

Observation of a Pressure-Induced First-Order Polyamorphic Transition in a Chalcogenide Glass at Ambient Temperature

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An apparently first-order polyamorphic transition has been observed with increasing pressure at ambient temperature in a molecular glass of composition $\text{Ge}_{2.5}\text{As}_{51.25}\text{S}_{46.25}$. Raman spectroscopic measurements on pressure-quenched samples and *in situ* x-ray diffraction measurements indicate that this transition corresponds to a collapse of the ambient-pressure molecular phase to a high-pressure network phase. The high-pressure phase first appears at a pressure of ~ 8 – 9 GPa and the transformation becomes complete at ~ 14 – 15 GPa. Calorimetric measurements indicate that the low- and high-pressure phases are thermodynamically distinct and that they coexist in the transition range.

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The effects of pressure and temperature on glass structure are intimately related to a fundamental and currently highly debated issue in materials physics—which is whether, similar to crystalline polymorphs, structurally and thermodynamically distinct phases of the same composition exist also in the case of glasses and liquids. Such a phenomenon has been termed polyamorphism in the literature [1]. Strong experimental and/or theoretical evidence of polyamorphic transition has been observed or its presence has been suggested in elemental liquids such as S, Se, Te, P, C, and Si, in open tetrahedral networks such as H_2O , SiO_2 , BeF_2 , and GeSe_2 , as well as in complex binary liquids such as Y_2O_3 - Al_2O_3 [1–17]. Relatively sharp semiconductor-to-metal transitions in chalcogenide liquids as a function of pressure are well known and have originally been proposed to correspond to polyamorphic transitions in the liquid state [17]. However, it has since been realized that such property changes are in fact driven by percolation rather than by first-order structural and thermodynamic phase transitions [1]. Moreover, polyamorphic transitions are expected to be terminated by critical points that are typically located below the liquidus [1, 18, 19].

The two most well-studied and convincing cases of polyamorphism in literature pertain to the transitions between low- and high-density phases in phosphorus in the stable liquid state and in H_2O in the supercooled liquid state [3, 7, 12–14]. In these cases of experimentally observed polyamorphic phase transitions, the slope of the coexistence line in P - T space is negative due to the fact that the high-density phase has higher entropy compared to the low-density phase. The increase in entropy at high pressure is related to the fact that the low-density phase, which is molecular in nature, changes to a polymerized network structure at high pressure. In the case of H_2O *in situ* neutron diffraction measurements indicate a structural transformation from a low-density form with an open,

hydrogen-bonded tetrahedral “molecular” structure to a high-density network with interpenetrating tetrahedra with increasing pressure [13, 14]. However, it remains controversial as to whether this structural transformation is continuous or is truly first order in nature, characterized by the coexistence of the low- and high-density phases in the transformation region [20]. In the case of liquid phosphorus, x-ray diffraction and molecular dynamics simulation studies indicate that the low-pressure structure of the liquid consists of P_4 molecules, which transforms into a polymeric form with increasing pressure [3, 21, 22]. However, recent studies on phosphorus have conclusively demonstrated that, although the observed transition is first order in nature, it is not a true polyamorphic transition between two liquids but is in fact between a liquid and a dense fluid phase [7]. Thus, unequivocal experimental evidence of the existence of both structurally and thermodynamically distinct liquid or glassy phases of the same composition would be extremely valuable in understanding the fundamental nature of the phenomenon of polyamorphism. Unfortunately, such studies have been lacking in the literature due to experimental difficulties, and the existence of first-order structural phase transitions between two structurally and thermodynamically distinct amorphous phases has remained a strongly debated issue. Since density is the only relevant order parameter for phase transitions in classical glasses and liquids, an important question that naturally arises is whether polyamorphism is necessarily associated with a topological transformation of the structure. If that is indeed the case, then sharp structural transitions may be observed in glasses or liquids where the low- and high-density phases correspond to low- (e.g., molecular) and high-dimensional (e.g., network) structures, respectively.

