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VITREOUS GeO_2 RESPONSE TO SHOCK LOADING

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Abstract. Shock wave profiles in vitreous GeO_2 (6.56 Mg/m^3) under planar loading were measured using stress gauges to 14 GPa. New and previous data yield Hugoniot: D = 0.974 (km/s) + 1.711 u for shocks of 6 to 40 GPa. We show that the phase change from 4- to 6-fold coordination of Ge^{+4} with O^{-2} in vitreous GeO_2 occurs from 4 to 15 GPa. Hugoniots of vitreous GeO_2 and SiO_2 are found to approximately coincide if the pressure in SiO_2 is scaled by the ratio of SiO_2 to GeO_2 initial density.

INTRODUCTION

It has been long recognized that phase transitions in germanates occur at lower pressures than similar phase transitions in silicates. Jackson and Ahrens (1) reported Hugoniot data for GeO_2 for the high-pressure range, up to 160 GPa, and suggested that both vitreous and rutile phases transform to a common phase under high pressure, which is about 5 percent denser than the rutile-type structure. Chen et al. (2) speculated that vitreous GeO_2 undergoes an irreversible phase change when shock pressure exceeds 8 GPa. However, it was still unclear what pressure range is required for the phase change to occur under shock loading and if the response of GeO_2 to shock loading is similar to that of SiO_2. In order to investigate the GeO_2 phase transition pressure range and the similarity between GeO_2 and SiO_2 responses to shock loading, we conducted a series of planar impact experiments on vitreous GeO_2 with the Caltech 40 mm powder gun.

EXPERIMENTAL METHOD

Embedded piezoresistance manganin stress gauges (3) were employed to monitor stress wave profiles under planar impact. Two two-channel power supplies (CK-2, Dynasen, Inc.) were used to power four stress gauges (Mn4-50-EK, Dynasen, Inc.) among three GeO_2 slices in each experiment. The voltage change upon shock loading is converted to gauge resistance change (4). Stress wave profiles are deducted using the calibration relations (3). A cylindrical disc (100 mm diameter and 150 mm height) of bubble-free vitreous GeO_2 was cut into 40x40 mm cubic samples with the thickness ranging from 1.7 to 10 mm. The density is measured to be 3.655 Mg/m^3.

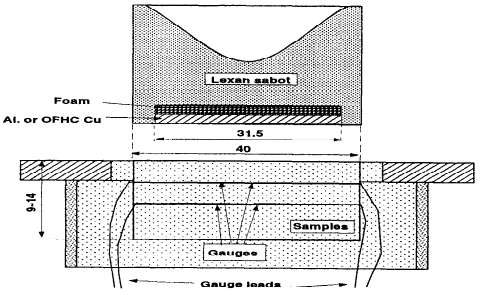

Figure 1: Target assembly for measuring shock profiles in GeO_2.

The samples used in the experiments were first polished to within 0.005 mm of uniform thickness. Then, stress gauges mounted on mylar film (0.013

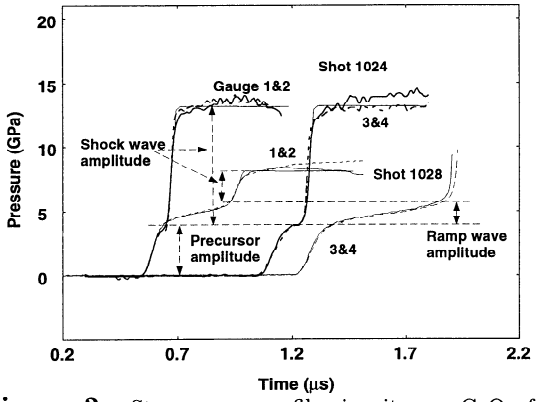

Figure 2: Stress wave profiles in vitreous GeO_2 for planar loading.

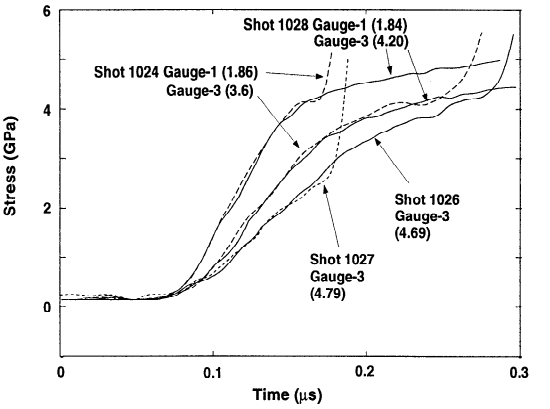

Figure 3: Vitreous GeO_2 elastic wave front rise time versus propagation distance. Number in brackets is distance (mm) between gauge and impact surface.

mm thickness) were sandwiched between samples. Epoxy was used to force air out of the contact surfaces between the gauges or samples and mylar film. After the epoxy cured (typically 24 hours), the whole sample assembly was encapsulated in epoxy as shown in Figure 1.

