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Direct Observation of Amorphous to Amorphous Apparently First-Order Phase Transition in Fused Quartz

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We report for the first time the direct observation of an apparently first-order phase transition in amorphous silica from the low density amorphous phase to the high density amorphous phase with a discontinuous volume change of about 20% from the dilatometric measurements using the piston cylinder apparatus at 36 kbar and 680 °C. Our Raman spectroscopy measurements on the retrieved samples quenched from high pressure and high temperature experiments do not show any Raman peaks indicating a large modification in the intermediate range order in the structure of amorphous silica.

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Amorphous quartz (a-SiO_2) or silica glass is one of the most well studied materials both theoretically and experimentally because of its importance in practical applications, in understanding the properties of the glassy systems, and its implications in geophysics. It has attracted attention also because of the controversies surrounding its detailed structure, namely, the degree of short range and of intermediate range order and their dependence on pressure and temperature [1].

Studies on a-SiO_2 at high pressures and room temperature have revealed a number of interesting and anomalous properties. Compressibility measurements on a-SiO_2 by Bridgman [2] have shown that the bulk modulus passes through a minimum at about 30 kbar and the changes in the bulk modulus are reversible up to 80 kbar. Irreversible densification of a-SiO_2 has been observed in static experiments around 100 kbar [3–5].

High pressure Raman spectroscopy study of a-SiO_2 at room temperature has revealed a gradual irreversible change in the Raman spectrum between 80 and 300 kbar [6]. A broadening of Raman bands and a loss of intensity have also been observed above 300 kbar [6]. The results from room temperature Brillouin scattering experiments on a-SiO_2 up to 400 kbar have shown that it transforms to a dense amorphous form of SiO_2 [7,8]. An irreversible densification is observed in the range 100–250 kbar, but no further significant densification is observed from 250 to 400 kbar [8]. Neutron scattering measurements on a-SiO_2 specimens quenched from 160 kbar, which had a 20% higher density, have shown that with respect to unpressurized a-SiO_2 there is a substantial change in the first sharp diffraction peak indicating a large modification in the intermediate range order [9]. All these experiments indicate that at room temperature there is a gradual low density amorphous (LDA) to high density amorphous (HDA) phase transition in SiO_2 at pressures 100–250 kbar. Similar pressure induced transformation has been observed in amorphous ice [10–13]. The LDA-HDA transition in amorphous ice is a first-order transition with a discontinuous volume change [12,13]. Recently on the basis of molecular simulations, Lacks [14] predicted that a kinetically hindered first-order amorphous to amorphous transition can occur in a-SiO_2. His calculations suggest that the LDA-HDA apparently first-order transformation of a-SiO_2 would be observed in the pressure range 30–50 kbar with a discontinuous volume change of about 19% below its glass transition temperature T_g [14]. At 1 atm, the T_g of fused quartz is nearly 1200 °C [15].

In an effort to resolve the controversy regarding the nature of the LDA-HDA transition in a-SiO_2, we have carried out high temperature (HT) high pressure (HP) quench experiments using the toroid anvil (TA) apparatus and dilatometric measurements using the piston-cylinder (PC) apparatus. At room temperature, the volume compression measurements have been extensively carried out on several materials using the PC apparatus [16]. The present study on a-SiO_2 probably represents the first application of the PC device for quantitative determination of the volume change at the HP and HT transformations.

The specimens of clear fused quartz of density $\rho = 2.18$ g/cc are sliced from cylindrical rods of 4–5 mm diam. The TA experiments are carried out using tungsten carbide (WC) toroid anvils of 32 mm face diam with internally heated pyrophyllite cell assembly [17]. The TA apparatus is calibrated using Bi I-II, Bi II-III, and Yb hcp to bcc transitions at 25.5, 26.5, and 40 kbar, respectively. The specimens of a-SiO_2 of 4 mm diameter and 5 mm long are surrounded by a boron nitride sleeve of 0.5 mm thickness and placed at the center of the graphite heater. The assembly is cold pressed to 40 kbar and the temperature is increased at the rate of 10 °C per minute. The final temperature is maintained for 15 min and then the heater power is cut off to quench the sample and then pressure is released slowly. Macroscopic density measurements are carried out on the retrieved sample by the water displacement method. The densities of the quenched specimens are $\rho = 2.24$ g/cc at 40 kbar, 450 °C (no transition); $\rho = 2.552$ g/cc at 40 kbar, 700 °C; $\rho = 2.582$ g/cc at