In this Letter we report experimental evidence suggesting a relatively abrupt pressure-induced structural and thermodynamic transition at ambient temperature in a

glass of composition $\text{Ge}_{2.5}\text{As}_{51.25}\text{S}_{46.25}$. The glass was synthesized by melting a mixture of the constituent elements ($\geq 99.9995\%$ purity, metals basis) in an evacuated (10^{-6} Torr) fused silica ampoule and subsequently quenching the ampoule in cold water. The small amount of Ge doping is necessary in stabilizing this As-rich sulfide glass from devitrification. This particular glass was chosen since previous studies have shown that its structure is unique, consisting mainly of isolated As_4S_3 molecules [23–25]. Such an open low-dimensional structure with weak intermolecular bonding results in a low glass transition temperature with the onset of T_g at ~ 302 K. These molecules in the corresponding As_4S_3 crystal phase consist of a 3-membered As_3 ring surmounted by an AsS_3 pyramid with each S atom being bonded to an As atom in the As_3 ring that is directly below it (Fig. 1). Isothermal compression of powdered samples of this glass was performed at pressures ranging from 3.0 to 14.4 GPa, at ambient temperature, in a 6–8 multianvil apparatus at the UC-Davis high-pressure laboratory. The glass powders were placed within a graphite capsule inside an 8 mm truncated edge length, castable MgO-ceramic octahedron. The samples were equilibrated at the desired pressure for 4 to 8 h before quenching at a rate of 1 to 4 GPa per hour.

Raman spectroscopy was used for structural characterization of the glass samples quenched from various pressures using a Fourier-transform Raman spectrometer (Bruker RFS100-S). A Nd:YAG laser operating at a wavelength of 1064 nm and a power level of 15 to 20 mW was used as the excitation source. Differential scanning calorimetry (DSC) experiments were performed on the same samples with a scanning calorimeter (Netzsch DSC 404) to measure the variation in T_g as a function of pressure. Energy-dispersive x-ray scattering measurements were carried out *in situ* at pressures of up to 15 GPa using a

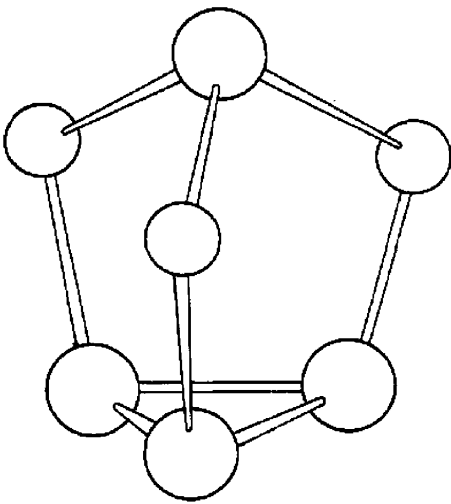


FIG. 1. Ball-and-stick model of the structure of an As_4S_3 molecule. The large and small spheres represent As and S atoms, respectively.

diamond-anvil cell (DAC) at a superconducting wiggler beam line (X17C) of the National Synchrotron Light Source at Brookhaven National Laboratory. A methanol-ethanol mixture was used as a pressure-transmitting medium and pressure was measured using ruby fluorescence. The x-ray beam was collimated to a spot size of ~ 20 to $30 \mu\text{m}$ to reduce background scattering from the steel gasket surrounding the sample as well as from other parts of the DAC. Ideally, for structure determination of glasses and liquids, energy-dispersive scattering data should be collected over a wide range of scattering angles 2θ to cover a large region of reciprocal space, i.e., Q values ($Q = 4\pi \sin\theta/\lambda$). Unfortunately, the geometry of the DAC, background diffraction, and the beam line instrumentation configuration did not allow data collection significantly beyond $2\theta = 12^\circ$ ($Q \leq 8 \text{ \AA}^{-1}$). However, as shown below, data over this relatively small Q range turned out to be sufficient to track the dramatic changes in position and intensity of the first sharp diffraction peak (FSDP) as a function of pressure.