EXPERIMENTAL RESULTS

Table 1 lists experimental parameters of the impactor and samples. Recorded stress wave profiles in vitreous GeO_2 (Figure 2) show that two stress gauges at the same interface gave nearly identical stress wave fronts, and showed only small differences in the peak stress behind the wave front. These differences are believed to be typical of the response from stress gauges (3). The wave profiles have a three wave structure: an elastic precursor with relatively long rise time, a ramp wave and then a normal shock wave when the peak stress is > 6 GPa.

The precursor rise-times are long, $\approx$ 100 and 150 ns at 1.8 and 4.2 mm from the impact surface (Figure 3), respectively. In order to verify that the long rise times are not the response of the measurement system, Figure 3 provides a comparison among the wave profiles that are aligned with respect to each arrival time. If the long rise time arose from the measurement system, it would not simply depend on wave propagation distance. However, Figure 3 clearly demonstrates that the precursor rise time increases with propagation distance. As a result, we infer that the longitudinal modulus of vitreous GeO_2 decreases with increasing stress during precursor wave loading and the precursor is an elastic ramp wave. Therefore, the whole elastic precursor can not be treated as a single wave with a constant wave velocity. Because the deformation rate associated with ramp wave loading is lower than that during shock loading, the ramp wave loading can be approximated as an isentropic process. In addition, the precursor stress does not decay with propagation distance (Figure 3), therefore, the phase velocity at constant particle velocity and stress is constant (5). The methods of (5) are used to determine the precursor parameters. Calculated results are shown in Figures 4 and 5. The peak stress of the initial ramp, its wave and maximum particle velocity are: 4 GPa, 3.5 km/s and 333 m/s, respectively. The above method also provides parameters of the ramp wave between 4 and 6 GPa. Results are shown in Figures 4 and 5.

Because the release wave from the rear impactor surface has not overtaken the shock front (in all experiments), the peak stress is assumed to be constant at two-stress gauge locations. Therefore, we averaged the peak stress from two gauges. A least square fit was obtained based on present data and previous data of (1). The Hugoniot relation for vitreous GeO_2 (3.655 Mg/m^3) in the pressure range of 6 to 40 GPa is

$$D = 0.974 + 1.711u, \quad \text{for } u > 0.6 \text{ km/s}, \quad (1)$$

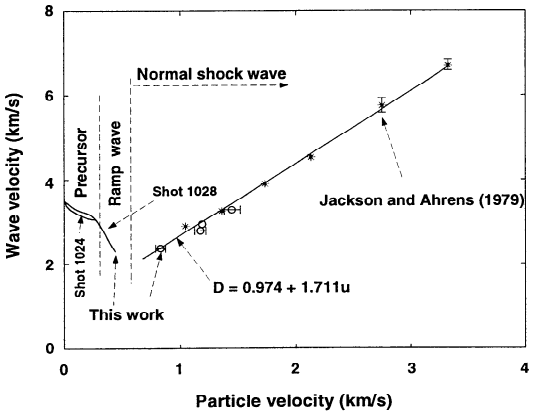

Figure 4: Shock wave velocity versus particle velocity for vitreous GeO_2.

where D and u are shock and particle velocity.

RESULTS OF ANALYSIS

Vitreous GeO_2 response

Based on the present data (Figure 5), the response of vitreous GeO_2 under planar shock loading is divided into three stress ranges: 0-4, 4-6, and 6 GPa and higher.

When the peak stress is below 4 GPa, the present data show that the compressibility of vitreous GeO_2 increases with increasing stress. This is also observed under hydrostatic loading (6). In general, a ramp wave results from densification processes like those which occur upon irreversible compression of lattice vacancies and upon coordination increases that accompany large shear deformations.

When the peak stress is between 4 and 6 GPa, the compressibility increases dramatically under both planar impact and hydrostatic loading (Figure 5). Smith et al. (6) found that the deformation is not reversible when pressure is higher than 4 GPa under hydrostatic loading. He suggested that a new phase (six-fold) starts to nucleate at 4 GPa. Grady (7) suggested that the large change of compressibility in brittle materials results from fracture incubation and nucleation, and melting along microfaults under shock loading when pressure is higher than material elastic limit. Because phase transition, melting and fracture processes result in compressibility increasing, it is possible that all the processes may occur in this pressure range.

