Memory Glass: An Amorphous Material Formed from $AlPO_4$

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A glass exhibiting structural memory has been produced through the compression of a single crystal of $AlPO_4$ berlinite to 18 gigapascals at 300 kelvin. The unique and extraordinary characteristic of this glass is that upon decompression below 5 gigapascals, it transforms back into a single crystal with the same orientation as the starting crystal. This glass has a "memory" of the previous crystallographic orientation of the crystal from which it forms.

THE RELATION OF ORDER TO DISORDER is of fundamental interest in the sciences (*1*). As an example of the disordered state, glass is a particularly significant material for its wide range of applications that are important to society (*2*). Normally, it is formed by quenching a melt sufficiently rapidly to prevent crystallization, the result being that glass is a metastable, kinetically frozen state of the liquid. Thus, it contains no long-range structural order; if recrystallized over geological time scales or by heating, glass generally converts to a polycrystalline aggregate (*3*).

Here we describe a different approach to making a glass, pressure-induced amorphization, as applied to crystalline $AlPO_4$ at 300 K. Though formed isothermally, unlike common glasses that are quenched from high temperature, the resulting phase is without long-range order. Hence it is a glass in the conventional sense, but we find that the pressure-amorphized $AlPO_4$ retains a "memory" of the crystal structure. When the pressure is reduced the material reverts back to the original structure and orientation of the single crystal from which it formed.

Two types of experiments, x-ray diffraction and mid-infrared absorption spectroscopy, show that $AlPO_4$ berlinite becomes amorphous under pressure (Fig. 1). In both cases, polycrystalline $AlPO_4$ was examined through a diamond cell as a function of pressure at 300 K (*4*).

The most conclusive line of evidence comes from x-ray diffraction (*5*). When the pressure is increased above 15 ± 3 GPa (150 kilobars), the powder diffraction pattern of the sample vanishes (Fig. 1, A to D). Because a calibrating standard was intermixed with the $AlPO_4$ sample, we are assured that the loss of the berlinite diffraction lines is not due to misalignments or other experimental artifacts. Furthermore, although no diffraction pattern is observed to the highest pressures of this study (40 GPa), the x-ray pattern of berlinite reappears upon decompression below 5 GPa. That is, the pressure-induced amorphization is reversible, but with a hysteresis of ~13 to 15 GPa.

Similarly, as pressure is increased above 15 ± 3 GPa, infrared absorption spectra of $AlPO_4$ change in a manner typical of crystals being converted to glass (*6, 7*). Specifically, the 1025 cm^{-1} band attributed to the antisymmetric tetrahedral P-O vibration broadens significantly, and the analogous Al-O vibration at 780 cm^{-1} vanishes altogether (Fig. 1, E to G). As with the x-ray diffraction pattern, the crystal-like infrared pattern of $AlPO_4$ reappears upon decompression below 5 to 7 GPa.

That berlinite becomes amorphous under compression at 300 K is not surprising. Indeed, our results merely confirm the suggestion (*8*) that $AlPO_4$ amorphizes above 12 GPa, on the basis of the Raman spectrum vanishing; in that case too, the sample was crystalline after decompression to zero pressure [see also (*9*)]. In addition, the isostructural and isoelectronic analog SiO_2 quartz is known to become amorphous under pressure, as is the coesite polymorph of SiO_2 (*10*). The only differences are that higher pressures are required to amorphize SiO_2 (25 and 30 GPa for quartz and coesite, respectively), and the crystalline phase does not reappear upon release of pressure. Presumably, the presence of the weaker Al-O bond allows $AlPO_4$ to become amorphous at a lower pressure than does the stronger Si-O bond of quartz and coesite (*11*).

We also note that a wide variety of materials have been found to pressure-amorphize if compressed at temperatures that are sufficiently low to kinetically hinder the equilibrium phase transitions. For example, crystalline SnI_4, $LiKSO_4$, and $Ca(OH)_2$ all amorphize upon compression above 10 to 15 GPa at 300 K (*12*). Like $AlPO_4$, these materials transform back from the glassy to the more stable crystalline state upon decompression to zero pressure. In contrast, H_2O ice I_h below 80 K, and $CaAl_2Si_2O_8$ anorthite and Fe_2SiO_4 fayalite at 300 K amorphize at pressures ranging from 5 to 40 GPa and remain in the glassy state (like SiO_2) after release of pressure (*13*).

To further investigate this phenomenon, single crystals of $AlPO_4$ berlinite have been compressed to pressures of 44 ± 1 and 28 ± 1 GPa at 300 K; that is, to pressures well above the crystal → glass transition (*14*). The specimens were thin plates, 18 ± 1 μm thick and over 50 μm in lateral dimensions. Before compression, the samples had an apparent birefringence of $\delta = 0.005$ (*15*), well within the range expected for berlinite and showing that our specimens were oriented with the *c* crystallographic axis at 45° to the plane of the plate (*16*).

After compression the two specimens were examined optically at ambient conditions, outside the diamond cell. The remarkable finding is that both exhibit a uniform value of $\delta = 0.005 \pm 0.001$ (Fig. 2), with a sample thickness identical to that prior to compression (within the quoted uncertainty). There is no evidence for any domain boundaries across either specimen. Thus, on decompression our samples reconverted from the glassy state to a single crystal with identical orientation (45° ± 6°) to the initial crystal from which the glass was made. The birefringence of the crystal quenched from 44 GPa is slightly mottled, but we interpret this as being due to defects produced by the (slightly) inhomogeneous stresses present at the peak pressures of that run. A similar texture of mottled birefringence caused by dislocations has been previously documented for single crystals that have been shock-compressed (*17*).