The Raman spectra of the $\text{Ge}_{2.5}\text{As}_{51.25}\text{S}_{46.25}$ glasses quenched from various pressures are shown in Fig. 2. The most intense band in the Raman spectrum at ambient pressure is centered at $\sim 273 \text{ cm}^{-1}$, corresponding to the breathing mode of the basal As_3 ring in the As_4S_3 molecule [23–25]. In addition, there are other sharp bands at 180, 200, 220, and 357 cm^{-1} that can also be assigned to vibrational modes of the As_4S_3 molecule [26]. On increasing pressure the Raman spectra of the quenched samples do not change significantly up to 7.3 GPa (Fig. 2). With further increase in pressure the Raman spectra of the quenched glasses show marked changes. The most pronounced change is an abrupt drop in the relative intensity of the sharp bands at 180, 200, 220, and 273 cm^{-1} corresponding to the As_4S_3 molecular entities. For example, at 9.8 GPa the relative intensity of the 273 cm^{-1} peak is nearly halved and it virtually disappears on increasing the pressure to 14.4 GPa (Fig. 2, inset). Concomitantly the band at $\sim 235 \text{ cm}^{-1}$ broadens and its relative intensity increases sharply with increasing pressure (Fig. 2). This band has been assigned to As-As stretching in the network by Ewen and Owen, on the basis of their resonance Raman experiments [27]. Besides these major changes, the bands near ~ 375 and 330 cm^{-1} , which have been assigned to symmetric stretching of AsS_3 pyramids in As sulfide glasses [23–25], also broaden and their relative intensities increase with rising pressure in this range.

The pronounced decrease in the intensity of the sharp molecular peaks at 180, 200, 220, and 273 cm^{-1} and the concomitant increase in the intensity of the broad “network” peaks at 235 and $330\text{--}375 \text{ cm}^{-1}$ clearly indicate a relatively rapid molecular-to-network structural transformation of the glass at pressures above ~ 8 to 9 GPa. A small amount of intensity from the molecular peak at 273 cm^{-1} is still observable in the Raman spectrum of

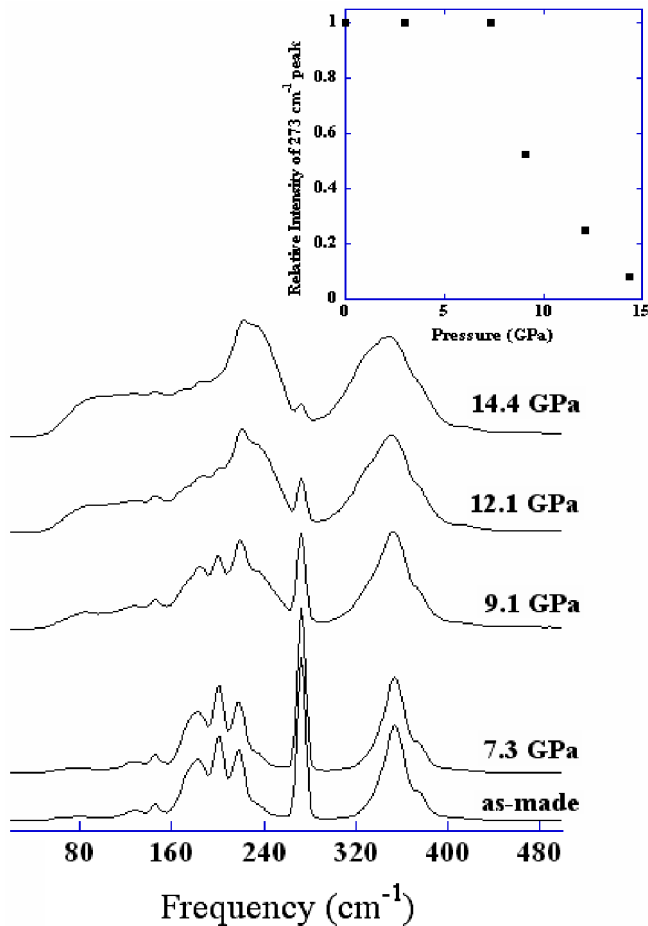


FIG. 2 (color online). Raman spectra of the $\text{Ge}_{2.5}\text{As}_{51.25}\text{S}_{46.25}$ glass quenched from various pressures. All spectra were normalized to the intensity of the peak at $\sim 352\text{ cm}^{-1}$. The inset shows the variation in the relative intensity of the peak at $\sim 273\text{ cm}^{-1}$ in these spectra, above a smoothly varying local background. The error bars for the intensity are within the size of the symbols.

