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In-situ Raman and Brillouin light scattering study of the international simple glass in response to temperature and pressure

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ABSTRACT

International simple glass (ISG) is a six-component boroaluminosilicate glass recently developed as a reference benchmark glass for international collaborative studies on high level nuclear waste encapsulation. In this work, structure and elastic properties of the ISG in response to temperatures up to 700 °C and pressure up to 5.5 GPa were studied by in-situ Raman and Brillouin light scattering. Structural integrity of the ISG was evidenced from room temperature to 550 °C by negligible changes in its Raman spectra and elastic moduli. Raman and Brillouin light scattering measurements showed that the ISG was only elastically deformed throughout the tested pressure range.

1. Introduction

A requirement for general acceptance of increased worldwide utilization of nuclear energy is the demonstration of robust materials to immobilize high level waste (HLW) for long-term emplacement in geologic repositories. Cement [1–4], ceramics [5], and glass-ceramic composites [6–14] have been proposed as encapsulation materials, as well as glasses of various compositions [5,15]. Glass is promising for its innate ability of the amorphous network to accommodate a wide variety of elements, including the heavy actinides and fission products that result from nuclear energy generation or other processes such as nuclear weapons reclamation and medical treatments. Borosilicate glass has emerged at the forefront of nuclear waste forms due to its ease of processing [16] and its good environmental durability, with groundwater leaching being of primary concern for safe long-term storage [17]. An international simple glass (ISG) is currently being used in a few countries as a standard representation of waste glasses in collaborative studies to predict waste form behavior over geological time scales [18].

Nuclear waste forms containing typical HLW loadings will, when placed in a repository, generate enough heat to result in an initial storage temperature rise as high as 250 °C or even 600 °C by some estimates [19,20]. It is also well known that ballistic decay events can swell the matrix and helium or oxygen bubbles can form under irradiation [19]. This can lead to volume change and static pressure build-up in the glass matrix. To determine the suitability of nuclear waste glass in typical repository conditions, it is important to understand the evolution of its structure through the expected range of temperatures and pressures. Though addition of HLW will affect the structure and the behavior of the glass by network modification and ballistic nuclear decay processes, we offer a starting point by determining the response of the pristine ISG to a range of temperatures and pressures that include and exceed expected repository conditions.

2. Experimental

To provide homogeneity between samples, a single batch of the ISG was produced in May 2012 by MoSCI Corporation (Rolla, MO). Three individual batches yielding approximately 25 kg of glass cullet each were produced by blending powdered raw materials in a V-blender. Each batch was melted in high purity fused silica crucibles in an electric furnace at 1300 °C and water quenched to produce glass frit. After drying in an electric oven, the three batches of frit were blended together in a V-blender to create a master lot. This frit was then re-melted in platinum–rhodium crucibles in an electric furnace at 1300 °C for approximately 4 h, stirred once with a quartz rod, and cast into graphite molds. The ingots were annealed at 569 °C for 6 h (in an electric oven) and cooled to room temperature at a rate of 50 °C per hour. Glass ingots of 500 g each were distributed for study.[1] Samples used in this study were cut from one of such ingots.

The nominal target and measured compositions of the ISG are shown in Table 1, of which the main components are common to most boroaluminosilicate nuclear glasses. The ratios between components are similar to SON68, the French glass for waste encapsulation produced by Areva at La Hague [17,18]. Composition of two bars

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[1] Dr. James C. Marra kindly provided information on the synthesis of the ISG.

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Table 1
Nominal target and measured composition of the ISG [21].

Oxide	Target (mol%)	Target (wt.%)	Tolerances (wt.%)	Composition of bar 1 (wt.%)	Composition of bar 2 (wt.%)
SiO_2	60.2	56.2	±1.5	56.4	56.2
B_2O_3	16.0	17.3	±0.9	17.8	17.5
Na_2O	12.6	12.2	±0.7	12.2	12.6
Al_2O_3	3.8	6.1	±0.8	5.84	5.96
CaO	5.7	5.0	±0.6	4.60	4.54
Zr_2O	1.7	3.3	±0.5	3.15	3.24

of 500 g each was measured at Savannah River National Laboratory (SRNL), by using inductively coupled plasma-atomic energy spectroscopy (ICP-AES) and ion chromatography (IC) for cation and anion analysis, respectively. Reported values in Table 1 are the normalized averages of 12 measurements on each of the two bars [21]. There are some statistical differences in the composition between the two bars, but each bar is within the compositional tolerances. We expect that the composition of the ingot used in this study is within the compositional specifications in Table 1.

A Metricon Model 2010/M Prism Coupler was used to measure the room temperature refractive index of the ISG. Density was measured by the Archimedes method in distilled water. Shimadzu DTG-60 was used for differential thermal analysis (DTA) in N_2 environment with 20 mL/min gas flow, heating rate of 10 °C/min, with a powdered glass sample weight of 58.934 mg in a Pt pan. Theta Dilatronic model 292 was used to determine the linear coefficient of thermal expansion (CTE) to 690 °C by heating at 5 °C/min.

Raman spectroscopy was used to study the glass structure by monitoring modes of molecular vibration excited by the oscillating electric field of an incident light source [22]. Brillouin light scattering (BLS) was used to determine the elastic moduli of the ISG by measuring both longitudinal (V_L) and shear (V_T) velocities of thermal excitations (phonons), which naturally exist in a condensed matter at finite temperatures [23]. A six-pass high contrast Fabry–Pérot interferometer (JRS Scientific Instruments) was used to measure Brillouin frequency shift, and a Horiba LabRAM HR800 spectrometer was used for Raman measurements. A continuous wave 532 nm green laser was used as the probing light source for both Raman and BLS, and a sliding mirror was used to direct the scattered light to either spectrometer without disturbing the sample during in-situ studies under high temperatures or high pressures.

