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High-pressure structural study of GeI₄

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We have measured x-ray diffraction from a disordered phase of GeI₄, formed by reversible pressure-induced amorphization above 33 GPa. These are the first quantitative, *in situ* diffraction measurements on a pressure-amorphized material, and they show that the x-ray scattering from disordered GeI₄ significantly exceeds that of conventional amorphous materials. For this phase, the peak positions in the structure factor [$S(Q)$] resemble low-pressure Bragg diffraction and the interatomic correlations [$G(r)$] are similar to the low-pressure crystalline structure over distances of 16 Å. [S0163-1829(97)09301-6]

In recent years, there has been considerable interest in the properties of pressure-induced amorphization.¹⁻¹⁶ These transitions appear to involve direct transformation of crystalline to amorphous materials through increases in pressure at kinetically low temperatures. Some of the transitions are reversible.^{6,7} In general, structural measurements on pressure-amorphized phases have been indirect. All structural measurements by diffraction have been performed on quenched materials at ambient pressures and there have been no quantitative, *in situ* diffraction measurements on an amorphized phase.^{14,17,18} Such information is critically needed to understand the transformation mechanisms in pressure-induced amorphization and to assess the nature of amorphized materials compared to crystalline materials and conventional glasses.

Recently, techniques have been developed to allow structural measurements of amorphous materials at high pressures using synchrotron x-ray diffraction.¹⁹ Here we apply these methods to a study of pressure amorphized GeI₄. The reversible amorphization transition in GeI₄ has been well characterized by measurements of x-ray diffraction, Mössbauer spectroscopy, extended x-ray-absorption fine structure, and electrical conductivity.^{15,20} GeI₄ is an ideal compound to study with x-ray diffraction because of its relatively high Z,

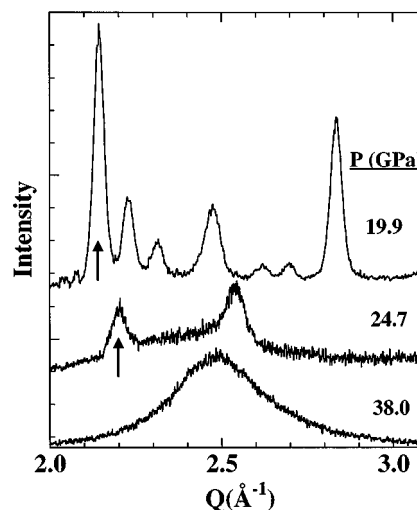


FIG. 1. Evolution of the diffraction pattern for GeI₄ with increasing pressure, indicated in GPa. The patterns are displayed at equivalent relative intensities. Above 24.7 GPa, the crystalline diffraction pattern is replaced by a mixture of broad peaks on an undulating background. By 38.0 GPa, the diffraction pattern is comprised of extremely broad peaks. The vertical arrows show the 222 line, which is the strongest reflection at ambient conditions.

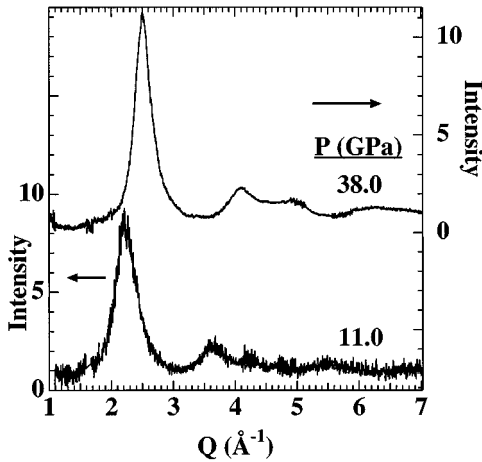


FIG. 2. Faber-Ziman structure factor, $S(Q)$, for GeI_4 at 38.0 GPa (on compression) and 11.0 GPa (on decompression). There is greater noise in the signal at 11.0 GPa because of a shorter acquisition time compared to 38.0 GPa.

chemical simplicity (only two types of atoms), and structural simplicity (cubic, $Pa3$ space group).

