Poisson's ratio increases with the addition of both TiO_2 and Na_2O . Adding Na_2O has a lesser effect from 0 to 10 mol% and then a constant effect between 10 and 25 mol%. The initial 10 Na_2O only increases Poisson's ratio by 0.015, after which adding Na_2O in 5 mol% increment increases it by 0.021, 0.020, and then 0.021. The effect of adding TiO_2 is dependent on the Na_2O content, with a change of 0.009 at 10 Na_2O when 10 TiO_2 is added. A similar increase occurs at 15 and 20 mol% Na_2O , but a decrease of -0.002 occurs at 25 Na_2O .

Data for number of bridging oxygen, density, index of refraction, and CTE in Figs. 1-3 are summarized in Table 3, and for Young's modulus, bulk modulus, shear modulus, and Poisson's ratio from Fig. 4 are summarized in Table 4.

Table 3. Number of bridging oxygen, density, index of refraction, and CTE for Na₂O-TiO₂-SiO₂, Na₂O-SiO₂ [32], TiO₂-SiO₂ [33], and SiO₂ glasses. Index of refraction values for TiO₂-SiO₂ glasses are from Shelby [42]. CTE values for Na₂O-SiO₂ glasses are from Shermer [43].

Glass Composition (mol%)	Number of Bridging Oxygen	Density (g/cm ³)	Index of Refraction	CTE (10 ⁻⁶ C ⁻¹)
10 Na ₂ O - 4 TiO ₂ - 86 SiO ₂	3.82	2.358	1.4980	5.63
10 Na ₂ O - 7 TiO ₂ - 83 SiO ₂	3.86	2.405	1.5104	5.77
10 Na ₂ O - 10 TiO ₂ - 80 SiO ₂	3.89	2.423	1.5283	5.73
15 Na ₂ O - 4 TiO ₂ - 81 SiO ₂	3.69	2.404	1.5133	8.17
15 Na ₂ O - 7 TiO ₂ - 78 SiO ₂	3.73	2.456	1.5308	8.28
15 Na ₂ O - 10 TiO ₂ - 75 SiO ₂	3.76	2.507	1.5593	8.20
20 Na ₂ O - 4 TiO ₂ - 76 SiO ₂	3.55	2.455	1.5235	10.08
20 Na ₂ O - 7 TiO ₂ - 73 SiO ₂	3.59	2.499	1.5418	10.04
20 Na ₂ O - 10 TiO ₂ - 70 SiO ₂	3.63	2.544	1.5668	9.92
25 Na ₂ O - 4 TiO ₂ - 71 SiO ₂	3.39	2.498	1.5263	12.06
25 Na ₂ O - 7 TiO ₂ - 68 SiO ₂	3.43	2.541	1.5498	11.96
25 Na ₂ O - 10 TiO ₂ - 65 SiO ₂	3.47	2.581	1.5627	11.82
10 Na ₂ O - 90 SiO ₂	3.78	2.266	1.4760	5.00
15 Na ₂ O - 90 SiO ₂	3.65	2.320	1.4795	7.20
20 Na ₂ O - 90 SiO ₂	3.50	2.365	1.4945	9.00
25 Na ₂ O - 90 SiO ₂	3.33	2.411	1.5013	10.80
5.4 TiO ₂ - 94.6 SiO ₂	4.00	2.200	1.4844	-0.05
8.3 TiO ₂ - 91.7 SiO ₂	4.00	2.210	1.5018	-0.29
SiO ₂	4.00	2.200	1.4600	0.50

Table 4. Elastic moduli and Poisson's ratio for Na₂O-TiO₂-SiO₂, Na₂O-SiO₂ [32], TiO₂-SiO₂ [33], and SiO₂ glasses measured through Brillouin light scattering.

