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Structure and thermo-mechanical response of TiO_2-SiO_2 glasses to temperature

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ABSTRACT

Structure and elastic moduli of $xTiO_2$ - $(1 - x)$ SiO_2 ($x = 0$–10 mol%) glasses prepared via the sol-gel process have been investigated through *in-situ* high temperature Raman and Brillouin light scattering from room temperature to 1200 °C. Three other synthetic glasses prepared by the flame hydrolysis deposition (FHD) process, namely, synthetic silica glass (Corning 7980) and two titania silicate glasses ($x = 5.4$ and 8.3), were also examined under the same conditions. The coefficients of thermal expansion of sol-gel glasses were measured up to 800 °C. Differences in properties of sol-gel glasses, FHD glasses, and literature values are presented and discussed. Changes in elastic moduli and Raman peak positions with composition and temperature are discussed. Young's modulus, bulk modulus, and shear modulus were found to decrease with increasing TiO_2 content and increase with temperature. A possible explanation for the anomalies in TiO_2-SiO_2 glasses is suggested based on the response of elastic moduli, Raman spectra, and coefficients of thermal expansion to temperature.

1. Introduction

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

In addition, other properties of titania silicate glasses have been found to behave anomalously with increasing TiO_2 content. Shelby showed that the density is almost independent of the TiO_2 content below 10 wt% (7.7 mol%) TiO_2, while the sensitivity of density to fictive temperature increases with increasing TiO_2 [6,7]. An anomalous response of transverse sound velocity to temperature has been shown in several titania silicate glasses from 0 to 300 K, where a minimum occurs around 80 K, above which it increases with increasing temperature [8]. Young's modulus and Poisson's ratio were shown to increase with temperature from room temperature to 900 °C for Corning 7971 ULE™ glass [9]. Young's modulus, bulk modulus and shear modulus of a TiO_2-SiO_2 glass with 8.4 wt% of TiO_2 were observed to decrease with pressure up to 2 GPa [10]. It has been suggested that the anomalous response of elastic moduli to temperature is connected to low thermal expansion of titania silicate glasses [8].

The structure of TiO_2-SiO_2 glasses has been studied frequently over the last several decades. Sandstrom et al. examined the glasses through extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge spectroscopy (XANES) to measure the coordination of Ti in the glass [11]. They showed that Ti^{4+} occupies primarily four-fold coordination, with a small concentration of six-fold coordinated atoms. More recent XANES experiments by Henderson et al. [12] showed that Ti^{4+} actually occupies five-fold coordinated sites at concentrations below 3.6 wt% with further additions of Ti occupying primarily four-fold coordinated sites. Chandrasekhar et al. [13] examined TiO_2-SiO_2 glasses through infrared (IR) and Raman spectroscopy. Henderson and Fleet provided a more detailed Raman peak analysis [14] for a variety of TiO_2 containing glasses. The structure of TiO_2-SiO_2 glasses has also been studied through neutron diffraction by Pickup et al. [15], and through quantum-chemical calculations by Sokolov et al., who estimated their vibrational frequencies, IR and Raman spectra [16]. These structural studies have generally been in agreement about the behavior of Ti^{4+} cations in the glass at room temperature. They replace Si^{4+} cations in the glass structure, initially with a higher coordinated state, either five- or six-fold. After approximately 2 mol%, Ti^{4+} becomes primarily four-fold coordinated until it phase separates into six-fold coordinated crystals above 10 mol%. To date, the structure of TiO_2-SiO_2 glasses under conditions other than ambient has been much less well studied.

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In order to understand the role of TiO_2 in silica glass, particularly, to gain a fundamental understanding of the anomalous thermal and elastic responses to temperature from the structure point of view, it is helpful to examine how the structure of the glass changes over a large composition and temperature range. In this study, we examined TiO_2-SiO_2 glasses from 0 to 10 mol% TiO_2 produced through the sol-gel process and three synthetic glasses with 0, 5.4, and 8.3 mol% TiO_2 prepared by the flame hydrolysis deposition (FHD) process by using *in-situ* high temperature Raman and Brillouin light scattering from room temperature to 1200 °C. Density and CTE up to 800 °C of these glasses were also measured. Glasses produced through the sol-gel method are compared with other synthetic glasses by FHD in terms of density, thermal expansion, elastic moduli, and Raman spectra. Correlations are drawn between changes in Raman peak shifts with temperature, and changes in responses of elastic moduli and thermal expansion to temperature. A possible explanation for the anomalous responses of TiO_2-SiO_2 glasses to temperature is suggested.

2. Methods

TiO_2-SiO_2 glasses were synthesized through the sol-gel process over the range of 0–10 mol% TiO_2, based on the procedure used by Huang et al. [17]. TiO_2 content was limited in this range to avoid the tendency of glasses to crystallize [2,18]. Tetraethyl orthosilicate (TEOS) and titanium butanate were used as the silica source and the titania source, respectively. Methanol was used as the solvent, water and 0.1 M hydrochloric acid were used as catalysts for the hydrolysis process, and dimethyl formamide (DMF) was used as a drying control agent. Molar ratios of chemicals are 1:12.8:0.0025:4.75:0.85 for alkoxides: methanol: HCl:H_2O:DMF. Methanol and TEOS were mixed together, then the HCl and about half of the water were added to start the hydrolysis process. Titanium butanate was added dropwise with continuous stirring. Then the second portion of the water was added along with the DMF. The sol was stirred for approximately 30 min before being transferred to sample molds (plastic tubes with caps). The sols were gelled for one day at room temperature and then three days at 60 °C. The gelled samples were removed from the molds and soaked in methanol for three days to remove any remaining water.