the sample quenched from 14.4 GPa. However, the transformation is probably complete at such a pressure, since the high-pressure–high-density structure is not likely to be entirely quenchable at atmospheric pressure. The Raman spectra of these pressure-quenched samples are found to remain unchanged even several months after quenching. This result indicates that the T_g of the high-density phase must be significantly higher than the ambient temperature, thus making the structural relaxation rate extremely slow. Experimental evidence corroborating this hypothesis comes from DSC measurements which show the existence of two separate T_g with onset temperatures at ~ 302 and 331 K corresponding to the low- and high-density phases, respectively, in glass samples quenched from an intermediate pressure 9.1 GPa (Fig. 3). The ratio of these two endothermic signals at low and high temperatures is found to decrease with increasing pressure and becomes nearly zero at the highest pressure of 14.4 GPa (Fig. 3). The T_g

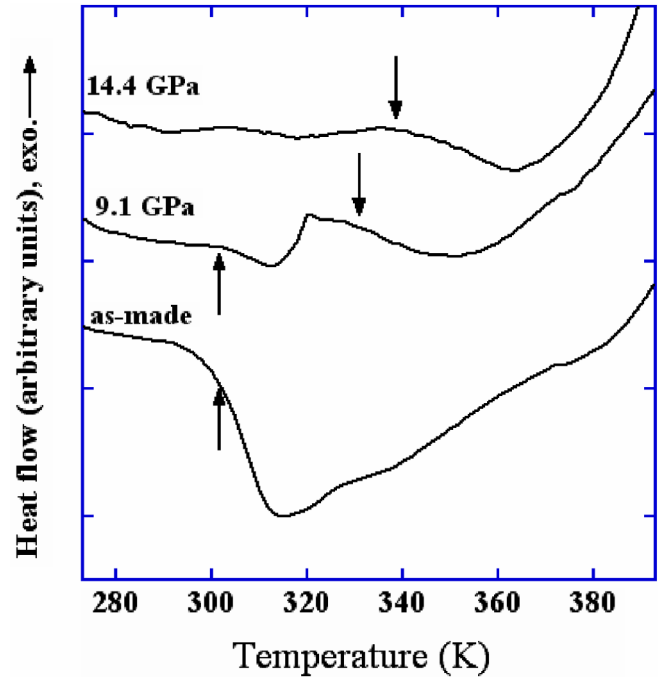


FIG. 3 (color online). DSC traces of $\text{Ge}_{2.5}\text{As}_{51.25}\text{S}_{46.25}$ glass quenched from various pressures. A heating rate of 30 K/min was used in all cases. The sample masses used for DSC experiments were 30 mg for the as-made glass and 15 mg each for the glasses quenched from 9.1 and 14.4 GPa. The arrows pointing upward and downward represent the T_g onset temperatures for the low- and high-density glassy phases, respectively. Only the low temperature range ($273\text{--}393\text{ K}$) is shown here to emphasize the glass transition behavior. At higher temperatures all glasses show crystallization exotherms at 423 K and melting endotherms at 498 K .

onset temperature for the endothermic signal at higher temperature is also found to shift slightly from 331 to $\sim 338\text{ K}$ at the highest pressure of 14.4 GPa (Fig. 3). This result provides clear evidence of the coexistence of the low- and high-density glassy phases with lower and higher T_g , respectively, in samples quenched from intermediate pressures. Such coexistence of structurally and thermodynamically distinct phases is characteristic of a classic first-order phase transition.

