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Pressure-induced instabilities of low-dimensional structural units in chalcogenide glasses at ambient temperature

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Relatively abrupt pressure-induced structural changes have been observed at ambient temperature in low-dimensional chalcogenide glasses in the Ge-As-P-S system. Raman and ^{31}P NMR spectroscopic measurements on pressure-quenched samples indicate that these structural changes correspond to a collapse of the low-dimensional molecular and ring-like structural units in these glasses into 3-dimensionally connected network at high pressure. The molecular-to-network transition is found to be reversible at high temperature above Tg and kinetic studies indicate that the extent of these structural changes is time-dependent at ambient temperature.

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1. Introduction

A wide variety of diffraction and spectroscopic techniques have been applied to investigate the atomic structure of glasses and less frequently of the melts from which they derive. These studies have helped in establishing structure-property relationship in a wide variety of glasses [1]. However, almost all of our knowledge about the structure of glasses and their molten precursors is limited to ambient pressure. Pressure is an important thermodynamic variable that is known to exercise dramatic control on density, diffusivity and viscosity of glasses and melts as well as solubility of volatiles in them [2]. Glassy materials can undergo permanent pressure-induced densification due to their structural freedom accompanied with slow structural relaxation kinetics. The effects of pressure on tetrahedral network structures in AX_2 glasses (A= Si, Ge; X= Se, O) have been studied in the past in detail using various spectroscopic and diffraction techniques [3-9]. As the pressure is increased, the open regions of these networks are found to collapse and eventually structural transitions associated with changes in local coordination numbers may occur [4]. On the other hand, increasing pressure is known to destabilize 2-dimensional ring-like structural units in B_2O_3 glass and promote the conversion of BO_3 units to BO_4 units, resulting in the formation of a higher-dimensional network [10]. However, little is known regarding pressure-induced densification mechanisms and structural changes in low-dimensional chalcogenide glasses [11].

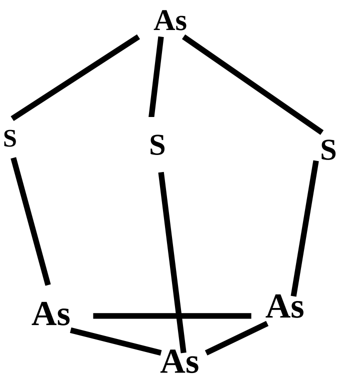

Fig. 1. Sketch of the structure of As_4S_3 molecule.

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In this paper we report experimental evidence suggesting the presence of relatively abrupt pressure-induced structural and topological transitions at ambient temperature in three chalcogenide glasses in the Ge-As-P-S system. One is a glass of composition $Ge_{2.5}As_{51.25}S_{46.25}$. This particular glass has a rather unique structure consisting primarily of isolated As_4S_3 molecules (Fig. 1) [11-14]. Such an open zero-dimensional structure with weak intermolecular bonding results in an unusually low calorimetric glass-transition temperature Tg ~312 K and a large thermal expansion coefficient of 96 ppm/K for this glass. Some of the preliminary results regarding the role of pressure in resulting structural transformations in this glass have been presented by us in an earlier publication [11]. These results are reviewed here and new results on the kinetics and reversibility of these structural transformations are presented. In addition, a second glass of composition $Ge_3P_{1.3}As_{50.7}S_{45}$ is studied where a small amount of As (1.3 atom%) in the original composition $Ge_{2.5}As_{51.25}S_{46.25}$ is replaced with P such that ^{31}P NMR spectroscopy can be used as a probe for studying the pressure induced structural changes. The third glass is of composition $As_2P_2S_8$. Previous Raman and ^{31}P NMR spectroscopic studies [15,16] have indicated that the structure of this glass (T_g ~ 453 K) consists primarily of 2-dimensional $As_2P_2S_8$ rings (Fig. 2).