Glass Composition (mol%)	Young's Modulus (GPa)	Bulk Modulus (GPa)	Shear Modulus (GPa)	Poisson's Ratio (GPa)
10 Na ₂ O - 4 TiO ₂ - 86 SiO ₂	69.0	36.2	29.2	0.182
10 Na ₂ O - 7 TiO ₂ - 83 SiO ₂	71.0	37.3	30.0	0.183
10 Na ₂ O - 10 TiO ₂ - 80 SiO ₂	75.3	40.6	31.6	0.191
15 Na ₂ O - 4 TiO ₂ - 81 SiO ₂	67.6	37.9	28.1	0.203
15 Na ₂ O - 7 TiO ₂ - 78 SiO ₂	70.0	40.2	28.9	0.210
15 Na ₂ O - 10 TiO ₂ - 75 SiO ₂	70.8	41.2	29.2	0.214
20 Na ₂ O - 4 TiO ₂ - 76 SiO ₂	63.6	38.2	26.0	0.223
20 Na ₂ O - 7 TiO ₂ - 73 SiO ₂	65.6	40.6	26.7	0.231
20 Na ₂ O - 10 TiO ₂ - 70 SiO ₂	67.5	42.8	27.3	0.237
25 Na ₂ O - 4 TiO ₂ - 71 SiO ₂	61.8	40.3	24.8	0.244
25 Na ₂ O - 7 TiO ₂ - 68 SiO ₂	63.7	41.6	25.6	0.245
25 Na ₂ O - 10 TiO ₂ - 65 SiO ₂	67.4	43.5	27.2	0.242
10 Na ₂ O - 90 SiO ₂	65.4	34.7	27.6	0.180
15 Na ₂ O - 90 SiO ₂	63.6	36.0	26.4	0.197
20 Na ₂ O - 90 SiO ₂	61.2	36.5	25.1	0.220
25 Na ₂ O - 90 SiO ₂	60.3	38.4	24.3	0.234
5.4 TiO ₂ - 94.6 SiO ₂	69.8	35.3	29.8	0.170
8.3 TiO ₂ - 91.7 SiO ₂	67.4	35.0	28.6	0.179
SiO ₂	72.7	36.4	31.2	0.167

Fig. 5. Raman spectra of $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ glasses at room temperature. Spectra are offset vertically for clarity, with Na_2O compositions of 10, 15, 20, and 25 mol% in large offsets, and TiO_2 compositions of 4, 7, and 10 mol% in small offsets.

Raman spectra for $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ glasses are shown in Fig. 5. Spectra are offset vertically, with different Na_2O contents having large offsets and different TiO_2 contents having small offsets. Spectra were corrected for frequency and temperature [44] and then normalized to the maximum intensity in the 400-600 cm^{-1} range. These Raman spectra were then fit with Gaussian peaks using Fityk [45]. An example of the deconvoluted spectrum for the 15 Na_2O - 4 TiO_2 - 81 SiO_2 glass is shown in Fig. 6. Peaks are observed at 340, 460, 490, 540, 600, 720, 800, 840, 900, 980, 1080, and 1100 cm^{-1} . The fitted peak positions are given in Table 5. The intensities of the peaks are shown in Table 6.

Fig. 6. Deconvoluted Raman spectrum of 15 Na₂O - 4 TiO₂ - 81 SiO₂ glass. Individual peaks are given in red, the overall fitted spectrum in green, and the measured Raman spectrum in black.

Table 5. Position of Raman peaks for Na₂O-TiO₂-SiO₂ glasses at room temperature.

Composition (Na ₂ O-TiO ₂ - SiO ₂)	Wavenumber of Fitted Peaks (cm ⁻¹)												
	340	Main Band	460	490	540	600	720	800	840	900	980	1080	1100
10-4-86		457	458	488	539		730	794	841	906	977	1072	1087
10-7-83	336	458	455	488	536		725	797	848	907	973	1063	1086
10-10-80	332	458	453	487	533		728	802	851	908	970	1052	1082
15-4-81	341	476	458	490	534	590	720	794	849	906	975	1083	1090
15-7-78	342	470	457	491	535	576	718	799	851	908	976	1070	1091
15-10-75	336	474	462	493	533	571	722	802	852	908	973	1067	1088
20-4-76	343	498	459	490	537	592	720	794	851	905	975	1089	1094
20-7-73	340	494	462	491	540	592	722	790	849	906	975	1080	1094
20-10-70	337	484	450	491	537	580	724	795	849	908	976	1074	1093
25-4-71	340	528	452	500	548	589	725	788	848	897	973	1091	1099
25-7-68	341	529	465	497	552	600	717	790	849	899	972	1087	1098
25-10-65	336	534		493	557		715	791	843	897	969	1078	1099

Table 6. Intensity of Raman peaks for Na₂O-TiO₂-SiO₂ glasses at room temperature. Intensity is normalized to the maximum intensity in the 400-600 cm⁻¹ range.