The pressure dependence of the x-ray diffraction patterns for this glass is shown in Fig. 4. The diffraction pattern at ambient pressure displays an unusually strong FSDP at 1.2 \AA^{-1} corresponding to a strong intermediate-range order in this glass which is to be expected in a structure predominantly consisting of well-defined molecules [28]. The corresponding characteristic length scale $d \sim 2\pi/Q = 5.2\text{ \AA}$ may correspond to intermolecular separation distances in the glass structure. As pressure is increased, both the FSDP and the second peak at $\sim 2.2\text{ \AA}^{-1}$ move to larger Q values. Such changes are partly due to the densification of the glass structure at higher pressures since $(V/V_0)^{1/3} \sim (d/d_0) \sim Q_0/Q$, where the subscript 0 for

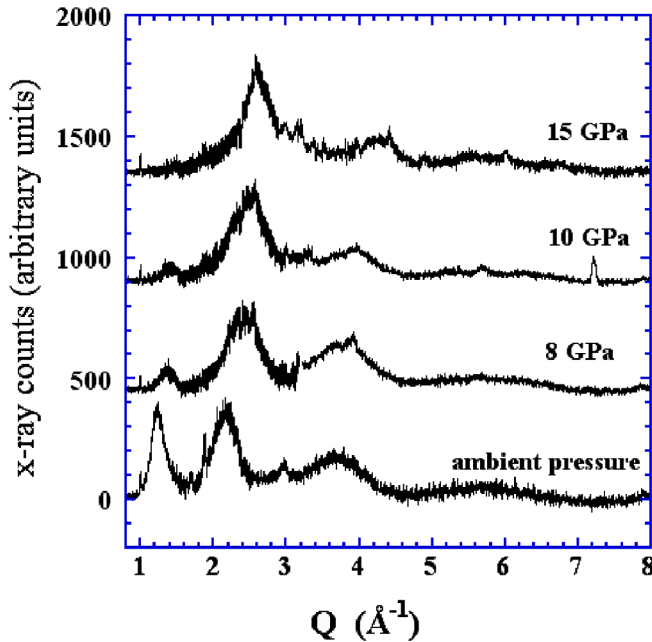


FIG. 4 (color online). Pressure dependence of the x-ray diffraction patterns for $\text{Ge}_{2.5}\text{As}_{51.25}\text{S}_{46.25}$ glass at ambient temperature. The sharp spikes in these patterns correspond to unavoidable diffraction peaks from the background including those from the gasket material inside the diamond-anvil cell.

volume V , real-space distance d , and wave vector Q correspond to values at ambient pressure (Fig. 4) [28]. The magnitude of the change in Q due to densification could not be estimated at this stage since the bulk compressibility of this glass is unknown. However, the most remarkable change in these diffraction patterns as a function of pressure is shown by the intensity of the FSDP, which remains nearly unchanged up to at least 5 GPa and then drops by a factor of 4 at 8 GPa and almost completely disappears at 15 GPa (Fig. 4). Such a dramatic decrease in the intensity of the FSDP at high pressures points toward a complete collapse of the strong intermediate-range order in the glass structure resulting from a molecular-to-network structural transition at ambient temperature. Unfortunately, the quality of the energy-dispersive diffraction data presented here is not sufficient for further processing and detailed structural analyses of the glass as a function of pressure. *In situ* angle-dispersive x-ray diffraction studies at high pressure are currently underway at the Advanced Photon Source at Argonne National Laboratory to address this issue.

In summary, the Raman spectroscopic and x-ray diffraction measurements provide clear evidence of a relatively sharp pressure-induced structural transition at ambient temperature in a glass of composition $\text{Ge}_{2.5}\text{As}_{51.25}\text{S}_{46.25}$. This transition corresponds to the transformation of the ambient-pressure molecular phase with low T_g (~ 302 K) and strong intermediate-range order to a high-pressure

network phase with higher T_g (~ 338 K). Calorimetric measurements indicate that the low- and high-pressure phases coexist in the transition range implying a first-order phase transition. As discussed earlier, such “molecular-to-network” topological transitions have also been observed in supercooled water and liquid P and may turn out to be the hallmark of polyamorphic transitions in glass-forming liquids.

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