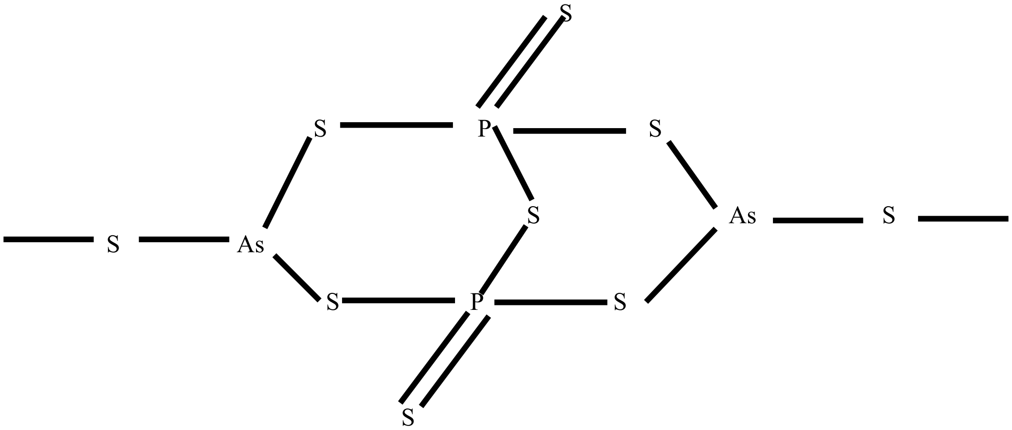

Fig. 2. Structure of $As_2P_2S_8$ ring.

2. Experiments

2.1. Sample synthesis

The chalcogenide glasses were synthesized by melting a mixture of the constituent elements (≥99:9995% purity, metals basis) in an evacuated (10^{-6} Torr) fused silica ampoule and subsequently quenching the ampoule in cold water.

Isothermal compression of powdered samples of these glasses were performed at pressures ranging from 3.0 to 14.4 GPa, at ambient temperature, in a 6-8 multi anvil apparatus at the UC-Davis high-pressure laboratory. The glass powders were placed within a graphite capsule inside a 8mm truncated edge length, castable MgO-ceramic octahedron. The samples were equilibrated at the desired pressure for 12 hours before quenching at a rate of 1 to 4 GPa per hour.

2.2. Spectroscopy

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.

Preliminary ^{31}P magic-angle-spinning (MAS) NMR spectra of pressure-quenched $Ge_3P_{1.3}As_{50.7}S_{45}$ glass samples are reported here. Similar experiments on pressure-quenched $As_2P_2S_8$ glass samples are currently underway and will be published elsewhere [17]. All ^{31}P MAS NMR spectra were collected with a Bruker Avance 500 solid-state spectrometer equipped with a 11.74 T wide bore magnet (^{31}P Larmor frequency of 202.45 MHz) and a 4 mm Bruker CPMAS probe. Crushed glass samples were taken in ZrO_2 rotors and were spun at a rate of 15 kHz. A magnetization tip angle of 60° (1 μs pulse duration) and a recycle delay of 30 s were used and 32 transients were averaged to obtain the MAS spectrum. The ^{31}P chemical shift was externally referenced to 85% H_3PO_4 in all experiments.

3. Results and discussion

3.1. $Ge_{2.5}As_{51.25}S_{46.25}$ and $Ge_3P_{1.3}As_{50.7}S_{45}$ glasses

The Raman spectra of the $Ge_{2.5}As_{51.25}S_{46.25}$ glasses quenched from various pressures are shown in Fig. 3. The most intense band in the Raman spectrum at ambient pressure is centered at ~ 273 cm^{-1}, corresponding to the breathing mode of the basal As_3 ring in the As_4S_3 molecule [12-14]. 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 [18]. On increasing pressure the Raman spectra of the quenched samples do not change significantly up to 7.3 GPa (Fig. 3). 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. 3, inset). Concomitantly the band at ~ 235 cm^{-1} broadens and its relative intensity increases sharply with increasing pressure (Fig. 3). This band has been assigned to As-As stretching in the network by Ewen and Owen, on the basis of their resonance Raman experiments [19]. 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 [12-14], also broaden and their relative intensities increase with rising pressure in this range.