Composition (Na ₂ O-TiO ₂ - SiO ₂)	Normalized Intensity of Fitted Peaks (a.u.)												
	340	Main Band	460	490	540	600	720	800	840	900	980	1080	1100
10-4-86		0.91	0.07	0.13	0.04		0.27	0.48	0.35	1.72	0.66	0.98	0.38
10-7-83	0.02	0.92	0.05	0.12	0.09		0.42	0.67	0.54	2.43	1.23	0.98	0.25
10-10-80	0.05	0.92	0.04	0.10	0.13		0.68	0.86	0.69	2.62	1.60	0.86	0.16
15-4-81	0.02	0.82	0.05	0.13	0.25	0.04	0.19	0.52	0.37	2.16	1.01	1.38	0.48
15-7-78	0.05	0.83	0.04	0.13	0.25	0.05	0.33	0.68	0.46	2.93	1.46	1.23	0.28
15-10-75	0.08	0.79	0.04	0.11	0.27	0.07	0.49	0.81	0.56	3.11	1.84	1.03	0.17
20-4-76	0.03	0.65	0.05	0.10	0.40	0.09	0.06	0.35	0.27	1.93	0.90	1.48	0.53
20-7-73	0.06	0.69	0.05	0.06	0.36	0.05	0.19	0.47	0.55	3.00	1.32	1.48	0.33
20-10-70	0.06	0.74	0.02	0.11	0.31	0.06	0.32	0.56	0.53	3.06	1.48	1.30	0.22
25-4-71	0.04	0.51	0.02	0.11	0.38	0.26	0.02	0.23	0.17	1.69	0.74	1.73	0.50
25-7-68	0.07	0.59	0.02	0.10	0.40	0.13	0.05	0.32	0.34	2.42	1.01	1.69	0.40
25-10-65	0.12	0.70		0.06	0.31		0.25	0.56	0.49	3.85	1.37	1.62	0.29

In the low frequency region, the main silica band at ~460 cm⁻¹ decreases in intensity and shifts to higher frequencies with increasing Na₂O, and with increasing TiO₂ it increases in intensity and shifts to lower frequencies. Increasing TiO₂ increases intensity more at 20 and 25 Na₂O contents and shifts the position less at 10 and 25 Na₂O. The shoulder at 340 cm⁻¹ increases in intensity with increasing TiO₂ and this increase is larger for higher Na₂O contents. The 490 cm⁻¹ peak remains relatively unchanged in intensity and shifts slightly to higher frequencies with increasing Na₂O and does not change significantly with increasing TiO₂. The 540 cm⁻¹ peak position does shifts only slightly between 10 and 20 Na₂O before shifting significantly to higher frequencies between 20 and 25 Na₂O. Intensity of the 540 cm⁻¹ peak does the opposite, increasing steadily between 10 and 20 Na₂O and then remaining almost constant between 20 and 25 Na₂O. Changes in the TiO₂ content have mixed effects on the peak position and intensity, increasing intensity and shifting to lower frequencies at 10 Na₂O and decreasing intensity and shifting to higher frequencies at 25 Na₂O. The 600 cm⁻¹ peak was too small to fit in the 10 Na₂O glasses, and generally shifted slightly to higher frequencies with increasing Na₂O and to lower frequencies with increasing TiO₂. At 15 and 20 Na₂O, the intensity remains largely unaffected by Na₂O and TiO₂ content. A large increase in intensity occurs at 25 Na₂O, with increasing TiO₂ decreasing the intensity significantly. A small peak appears at 460 cm⁻¹. This peak does not change significantly in position or intensity with changing TiO₂ or Na₂O content.

The 720 cm⁻¹ peak shifts to higher frequencies with increasing TiO₂ and to lower frequencies with increasing Na₂O. It also increases in intensity with increasing TiO₂ and decreases in intensity with increasing Na₂O. The 800 cm⁻¹ peak shows the same response to the addition of TiO₂, increasing in both frequency and intensity, although the change in position is

larger than that seen in the 720 cm^{-1} peak. The 840 cm^{-1} peak behaves in the same manner as the 720 and 800 cm^{-1} peaks in intensity, but does not shift in position with either Na_2O or TiO_2 .