For this work, we measured energy dispersive x-ray diffraction spectra from GeI_4 in the diamond anvil cell on increasing and decreasing pressure between 0 and 38 GPa. The experiments were performed at the superconducting wiggler beamline (X-17C) of the National Synchrotron Light Source. A sample of GeI_4 was compressed without a pressure medium to minimize unwanted background diffraction and Compton scattering. Detailed diffraction measurements on the high-pressure phase of GeI_4 were performed at 38 GPa and on decompression at 11 GPa. For these measurements, energy dispersive diffraction spectra were measured at scattering angles in the range $6.5^\circ < 2\theta < 20^\circ$. For each measurement, the Compton scattering from the diamonds were subtracted, the continuum of escape peaks were removed, and the intensities were normalized to the measured source spectrum for the synchrotron. The individual measurements at each 2θ were then combined and averaged to form a single x-ray spectrum over the range $1 < Q < 12 \text{ \AA}^{-1}$. Throughout the experiment, pressures were measured with the ruby fluorescence scale. Because GeI_4 is a soft material, we estimate that the maximum pressure variation over the x-rayed sample ($15\text{--}25 \mu\text{m}$ in length) was less than ± 0.1 GPa.

We recorded diffraction from GeI_4 at 0, 2.3, 8.0, 19.9, 24.7, 33.5, and 38.0 GPa on compression. On decompression, diffraction was measured at 11.0, 3.0, and 0.3 GPa. Consistent with previous results, our measurements show a pressure-induced transition between crystalline GeI_4 and a disordered structure (Fig. 1). In the present experiments, we observed a mixture of these phases between 24.7 and 33.5 GPa on increasing pressure and that the transition was complete by 38 GPa. Again, in agreement with previous work, we find that the crystal-glass transition is reversible; on decompression GeI_4 recrystallizes between 3.0 and 0.3 GPa.¹⁵ In detail, the pressures for the transitions (crystal \rightarrow glass and glass \rightarrow crystal), the region over which the mixed phase occurs, and the elastic compression for the crystalline phase were consistent with previous results.¹⁵

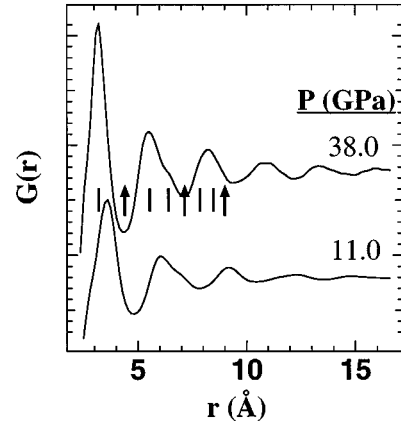


FIG. 3. Average pair distribution function [$G(r)$] for GeI_4 at 38.0 and 11.0 GPa determined from the sine transform of the structure factor [$S(Q)$]. I-I correlations constitute approximately 80% of the signal. The vertical lines and arrows show the I-I distances for crystalline ($Pa3$) structured GeI_4 at 38.0 GPa scaled to the first peak in $G(r)$. The arrows indicate atomic pairs that produce no Bragg diffraction due to interference effects (200, 310, and 100).

We obtain the Faber-Ziman structure factor [$S(Q)$], which is the normalized coherent scattering, from our diffraction data using the relation

$$S(Q) = \frac{I(Q) - \langle f^2(Q) \rangle}{\langle f(Q) \rangle^2} + 1, \quad (1)$$

where $I(Q)$ is the coherent scattering intensity and $\langle f(Q) \rangle^2$ and $\langle f^2(Q) \rangle$ are the square of the average and average of the squared atomic scattering factors for GeI_4 . Scaled in this manner, the diffraction spectra at 38 GPa consisted of a single large peak at $Q \sim 2.5 \text{ \AA}^{-1}$ with lower intensity peaks at 4.0 and 4.9 \AA^{-1} (Fig. 2). For $Q > 6 \text{ \AA}^{-1}$, the spectra were featureless. On decompression to 11 GPa, the spectra were broadly similar, though the peaks were shifted to smaller values of Q , corresponding to larger interatomic separations (Fig. 2). At 11 GPa, the first diffraction peak occurs at 2.1 \AA^{-1} . The change in $S(Q)$ for GeI_4 suggests that the structural response is largely elastic between 38 and 11 GPa. This behavior is in contrast to the dramatic changes in $S(Q)$ for SiO_2 associated with changes in coordination and medium-range order at high pressures.¹⁹