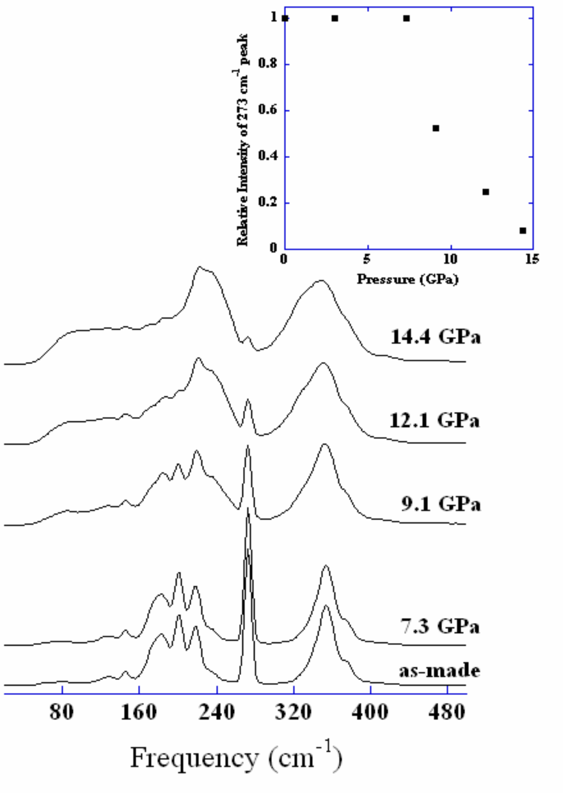

Fig. 3. Raman spectra of the $Ge_{2.5}As_{51.25}S_{46.25}$ glass quenched from various pressures. All spectra were normalized to the intensity of the peak at ~352 cm^{-1}. The inset shows the variation in the relative intensity of the peak at ~273 cm^{-1} in these spectra, above a smoothly varying local background. The error bars for the intensity are within the size of the symbols.

The 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 330-375 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 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.

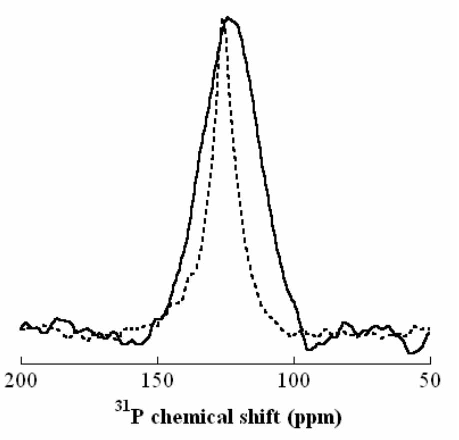

Fig. 4. ^{31}P MAS NMR spectra of the uncompressed $Ge_3P_{1.3}As_{50.7}S_{45}$ glass (dashed line) and the same glass quenched from 12 GPa at ambient temperature (solid line).

^{31}P MAS NMR spectra of the uncompressed and pressure-quenched (from 12 GPa) $Ge_3P_{1.3}As_{50.7}S_{45}$ glasses completely corroborate with this scenario of molecular-to-network structural transformation at high pressure (Fig. 4). P atoms at such small doping levels are known to preferentially replace the apical As atoms in the As_4S_3 molecules to form the top PS_3 pyramid of PAs_3S_3 molecules [20]. This atomic environment for the P atoms is corroborated by the ^{31}P MAS NMR spectrum (Fig. 4) of the uncompressed $Ge_3P_{1.3}As_{50.7}S_{45}$ glass that shows a single unusually narrow peak (FWHM = 1.8 kHz) at a chemical shift of ~ 126 ppm. Such a narrow peak is consistent with a phosphorus atom bonded to three nearest-neighbor sulfur atoms in a highly ordered molecular environment [16]. This ^{31}P MAS NMR peak shows a remarkable broadening in the spectrum of the sample quenched from 12 GPa, with a FWHM of ~ 4.9 kHz characteristic of a 3-coordinated P species in a network environment [16]. The corresponding Raman spectra of these two $Ge_3P_{1.3}As_{50.7}S_{45}$ glass samples are shown in Fig. 5. It is interesting to note that besides the typical Raman bands corresponding to the $Ge_{2.5}As_{51.25}S_{46.25}$ glass, the spectrum of the uncompressed sample contains a small but sharp peak at 308 cm^{-1} corresponding to stretching of the PS_3 pyramid against the As_3 basal triangle in the PAs_3S_3 molecules (Figs. 1,5). This mode completely disappears in the spectrum of the sample quenched from 12 GPa, again indicating a pressure-induced molecule-to-network transformation in this glass.