The high frequency peaks tend to have larger changes with composition. The 900 cm^{-1} peak shifts to higher frequencies with added TiO_2 and to lower frequencies with added Na_2O . Similar to the reaction of the 800 cm^{-1} peak, there is a large shift to lower frequencies between 20 and 25 Na_2O . It increases in intensity with increasing TiO_2 . Increasing Na_2O decreases its intensity at low TiO_2 contents and increases the intensity at high TiO_2 contents. The 1100 cm^{-1} peak shows the opposite response to composition changes, decreasing in frequency with added TiO_2 and increasing in frequency with added Na_2O . With this peak the shift is fairly constant with Na_2O between 15 and 25 mol%. The 1100 cm^{-1} peak increases in intensity with Na_2O and decreases with TiO_2 . The 1080 cm^{-1} peak decreases in intensity with increasing TiO_2 and increases in intensity slightly with increasing Na_2O . It shifts slightly to higher frequencies with increasing Na_2O and shifts significantly to lower frequencies with increasing TiO_2 . The 980 cm^{-1} peak experiences no significant peak shift with composition changes, but it does generally increase in intensity with increasing TiO_2 .

To summarize the peak changes, adding TiO_2 increases the intensity of the 340, main band, 720, 800, 900, and 980 cm^{-1} peaks, while decreasing the intensity of the 1080 and 1100 cm^{-1} peaks. Na_2O increases the intensity of the 540 and 1080 cm^{-1} peaks while decreasing the intensities of the main band, 720, 800, and 840 cm^{-1} peaks. Adding Na_2O shifts the main band, 540, 1080, and 1100 cm^{-1} peaks to higher frequencies and the 720, 800, and 900 cm^{-1} peaks to lower frequencies. Adding TiO_2 shifts the main band, 1080, and 1100 cm^{-1} peaks to lower frequencies and the 720, 800, and 900 cm^{-1} peaks to higher frequencies. The 340, 490, 840, and 980 cm^{-1} peaks do not shift significantly with changes in either Na_2O or TiO_2 content.

Discussion:

The changes in properties with respect to the addition of Na_2O to the ternary system are basically the same as observed in the binary Na_2O - SiO_2 system. Density [9,32,34] and refractive index increase [2], Young's modulus and shear modulus decrease [9,32], bulk modulus and Poisson's ratio increase [32] (note: there is a shallow minimum in the bulk modulus around 10 Na_2O in the binary system), and thermal expansion increases [2,10]. The response to the addition of TiO_2 differs notably between the ternary and binary systems. In both cases the refractive index [34,42] and Poisson's ratio [33] increase with TiO_2 ; however, in the ternary system the density increases instead of remaining basically constant in the binary system [42], the elastic moduli increase instead of decreasing [34], and thermal expansion increases instead of decreasing [46,47].

Since Ti should be four-fold coordinated in a tetrahedral geometry in both the binary and ternary systems at low Ti contents [1,31], with square pyramidal ^{51}Ti beginning to appear in the ternary glasses above 5 mol% TiO_2 [31] (and dominate at 15 mol% [16]), this difference in response of material properties is somewhat non-intuitive. To unravel this mystery, we will begin with a review of the Raman peak assignments and a discussion of the implications of the shifts in position and the changes in intensity. To show the evolution of peak position and intensity with composition, the peak positions and intensities of select peaks versus the number of bridging oxygen are shown in Fig. 7.

Fig. 7. Raman peak positions and intensity versus the number of bridging oxygen.

Peak assignments in the 400-600 cm⁻¹ range are generally in agreement, with the main band at ~460 cm⁻¹ peak assigned to symmetric oxygen vibrations in Si-O-Si bonds, the 490 cm⁻¹

peak assigned to a breathing mode vibration in four-member Si-O rings, and the 540 cm^{-1} peak assigned to delocalized vibrational modes arising from non-bridging oxygen in the silica network [48]. The peak occurring at 340 cm^{-1} is harder to assign. Kusabiraki et al. [20] suggested that it was due to antisymmetric bending of ^{6}Ti ; however, the population of ^{6}Ti should be extremely small in our glasses [1,16,31]. To our best knowledge, the small peak at 460 cm^{-1} has not been reported previously for these glasses. The behavior of this peak is similar to that of the 490 and 600 cm^{-1} peaks, in that it is resistant to changes in position and intensity with composition. Given this, it would make sense for this peak to be related to vibrations of rings within the silica network. As 460 cm^{-1} is generally lower than the main band, which is associated with six-member rings, it could correspond to the breathing mode of larger, e.g., seven- or eight-member rings. However, larger rings are generally quite flexible and unlikely to have symmetric vibrations. Thus it seems more likely that this vibration would correspond to a rocking-mode between two smaller, adjacent rings.