After soaking, the gels were dried under atmospheric conditions for one week. They were then heated at 60 °C for three days to remove any remaining methanol/water. The dried gels were sintered in a programmable tube furnace from room temperature to 1100 °C through the following steps (Fig. 1): ramp from room temperature to 70 °C at 1.5 °C/min; dwell at 70 °C for 60 min; ramp from 70 °C to 150 °C at 0.5 °C/min; dwell at 150 °C for 120 min; ramp from 150 °C to 200 °C at 0.2 °C/min; dwell at 200 °C for 120 min; ramp from 200 °C to 300 °C at 0.1 °C/min; dwell at 300 °C for 60 min; ramp from 300 °C to 350 °C at 0.2 °C/min; ramp from 350 °C to 400 °C at 0.5 °C/min; ramp from 400 °C to 700 °C at 1.0 °C/min; dwell at 700 °C for 240 min; ramp from 700 °C to 900 °C at 0.5 °C/min; ramp from 900 °C to 1100 °C at 6.0 °C/min; dwell at 1100 °C for 20 min; cool to room temperature in the furnace. Between 150 °C and 700 °C oxygen was flowed through the tube furnace at a rate of 60 ml/min to facilitate the decomposition of residual organics in the glass.

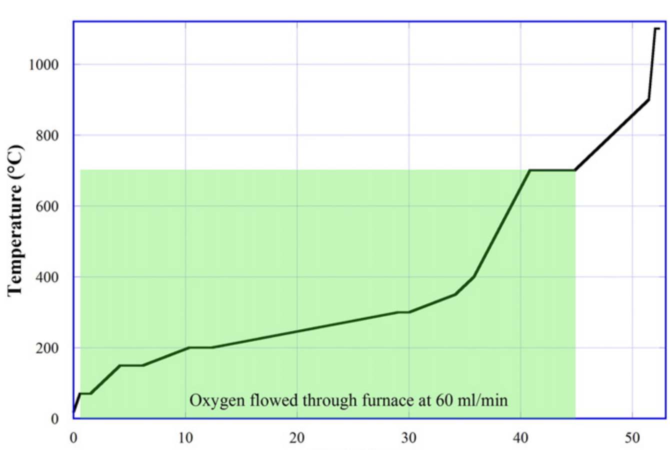

Fig. 1. Time-temperature profile for the sintering of sol-gel glasses. The area high-lighted in green represented time when oxygen flowed through the furnace.

Table 1
Compositions and standard deviations (in mol%) of TiO_2-SiO_2 sol-gel glasses.

Sample	SiO_2	SiO_2 Std	TiO_2	TiO_2 Std
4 TiO_2–96 SiO_2	96.28	0.026	3.72	0.026
5.4 TiO_2–94.6 SiO_2	94.51	0.039	5.49	0.039
8.3 TiO_2–91.7 SiO_2	91.68	0.034	8.32	0.034
10 TiO_2–90 SiO_2	90.23	0.043	9.77	0.043

Through this process cylindrical, bulk glass samples of up to 20 mm in length and 3 mm in diameter were prepared. As a reference, commercial synthetic silica glass (Corning 7980) and two TiO_2-SiO_2 glasses ($x = 5.4$ and 8.3) prepared by FHD were used. The commercial synthetic silica glass was produced by the direct deposition of combusted silica precursor to transform into glass boule. On the other hand, TiO_2-SiO_2 glasses in this study were prepared through soot process. Fine soot particles of TiO_2-SiO_2 were produced by hydrolysis of gaseous silicon tetrachloride and titanium tetrachloride in oxygen-hydrogen flame. The porous soot preform was heat-treated at 1200 °C for 3 h in air, at 1400 °C for 4 h in vacuum, and at 1700 °C for 4 h in vacuum. Then, the glasses were annealed at 1100 °C for $x = 5.4$ and 1040 °C for $x = 8.3$.

Density of samples was measured through the Archimedes method, using water as the liquid medium. Each sample was measured ten times, resulting in standard deviations between 0.005 and 0.01 g/cm^3. Sintered sol-gel samples have densities between 2.15 and 2.18 g/cm^3, very close to the values of TiO_2-SiO_2 glasses prepared through other methods [6–8], but lower than the 2.20 g/cm^3 of other synthetic glasses produced by FHD that were measured using the same method. Shelby [6] summarized densities of TiO_2-SiO_2 glasses from eight studies, where the majority of measured values are between 2.19 and 2.21 g/cm^3 with the rest between 2.15 and 2.28 g/cm^3. Densities of TiO_2-SiO_2 glasses prepared through the sol-gel process have been reported in the range of 2.10 to 2.36 g/cm^3 [15], so the densities of our sol-gel samples seem reasonable, if generally slightly low.

Electron microprobe analysis (EMPA) was used to determine the composition and the homogeneity of four sol-gel TiO_2-SiO_2 glasses. Quartz and rutile were used as the Si and Ti references, respectively. Compositions were measured at 40 points across the surface for each sample. Nominal compositions, measured compositions, and standard deviations are shown in Table 1. Compositions are within 0.3 mol% of the nominal values, and have standard deviations of 0.04 mol% or less.

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

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

Glass	OH content (ppm)
5.4 TiO_2–94.6 SiO_2 by sol-gel	2250
8.3 TiO_2–91.7 SiO_2 by sol-gel	2965
Synthetic silica, FHD	800
5.4 TiO_2–94.6 SiO_2, FHD	50
8.3 TiO_2–91.7 SiO_2, FHD	50