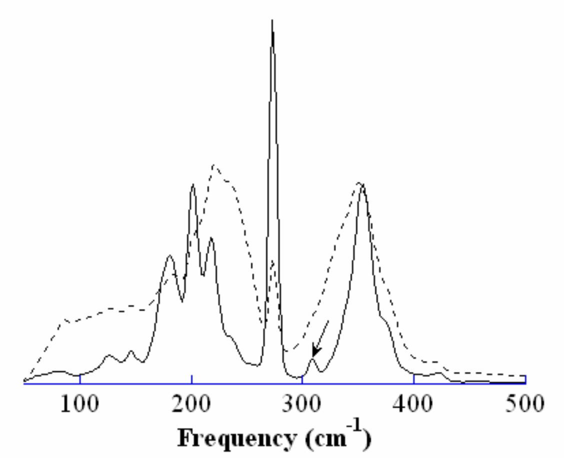

Fig. 5. Raman spectra of the uncompressed $Ge_3P_{1.3}As_{50.7}S_{45}$ glass (solid line) and the same glass quenched from 12 GPa at ambient temperature (dashed line). The arrow marks the band at 308 cm^{-1} that corresponds to the stretching of the PS_3 pyramid in PAs_3S_3 molecule (see text for details).

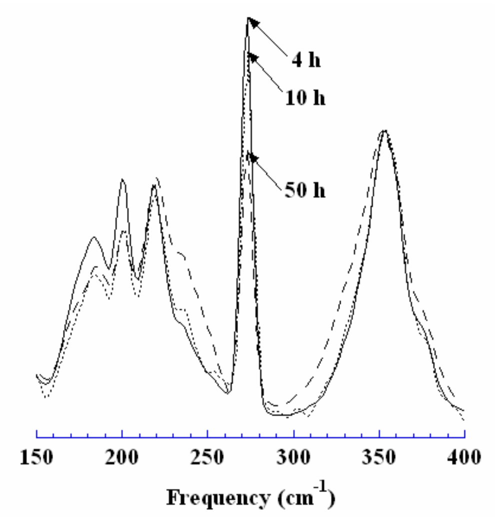

Fig. 6. Raman spectra of the $Ge_{2.5}As_{51.25}S_{46.25}$ glass quenched after holding at ambient temperature at 10 GPa for 4 hours (solid line), 10 hours (dotted line) and 50 hours (dashed line). All spectra are normalized to the intensity of the peak at ~352 cm^{-1}. Arrows indicate progressive decrease in the relative intensity of the peak at ~273 cm^{-1} corresponding to the molecular phase, with increasing holding time.

Raman spectra of $Ge_{2.5}As_{51.25}S_{46.25}$ glass samples held at 10 GPa for various lengths of time show that the degree of transformation from the molecular to the network phase is strongly time dependent at least up to 50 hours at pressures in the transformation range (Fig. 6). This result indicates that sluggish transformation kinetics is indeed responsible for the observed broadening of the pressure interval associated with the transformation. This result is consistent with the scenario of nucleation and growth of a network phase within the matrix of the molecular phase with increasing pressure. $Ge_{2.5}As_{51.25}S_{46.25}$ glass samples quenched from 12 GPa at ambient temperature, when annealed for 3 hours at 313 K showed significant increase in the intensity of the intra-molecular vibrational modes of As_4S_3 molecules at 180, 200, 220 and 273 cm^{-1} while the intensity of the network bands at 235 and 330-375 cm^{-1} decreased (Fig. 7). This preliminary result indicates that the molecular-to-network transition is indeed reversible in this material at ambient pressure.