The 1080 cm^{-1} and 1100 cm^{-1} peaks are likely associated with Ti and Si non-bridging oxygen, respectively. A similar peak appears at $\sim 1100\text{ cm}^{-1}$ in both binary systems; assigned to Q^3 species in $\text{Na}_2\text{O-SiO}_2$ glasses [48] and to anti-symmetric oxygen vibrations in $\text{TiO}_2\text{-SiO}_2$ glasses (either Ti-O-Si bonds [33] or Si-O $^-$ non-bridging oxygen caused by the added Ti [24]). The Q^3 peak appears at 1080 cm^{-1} for Si-O-Li non-bridging oxygen [48] as opposed to at 1100 cm^{-1} for Si-O-Na. This suggests that the difference in position is caused by an increase in the range of motion available to the oxygen rather than a change in the Si-O bond. As ^{4}Ti has a longer and weaker bond than ^{4}Si , the Ti Q^3 species would tend to occupy a lower frequency than a Si Q^3 .

In earlier studies, the 900 cm^{-1} peak was assigned to the bridging oxygen vibrations of TiO_2 tetrahedra [24,49]. This peak shifts to lower frequencies as the TiO_2 content is increased. If it were caused by ^{4}Ti , this would correspond to an increase in the amount of corner sharing Ti tetrahedra, which would increase the free volume around the bridging oxygen, allowing for larger motions and a lower frequency. This matches Raman spectra for sodium titanates, which have peaks between 860 and 885 cm^{-1} depending on stoichiometry [50]. However, it has been observed that the fraction of ^{4}Ti decreases and that of ^{5}Ti increases as the TiO_2 content in the glass is increased [16,24,31]. ^{5}Ti has four Ti-O bonds and one titanyl Ti=O bond. Farges et al. [15,17] predicted that the vibrations of this titanyl oxygen would have frequencies between 850 - 910 cm^{-1} . In a later high temperature Raman study by Reynard and Webb, the 900 cm^{-1} peak was assigned to the titanyl oxygen vibrations [25].

The 980 cm^{-1} peak also have multiple possible assignments, as peaks at $\sim 950\text{ cm}^{-1}$ appear in both the $\text{TiO}_2\text{-SiO}_2$ and $\text{Na}_2\text{O-SiO}_2$ systems. In the $\text{Na}_2\text{O-SiO}_2$ system, this peak is assigned to the Si Q^2 species, which starts to become significant in intensity around 30 mol% Na_2O [32] and can shift towards 980 cm^{-1} as the Na_2O content reaches 40-50 mol% [48]. In the $\text{TiO}_2\text{-SiO}_2$ system, this peak has been assigned to either Si Q^2 species caused by the addition of TiO_2 [24] or Ti-O-Si bridging oxygen [33]. If it were due to the Q^2 species of Si caused by Na, then it would be expected that the peak intensity would be sensitive to the Na composition. As neither the peak intensity nor the position is sensitive to the Na_2O content (Fig. 7c,d), it makes more sense to assign it to a Ti-O vibration. The intensity of the 980 cm^{-1} peak is sensitive to the TiO_2 content and the shift from 950 to 980 cm^{-1} between the binary and ternary systems.

The 720 and 800 cm^{-1} peaks have been assigned to several different vibration modes in previous literature. Inoue et al. assigned them to vibrations around ^{6}Ti and ^{5}Ti , respectively [1]. Reynard and Webb assigned the 720 cm^{-1} peak to the motion of bridging oxygen in Q^2 and

Q^3 species [25]. Reynard additionally pointed out that ^{61}Ti has peaks at $\sim 600\text{ cm}^{-1}$ in rutile and anatase, with peaks at 720 cm^{-1} only appearing in crystals with edge-sharing ^{61}Ti octahedra [51]. If the 720 cm^{-1} peak was associated with the presence of Q^2 and Q^3 species, then its intensity would increase with increasing Na_2O content. As the intensity of this peak decreases with Na_2O and increases with TiO_2 , this assignment seems unlikely (Fig. 7e). Rather, if we suppose that the 800 cm^{-1} continues to correspond to the motions of Si within its tetrahedral oxygen cage [48], then the 720 cm^{-1} peak could correspond to the motions of tetrahedral Ti. In this case the addition of Na_2O would create more non-bridging oxygen, which would break the symmetry around Q_4 species of Ti and Si and reduce the intensity of both peaks. This matches the behavior observed in Raman spectra (Fig. 7e). The 720 cm^{-1} peak is reported at frequencies of $\sim 750\text{ cm}^{-1}$ for higher TiO_2 contents [24,49] and has been compared to the 767 cm^{-1} TiO_4 band in Ba_2TiO_4 [24]. The 840 cm^{-1} peak was reported in pure SiO_2 glass by Kalampounias et al. [52], and assigned it to Si cation vibrations within "supertetrahedra" structures, with the 800 cm^{-1} peak assigned to Si cation vibrations within apex-bridged tetrahedra.