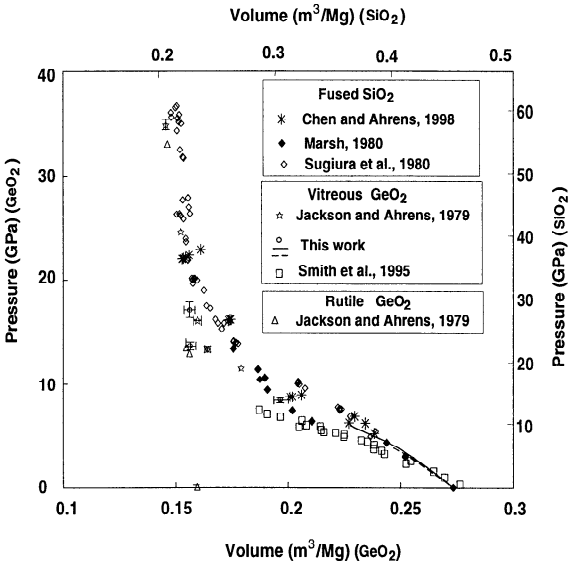

Figure 5: Pressure versus volume for vitreous GeO_2 and SiO_2. The P-V plot for SiO_2 is aligned to the GeO_2 plot so that initial volume and volume for completion of phase change to rutile phase coincides. Vertical axis of pressure for SiO_2 (right) is scaled by the ratio of initial SiO_2 to GeO_2 density.

When peak impact stress is > 6 GPa, a normal shock wave forms. Shock wave formation reveals that the compressibility of vitreous GeO_2 starts to decrease with stress increasing from 6 GPa. When shock stress is greater than ~ 15 GPa, vitreous GeO_2 compression data closely match that of rutile phase GeO_2 (1) (Figure 5). Therefore, we conclude that the phase transition to rutile phase in vitreous GeO_2 starts at ~ 4 GPa and is completed in the pressure range of 14 to 16 GPa. It is also inferred that the 4- to 6-fold GeO_2 transition occurs between 5.6 and 13 GPa under static loading (6).

GeO_2-SiO_2 similarities

Because vitreous GeO_2 has a similar structure to fused SiO_2, it is interesting to investigate their pressure-volume (P-V) relation similarities. Deformation or phase transition processes in materials are generally completed at the shock front because the energy needed for the processes is only available from stress or particle velocity gradient at the shock front. We use the density ratio

at zero-pressure of SiO_2 (glass) to GeO_2 (glass) to scale the pressures in SiO_2. Figure 5 shows the comparison between fused SiO_2 and vitreous GeO_2 P-V relations. When the shock pressure is between 10 to 30 GPa, the pressure in fused SiO_2 ((8) and (2)) appears to be slightly higher than the pressure in GeO_2. Grady (7) indicated that a possible misinterpretation of the SiO_2 data has occurred. The shock wave velocity in the 10 - 30 GPa pressure range was measured and reported as having a nearly constant shock velocity. (8). However, the stress wave profile measurements (7) suggest that a single wave is not stable in this pressure range in SiO_2. The shock wave velocity appears to be slightly lower than that given by Marsh (8). In spite of this problem, Figure 5 demonstrates a reasonable similarity of P-V relations of fused SiO_2 and vitreous GeO_2. This similarity demonstrates that the response of vitreous GeO_2 at lower shock pressure can be used to analyze the response of fused SiO_2 under higher pressure, especially in the phase transition regime.

CONCLUSIONS

Based on the present data and discussion, the features of a stress wave in vitreous GeO_2 to planar shock loading include an elastic precursor, with a peak amplitude of 4 GPa, and a peak particle velocity of 333 m/s, a ramp wave with an amplitude $\sim$ 2 GPa and then a normal shock wave form when the peak shock stress is higher than 6 GPa. The Hugoniot relation of vitreous GeO_2 is $D = 0.917 + 1.711u$, for $u > 0.6$ km/s. When shock stress is higher than $\sim$ 15 GPa, vitreous GeO_2 compression data appears to approach those of rutile GeO_2 ((1)). Therefore, the phase change from 4- to 6-fold GeO_2 starts at about $\sim$ 4 GPa and is completed at $\sim$ 15 GPa. A similarity between the pressure-volume relations for fused SiO_2 and GeO_2 appears when the ratio of SiO_2 to GeO_2 density is used to scale shock stress in SiO_2. This similarity provides the basis for using GeO_2 as an analogous material to SiO_2.

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Table 1: Experimental parameters for shock loading, GeO_2 glass.

Shot #	Impactor material	Impactor thickness (mm)	Impactor velocity (km/s)	H_1 (mm)	H_2 (mm)	H_3 (mm)
1024	OFHP Cu	5.997±0.001	1.547±0.006	1.857±0.0041	1.745±0.0034	10.378
1026	2024 Al	4.02±0.001	2.062±0.013	2.454±0.0021	2.238±0.0019	5.883
1027	2024 Al	6.015±0.005	2.310±0.001	2.202±0.0038	2.588±0.0021	6.192
1028	2024 Al	6.021±0.0043	1.304±0.001	1.836±0.004	2.360±0.005	5.298

H_1, H_2 and H_3 are thicknesses of three slices in each experiment.