40 kbar, 800 °C; $\rho = 2.54$ g/cc at 50 kbar, 900 °C. The powder x-ray diffraction data on the retrieved samples are collected using a Phillips PW1710 model diffractometer in the two theta range 10° to 145°, with filtered CuK_α radiation. The x-ray diffraction patterns of the quenched specimens show the amorphous phase, though the last two conditions are found to show weak coesite lines. Thus an irreversible densification of fused quartz associated with the LDA-HDA transformation is observed at 40 kbar and 700 °C in the TA experiments.

The HP dilatometric measurements are carried out in an end-loaded PC apparatus having a WC core of 12.7 mm diameter and 50 mm length. Two lever arms are attached to the WC piston. The piston displacement is monitored using two dial gauges having a least count of 0.0025 mm. In spite of careful alignment, the two dial gauges do not record the same displacements due to the lack of parallelism at various contacting surfaces. The average of displacements recorded by two gauges represents the true change in length of the specimen cell and gives reproducible results. The error in the determination of the volume change comes mainly due to uncertainty in the measurement of piston displacement and in the areas of cross section of the pressure vessel and piston. The internally heated cell assembly, commonly used for conducting high pressure melting experiments using the PC apparatus [18], is adapted for the HT dilatometric measurements. The specimens of the fused quartz, 5 mm in diameter and 12 mm long, surrounded by a pyrophyllite sleeve of 0.5 mm thickness is placed in the center of the 38 mm long tubular graphite heater of the cell assembly (Fig. 1). To minimize friction a thin lead foil is wrapped around the outer talc sleeve and Molykote paste lubricant is smeared around the foil and the piston. In these experiments the temperature is not determined using a thermocouple at the center of the cell, because this would have introduced errors in the determination of the volume change. The heater power versus temperature curve for the cell is determined from a separate experiment. The pressure is determined by applying friction correction assuming the friction to be symmetrical on the upstroke and downstroke pressure cycles.

In the PC experiments the pressure is raised to about 36 kbar and then the temperature is increased in small steps to about 600 °C. When the transition began, the piston displacement increased significantly and the gauge pressure started falling. At 2 min intervals the pressure is raised to the original value and piston displacement is recorded. The temperature is also increased in very small steps and measurements are continued until the piston displacement becomes extremely small signaling the end of the transition. The piston displacement versus temperature curve for the measurements taken on the upstroke pressure cycle in two different independent experiments are shown in Fig. 2. A large piston displacement is seen at about 680 °C indicating a discontinuous volume change of the cell assembly at about 36.3 kbar and 680 °C, which comes essentially from an apparently first-order phase transition of fused quartz. The spread in the transition is due to the sluggish nature of the transition and also may be due to temperature nonuniformity across the length of the specimen. The thermal expansion effect of the cell is very small in the temperature range 350–600 °C and is negligible in the transition region. The experiments are conducted essentially under isothermal, isobaric conditions. Hence the materials, talc, pyrophyllite, graphite, etc., in the cell do not contribute to the measurement of the volume change of fused quartz at the transition. Also to show that the observed volume change does not occur from some unknown cause in the pressure

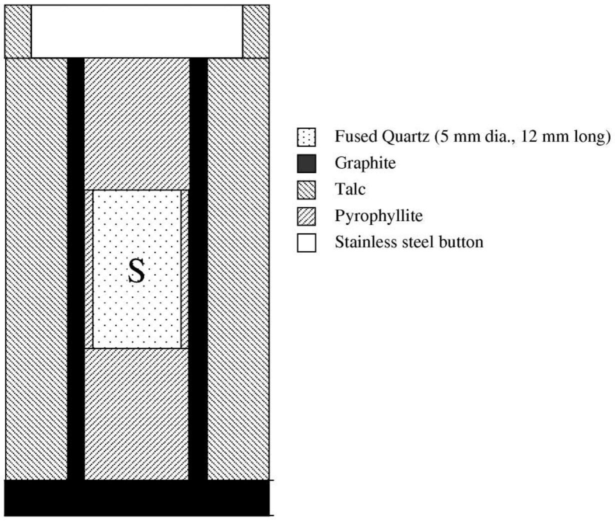

FIG. 1. Internally heated piston cylinder cell assembly of 12.7 mm diam used for the high pressure and high temperature dilatometric measurements.