Accepting these peak assignments, we can compare them to the changes in material and mechanical properties. To make the changes in the spectra with changing TiO_2 content easier to see, Raman spectra for glasses from 0 to 10 TiO_2 are plotted for 10 and 25 Na_2O in Fig. 8. As Na_2O and TiO_2 concentrations become higher, the density increases. The effect of Ti on the structure to increase density can be seen in the broadening of the main 460 cm^{-1} peak (Fig. 8). This broadening indicates a larger range of angles occupied by the network formers, which allows for more efficient packing. This arises from the longer and lower strength Ti-O bonds, which preserve the silica network integrity while making rearrangement easier. The role of Na is to make the structure less rigid and fills available free volume, as seen in Fig. 9, where the Na_2O content is increased from 0 to 25 mol% for 4 and 10 TiO_2 glasses. This is most clearly seen in the changes in the 460 cm^{-1} peak, with the loss of symmetry and shift to higher frequencies (Figs. 7a, 9a,b).

Fig. 8. Raman spectra of a) 10 Na₂O and b) 25 Na₂O glasses with TiO₂ contents between 0 and 10 mol%. Spectra are overlaid to make the differences in peak shape easier to observe. Spectra intensities are normalized to the peak maximum in the 400-600 cm⁻¹ range. Raman spectra for the Na₂O-SiO₂ system are included for comparison [32].

Fig. 9. Raman spectra of a) 4 TiO₂ and b) 10 TiO₂ glasses with Na₂O contents between 0 and 25 mol%. Spectra are offset vertically for clarity with increasing Na₂O. Spectra are normalized to the signal maximum in the 400-600 cm⁻¹ range. Raman spectra of binary TiO₂-SiO₂ glasses with 5.4 and 8.3 TiO₂ are included in a) and b), respectively, for comparison [33].

If $^{[4]}\text{Ti}$ is the primary species in these glasses, we might expect to see similar anomalous thermal expansion behavior in the binary system as Ti is substituted for Si. While there is an initial increase in CTE between 0 and 4 mol% TiO_2 , the CTE remains effectively constant between 4 and 10 TiO_2 (Fig. 3). TiO_2 reduces the CTE in the binary system by increasing the free volume [33], so it might be expected that this effect would be hindered as the Na_2O content is increased. The increase in CTE with initial additions of Ti, which should be almost completely four-fold coordinated, supports this idea. The constant CTE between 4 and 10 mol% could be due to TiO_2 entering the glass as a combination of $^{[4]}\text{Ti}$ and $^{[5]}\text{Ti}$. $^{[5]}\text{Ti}$ should generally promote an increased flexibility in the network due to the titanyl non-bridging oxygen, but also removes Na from the silica network. The balance of these two effects could explain why CTE remains relatively constant as TiO_2 is increased from 4 to 10 mol%.