Scaling the results to the relative intensity scale of (1), shows that the height of the first diffraction peak from the high-pressure phase is extremely large compared to that of conventional amorphous materials (e.g., liquids and melt-quenched glasses). At 38 GPa, the magnitude of the first peak in $S(Q)$ (~ 10) is 2–3 times the intensity of the first strong diffraction peak in $S(Q)$ for a wide range of liquids and melt-quenched glasses (Fig. 2).²¹ The height of the first peak at 11 GPa is similarly discrepant. Detailed comparisons between the results for the crystalline and high-pressure phases show that the integrated intensity of the first diffraction peak at 38 GPa is within 25% of the strongest Bragg reflection at ambient conditions (222). At 38 and 11 GPa, the peak positions in $S(Q)$ are also consistent with the strongest diffraction lines of crystalline GeI_4 . Specifically the first three peaks at 2.51 , 4.0 , and 4.9 \AA^{-1} can be indexed as 222,

440, and 622/444. Assuming the peaks in $S(Q)$ correspond to Bragg diffraction, and fitting linewidths to the Scherer equation, we obtain a correlation length of ~ 32 Å.

Structural details of the high-pressure phase are provided by the sine transform of the structure factor. Specifically, the average pair correlation function [$G(r)$], which describes the atomic distribution, is given by

$$G(r) = \frac{2}{\pi} \int_0^{\infty} Q(S(Q) - 1) \sin(Qr) dr. \quad (2)$$

Because GeI_4 contains more than one type of atom, $G(r)$ is a convolution of all the Ge-Ge, I-I, and Ge-I correlations, and it does not allow a direct measure of the coordination state. However, due to the large difference in Z between I and Ge, and the stoichiometry of GeI_4 , the I-I correlations contribute to $\sim 80\%$ of the signal in $G(r)$.

At 38 GPa, the first peak in $G(r)$ shows that the iodine radius is ~ 1.6 Å (i.e., 3.2/2) and that there are structural correlations to distances as large as 16 Å (Fig. 3). The extent of ordering is large compared to the atomic radii, and it is suggestive of significant short- and medium-range ordering in the structure. A comparison between $G(r)$ and the extrapolated interatomic distances in crystalline GeI_4 shows they are similar at 38 GPa (Fig. 3), suggesting that the high-pressure phase and the original crystalline phase are closely related. Notably, the atomic pairs that produce weak Bragg diffraction are absent from $G(r)$ (hkl of 200, 310 and 100). Combined with the observations of strong diffracted intensities and the spacing of the peak positions in $S(Q)$, the results for $G(r)$ suggest that the pressure amorphized phase of GeI_4 retains the structure of the parent crystalline phase to distances of ~ 16 Å (one-half the Scherer correlation length).

Thus, we conclude that the amorphization transition for GeI_4 arises from a reversible change in only the long-range order with increasing and decreasing pressure.

Previous studies indicate that the high-pressure transition in GeI_4 is driven by a change in the I \cdots I bonding associated with metallization.^{15,20} The present diffraction results show that this electronic transition is associated with a loss of the long-range order of GeI_4 . This conclusion is reasonable given that metallization largely affects the intertetrahedral bonding of the molecular crystal. It is also consistent with the reversibility of the crystal-glass transition at room temperature: the transformation could occur with small atomic displacements (less than ~ 2 Å).

Observations of antiferromagnetism in pressure-amorphized Fe_2SiO_4 (fayalite) suggest similar length scales of ordering to that of GeI_4 at high pressures (~ 10 – 20 Å).¹⁰ Also, recent high-pressure Raman measurements are consistent with extensive crystallinity in pressure-amorphized AlPO_4 .¹⁶ In the absence of quantitative diffraction data for other amorphization transitions, we are cautious about generalizing our observations of extensive short- and medium-range ordering for all materials formed by pressure-induced amorphization. Further structural measurements will be required to resolve this issue.

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