Temperature dependent light scattering was done using the Linkam TS1500 optical furnace, based on an emulated platelet geometry for BLS by placing the sample on a polished Pt plate [24]. An optically polished sample (~150 μm in thickness and ~1–1.5 mm in later dimensions) was used for the in-situ measurements. The sample was heated at a rate of 50 °C/min to the target temperature (±1 °C) and allowed to equilibrate for 5 min before Raman and Brillouin spectra were taken. From the measured longitudinal and transverse sound velocities by BLS, together with the sample density, Young's modulus (E), bulk modulus (K), shear modulus (G), and Poisson's ratio (ν) can be obtained through the following equations:

$$E = V_T^2\left(\frac{3V_L^2-4V_T^2}{V_L^2-V_T^2}\right)\rho \quad (1)$$

$$K = \left(V_L^2-\frac{4}{3}V_T^2\right)\rho \quad (2)$$

$$G = V_T^2\rho \quad (3)$$

$$\nu = \frac{V_L^2-2V_T^2}{2(V_L^2-V_T^2)}. \quad (4)$$

The volumetric thermal expansion ($3\alpha_L$) was considered for density input in modulus calculations through 700 °C. Relative errors for E, K and G were measured to be 0.38%, 0.45%, 0.59% respectively, by five measurements taken at room temperature.

For pressure dependent studies, a membrane-driven diamond anvil cell (DAC) was used to generate hydrostatic pressures. An optically polished glass sample (~100 μm × 100 μm × 20 μm in size), a ruby ball (5–10 μm in diameter, as pressure calibrant) [25,26] and methanol pressure transmitting medium (PTM) were loaded into a hole drilled in a stainless steel gasket [27]. Pressure in the DAC was determined from the pressure dependent ruby fluorescence shift [28]. After certain pressure was reached in the DAC, the sample was allowed to equilibrate for 15–20 min before any measurement was taken. Longitudinal frequency shift of the ISG under pressure in DAC was obtained using the back scattering geometry in BLS. Repeated measurements gave errors in Brillouin frequency shifts to be ~0.1 GHz, errors in pressures were estimated by repeated measurements to be within 0.1 GPa.

3. Results

Refractive index was measured to be 1.5315 (accuracy of ±0.0002). Density was taken as average of 5 measurements to be 2.50 g/cm^3, in good agreement with the value reported earlier [18]. The glass transition temperature (T_g) was determined from the heating curve of a DTA experiment to be 575 ± 3 °C by the method of intersecting tangents with visual selection (Fig. 1a). The glass transition temperature (T_g) from dilatometry was also measured to be 575 ± 3 °C by the method of intersecting tangents with visual selection (Fig. 1b). Errors reported in T_g are a generous estimate of error by visual alignment of tangents. Data between 120 °C and 550 °C were extrapolated to room temperature where the dilatometry measurements were not reliable. The linear CTE of the ISG in this temperature range was expressed as: $\alpha_L = (3.911 + 0.012651 \cdot T - 9.74\times10^{-6}\cdot T^2)\times10^{-6}/°C$. Then the tangent line between T_g and 690 °C was used to obtain $\alpha_L = (-158.84 + 0.28962 \cdot T)\times10^{-6}/°C$ for 600 °C ≤ T ≤ 700 °C.

Fig. 2 shows the Young's modulus (E), shear modulus (G) and bulk modulus (K) of the ISG, window glass [29] and silica glass. Composition of the window glass is 71.2SiO_2–13.6Na_2O–9.7CaO–4.0MgO (in wt.%) and T_g is 550 °C [29]. Silica glass used in this study is Suprasil 300 with low OH content (≤1 ppm) and T_g is ~1200 °C.

Evolution of the ISG Raman spectrum with increasing temperature to 700 °C is shown in Fig. 3(a). To obtain the peak position at each temperature as seen in Fig. 3(b), an asymmetric Gaussian function was used for fitting the main band, as described by Stancik and Brauns for fitting asymmetric infrared absorption spectra [30]. The normalized main band around 500 cm^{-1} was isolated from 0.8 to 1 to reduce asymmetry, then fit with the asymmetric Gaussian function having a smoothly varying full width at half maximum (FWHM). Error bars reflect the given fitting errors.

The measured longitudinal Brillouin frequency shift of the ISG as a function of pressure is shown in Fig. 4, in comparison with that of window glass [31] and silica glass. The composition of the window glass for the pressure-dependent study is 73.7SiO_2–10.6Na_2O–9.4CaO–3.1MgO–1.8Al_2O_3–1.1K_2O–0.2Fe_2O_3 (in wt.%) [31], which is slightly different from that used in the temperature-dependent study [29]. Raman spectra before compression and after decompression from 5.5 GPa are shown in Fig. 5.

4. Discussion

As it can be seen from Fig. 2, the ISG shows a slightly negative slope in E and G, and a nearly zero slope in K from room temperature to 550 °C. These behaviors are between those of abnormal glasses, such as silica glass, whose elastic moduli increase with temperature, and normal glasses, such as window glass [29], whose elastic moduli decrease with temperature. The nearly temperature-independent elastic moduli