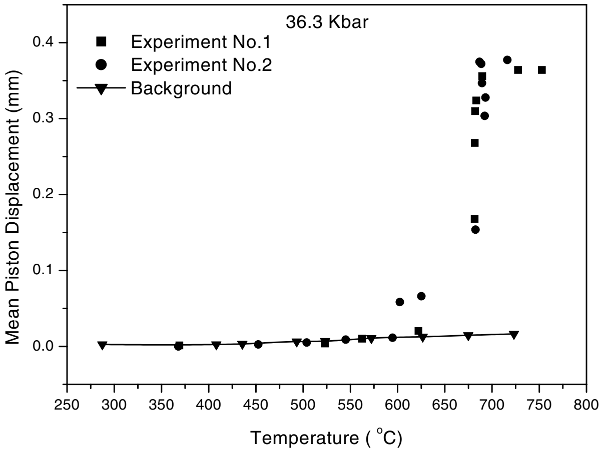

FIG. 2. The mean piston displacement versus temperature curve for measurements taken at 36.3 kbar on a-SiO$_2$ on the pressure upstroke cycle using the PC apparatus in two independent experiments and are compared with background experiment without a-SiO$_2$.

apparatus, we have conducted a background dilatometric experiment by replacing the fused quartz sample with a pyrophyllite rod of similar dimensions. The results of the HP and HT background dilatometric measurements show no anomalous behavior and are compared with the HP and HT dilatometric measurements on fused quartz in Fig. 2. This confirms that the observed volume change at 680 °C comes only from fused quartz. The recovered fused-quartz specimen at the end of the transition is found to be x-ray amorphous (Fig. 3) confirming an apparently first-order LDA to HDA phase transition in amorphous silica at 36.3 kbar and 680 °C. The volume change

$$\frac{\Delta V}{V_0} = \frac{A \Delta l}{V_0},$$

where Δl is the piston displacement at the transition and A is the average of the area of cross section of the pressure chamber and the piston. $\Delta V/V_0$ determined from two independent PC experiments are $(19.45 \pm 0.40)\%$ and $(19.89 \pm 0.40)\%$ at 36.3 kbar and 680 °C. These values compare well with the 17% change in density obtained from our TA experiments at 40 kbar and 700 °C and with the theoretical prediction of Lacks [14], $\Delta V/V_0 = 19\%$.

A similar first-order LDA-HDA transition has been observed in ice, at high pressures, and temperatures from 60 to 120 K, just below the glass transition temperature in ice, which is about 130 K [11]. Based on the work on ice, Lacks [14] conjectured that in fused quartz a similar transition would occur just below its glass transition temperature which is about 1200 °C at 1 atm. The earlier studies have shown that crystallization of fused quartz starts at 900 °C when pressurized to 25 kbar [19] and at 400 °C under a pressure of 100 kbar [20]. Our TA experiments show that at 40 kbar it starts to crystallize at 800 °C. The results of these studies indicate that the T_g of fused quartz decreases with an increase in pressure. And hence it can be inferred that the LDA-HDA transition has occurred in fused quartz at a temperature just below its glass transition temperature at 36 kbar.