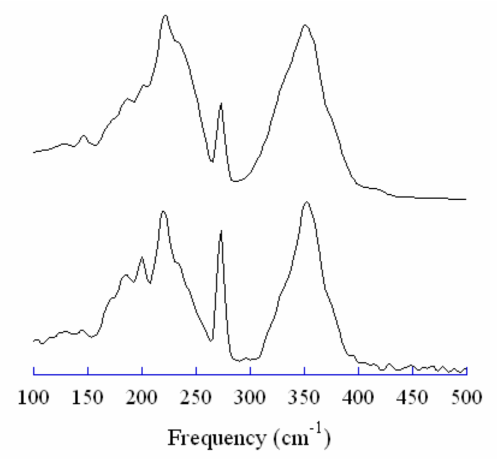

Fig. 7. Raman spectra of $Ge_{2.5}As_{51.25}S_{46.25}$ glass quenched from 12 GPa at ambient temperature (top) and of the same glass subsequently reheated to 313 K for 3 hours at ambient pressure (bottom). Both spectra are normalized to the intensity of the peak at ~352 cm^{-1}.

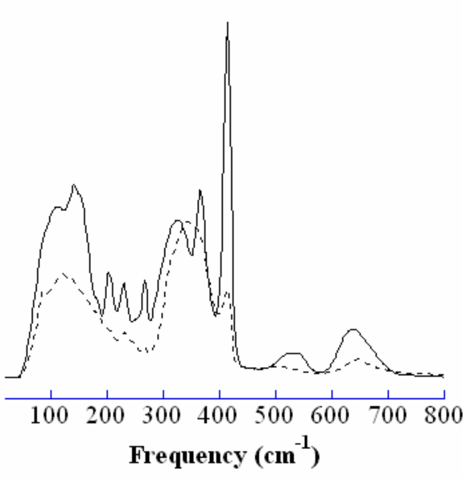

Fig. 8. Representative Raman spectra of the $As_2P_2S_8$ glass quenched from pressures between 0 and 6 GPa (solid line) and of the same glass quenched from pressures between 8.5 and 12 GPa, at ambient temperature (dashed line).

3.2. $As_2P_2S_8$ glass

The Raman spectra of the $As_2P_2S_8$ glasses quenched from various pressures are shown in Fig. 8. Detailed assignments of the vibrational bands in the Raman spectra of glasses in the As_2S_3-P_2S_5 system has been reported in a previous study by Koudelka and coworkers [15]. The most intense band in the Raman spectrum at ambient pressure, centered at ~ 414 cm^{-1} corresponds to the breathing mode of the 2-dimensional $As_2P_2S_8$ rings. Other strong bands at ~ 365 and 323 cm^{-1} have been assigned to stretching vibrations in $S{=}PS_3$ and AsS_3 units. Two highest frequency bands at ~532 and 637 cm^{-1} have been assigned to asymmetric P-S stretch and P=S stretch in $S{=}PS_3$ units. Three sharp bands at ~203, 230 and 267 cm^{-1} have been assigned to various P_xS_y molecules in this glass (Fig. 8). On increasing pressure the Raman spectra of the quenched samples do not change significantly up to 6 GPa. However, upon further increase in pressure to 8.5 GPa the Raman spectra of the quenched glasses show abrupt and marked changes that are essentially complete at this pressure, since no further change is observed upon increasing the pressure further to up to 12 GPa (Fig. 8). The most pronounced changes are an abrupt and marked drop in the relative intensities of the sharp bands at 414, 203, 230 and 267 cm^{-1}. These spectral changes clearly indicate that the low-dimensional structural elements such as the 2-dimensional $As_2P_2S_8$ rings and the P_xS_y molecules in this glass become unstable at high pressure with the Raman spectrum being dominated by a broad band centered at ~ 343 cm^{-1}. This broad band likely corresponds to the stretching vibrations of $S{=}PS_3$ and AsS_3 units that now form a 3-dimensionally connected network.

4. Summary

In summary, the Raman and ^{31}P MAS NMR spectroscopic measurements provide clear evidence of relatively abrupt pressure-induced structural transitions at ambient temperature in structurally low-dimensional chalcogenide glasses in the As-Ge-P-S system. These transitions correspond to the destabilization and transformation of the ambient-pressure molecular or ring-like low-dimensional structural units into a 3-dimensionally connected network structure with increasing pressure. Such topological transitions may turn out to be the telltale signs of the existence of polyamorphic transitions in glasses and glass-forming liquids.

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