This conjecture supports Farges et al.'s percolation model [16], where Ti atoms form clusters with localized high concentrations of Ti and Na. In these clusters $(^{[5]}\text{Ti}=\text{O})\text{O}_4$ square pyramids are at the boundary between the Na-rich regions and the Si-rich regions, with the $\text{Ti}=\text{O}$ titanyl oxygen on the Na-rich side of the boundary. If we adopt the percolation model into our explanation, the behavior of intensity of the 720, 800, 840, 900, 980, 1080, and 1100 cm^{-1} Raman peaks can be more easily explained. The addition of TiO_2 promotes further formation of these clusters, meaning that there will be less Na around Si. Thus the intensity of the 1100 cm^{-1} peak decreases (Fig. 7f), due to the reduced population of Si-O non-bridging oxygen contributing to this peak. This is consistent with the intensity increase in the 800 and 840 cm^{-1} peaks, indicating that a greater population of Q^4 Si exists (Fig. 7f). With more Ti the intensities of Ti related peaks, 720, 900, and 980 cm^{-1} , increase (Fig. 7d, e). Interestingly, the 1080 cm^{-1} peak decreases in intensity with increasing TiO_2 (Fig. 7f). This makes sense if titanyl oxygen acts to charge balance Na^+ in the network, corresponding to an increase in the $^{[5]}\text{Ti}$ population. Relating these peak changes to the mechanical properties, we see that as the TiO_2 content increases both Young's modulus and shear modulus increase. One possible explanation would be that the addition of Ti causes a reduction in the number of non-bridging oxygen around Si. That is, as Ti enters the glass and preferentially attracts Na to form clusters, it leaves an interconnected network of silica tetrahedra with few non-bridging oxygen. This would act to increase the overall integrity of the network and stiffness of the glass structure, and corresponds to the increased intensity of the main band, 800 and 840 cm^{-1} peaks (Fig. 7b, e). This mechanism of stiffening should be quite mild and certainly not increase the overall stiffness above that of pure silica. However, Inaba et al. reported Young's modulus for a 25 Na_2O - 15 TiO_2 - 60 SiO_2 glass of 74.2 GPa [9]. This follows the linear trend increase of Young's modulus with added TiO_2 seen in our 25 Na_2O glasses, to a greater value than pure silica. This suggests that the stiffening aspect is not primarily due to shielding the SiO_2 network from Na, but rather caused by an increase in the volume density of bonds in the network, tightening the network and increasing the packing density.

The shift in the 1080 and 1100 cm^{-1} peak positions match the free volume changes that would accompany the formation of these clusters (Table 3). As Na_2O content increases, the peaks shift to higher frequencies, indicating that the free volume decreases as the amount of Q^3 species increases. With the addition of TiO_2 , the peak shifts to lower frequencies as Na preferentially sits near titanyl oxygens and more free volume becomes available around non-bridging oxygen elsewhere in the glass. The fact that the 980 cm^{-1} peak changes its intensity, but its not position, with changes in either Na_2O or TiO_2 content (Fig. 7c, d) suggests that the population of the Ti and Na rich clusters changes, but not their size. A change in size should

result in a change in the average bonding environment around Ti, which would be expected to cause a shift in the peak position. Additionally, in the composition ranges we studied here it is possible that the population of clusters is not large enough for interactions between them to be appreciable; otherwise, the peak position would shift with the change of composition.

Both bulk modulus and Poisson's ratio increase with both TiO_2 and Na_2O content. This can generally be related to the reduction of free volume associated with both the number of non-bridging oxygen and the formation of Ti and Na rich clusters. For both bulk modulus and Poisson's ratio, the observed increase is reduced between 20 and 25 mol% Na_2O , compared to the change with TiO_2 at other Na_2O contents. This corresponds to the significant increase in the frequency of the 460 and 540 cm^{-1} peaks (Fig. 7a). It is possible that at 25 mol% Na_2O there is enough Na in the network that the formation of Ti rich clusters does not significantly alter the free volume available to the surrounding silica network.

Conclusions:

The structure, material and mechanical properties of Na_2O - TiO_2 - SiO_2 glasses have been studied with regards to composition through Raman spectroscopy, Brillouin light scattering, and dilatometry. Density, refractive index, elastic moduli, and Raman spectra agree well with literature values of similar glasses. The addition of Na_2O increases the density, refractive index, and CTE of glasses. It decreases Young's modulus and shear modulus while increasing the bulk modulus and Poisson's ratio. The addition of TiO_2 increases density, refractive index, Young's modulus, shear modulus, bulk modulus, and Poisson's ratio. CTE increases initially with TiO_2 , and then remains constant with further additions of TiO_2 .

Changes in the Raman spectra with composition have been discussed and related to the changes in properties. TiO_2 was observed to provide a stiffening effect by increasing the intensity and shifting to higher frequencies of peaks associated with network formers, namely the 720, 800, and 900 cm^{-1} peaks, while decreasing the intensity of the Si-O non-bridging oxygen peak at 1100 cm^{-1} . TiO_2 appears to reduce the effect of Na_2O on the silica network, and this shielding effect has been discussed in relationship to the percolation model proposed by Farges et al. [16]. TiO_2 stiffens the network by increasing the ordering and constraints in the network through the formation of clusters with higher local Ti and Na concentrations. While by increasing the number of non-bridging oxygen, Na_2O disrupts the network connectivity and fills available free volume.

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