Raman scattering, being an important structural probe, has been used in the study of the fused quartz and its HDA phase. The Raman spectra of the unpressurized (normal) a-SiO$_2$ and the specimens retrieved from HP and HT PC experiments, recorded at room temperature and 1 atm using SPEX RAMALOG 1403 Double Monochromator and with 5145 nm excitation in our study, are shown in Fig. 4. The spectrum of normal a-SiO$_2$ at room temperature and 1 atm pressure shows a strong but diffused peak at 433 cm^{-1}, with weaker features near 800 cm^{-1} [Fig. 4(a)]. In addition there are peaks at 498 and 609 cm^{-1} associated with the network structure of SiO$_4$ tetrahedra. These features are consistent with many reports in the literature [6,7]. But no Raman peaks other than a small hump at about 500 cm^{-1} are found in our spectrum of the retrieved a-SiO$_2$ quenched from 36.3 kbar and 700 °C [Fig. 4(b)] indicating a large broadening of bands. The small hump at 500 cm^{-1} seen in Fig. 4(b) is consistent with the Raman spectra of densified fused quartz obtained by quenching from pressures of 300 kbar [6] and 170 kbar [21] and room temperature. The absence of the peaks in our spectrum can be attributed to the complete breakdown of the intermediate range order and also probably to the modification of the short range order [6,9,22]. Hemley *et al.* [6] have observed at room temperature a gradual disappearance of the Raman bands in fused quartz in experiments up to 400 kbar. They have attributed this behavior to a gradual irreversible change in structure which starts at 80 kbar. The x-ray [23,24] and neutron diffraction [25] experiments on fused quartz at room temperature have shown that its structure, which consists of a network of SiO$_4$ tetrahedra joined at their vertices, becomes gradually more and more deformed as it undergoes the LDA-HDA transformation. The Raman spectrum [Fig. 4(b)] of the quenched a-SiO$_2$ following the apparently first-order transition around 36 kbar and

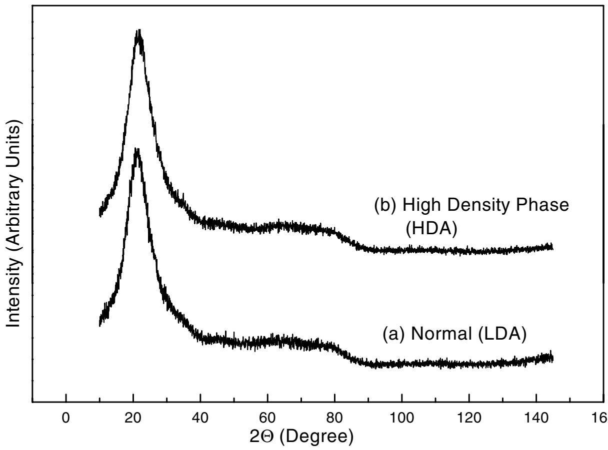

FIG. 3. XRD pattern of a-SiO$_2$ in (a) the LDA phase and (b) the HDA phase indicating the amorphous nature.

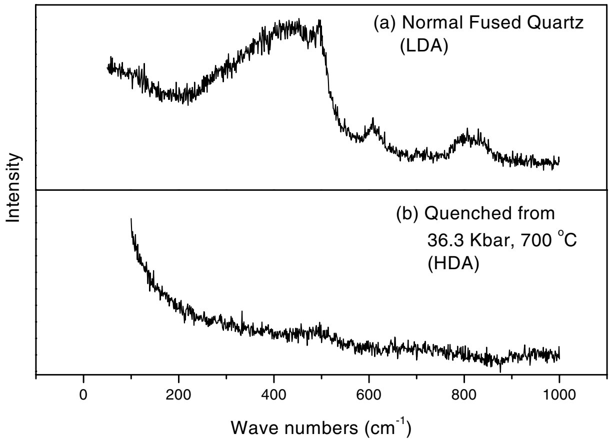

FIG. 4. Raman spectra of a-SiO$_2$ in (a) the LDA phase and (b) the HDA phase.

680 °C is similar to the Raman spectrum taken at 400 kbar at room temperature [6]. It appears that both methods lead to the same type of HDA phase and the continuous LDA-HDA transition at room temperature becomes an apparently first-order transition at high temperature.

To conclude, this Letter reports the first observation of an apparently first-order LDA-HDA phase transformation in fused silica with a discontinuous volume change of about 20% using the PC apparatus around 36 kbar and 680 °C. The experimental findings are consistent with the results of molecular simulations on fused quartz by Lacks [14], who suggested the possibility of a kinetically hindered first-order LDA-HDA transformation in fused silica. Similarity in the Raman spectra of the quenched samples of a-SiO$_2$ retrieved from the TA and PC experiments and the Raman spectrum of a-SiO$_2$ compressed to 400 kbar at room temperature suggests that the HDA phases obtained by the two different routes are similar.

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