The loss of the x-ray diffraction pattern on compression above 15 GPa proves that long-range order is lacking in the pressure-amorphized state. That this loss of diffraction is not simply due to crushing of the sample to an ultrafine grain size is demonstrated by the following observations: (i) the loss of diffraction occurs over a narrow pressure interval, rather than continuously or gradually; (ii) it is not correlated with the magnitude of shear stress present in the sample (*18*); (iii) it is reversible on decompression; and (iv) the amorphization is evident in infrared and Raman spectra, which probe a molecular length scale rather than

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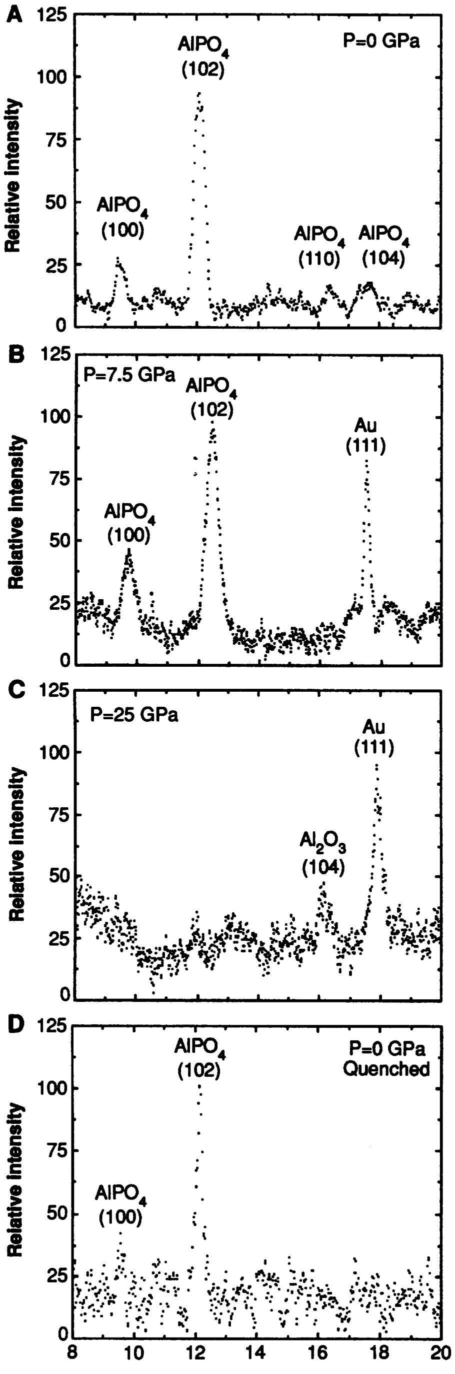

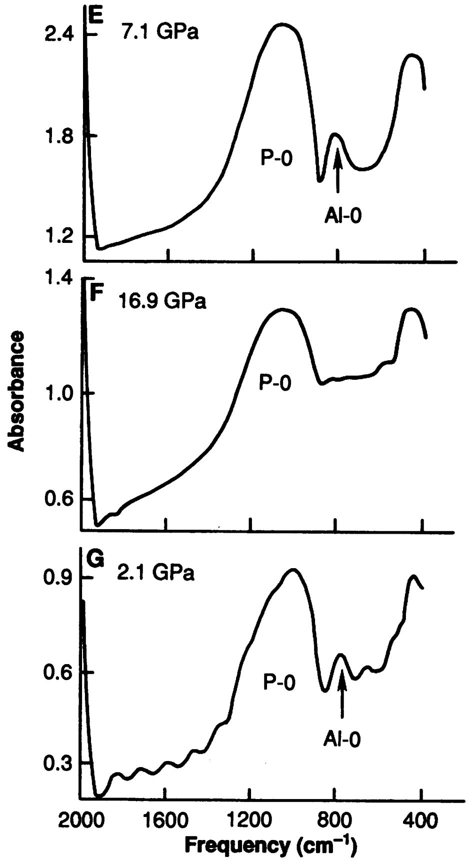

Fig. 1. (**A** to **D**) X-ray diffraction patterns (top to bottom) taken at zero pressure (before compression), at 7.5 ± 1 and 25 ± 2 GPa on increasing pressure, and at zero pressure after quenching from 40 GPa. The sample to film distance is 4.991 cm for the samples under pressure, and 2.865 cm for the samples at ambient conditions (*20*). The zero-pressure samples contain no gold (used for intensity calibration at high pressures), and the (104) diffraction line of Al_2O_3 is due to the presence of ruby that is used for pressure calibration (*4*). The signal-to-noise ratio is higher for the initial pattern ($P = 0$, before compression) because this was obtained from an amount of sample ~1 to 2 orders of magnitude larger than for the three other patterns. (**E** to **G**) Examples of infrared absorption spectra taken at 7.1 ± 0.2 and 16.9 ± 2 GPa on increasing pressure and at 2.1 ± 0.2 GPa on decreasing pressure. The Al-O and P-O antisymmetric tetrahedral stretching modes are indicated. The fringing evident in the 2.1-GPa spectrum is a result of interference effects due to the culets.

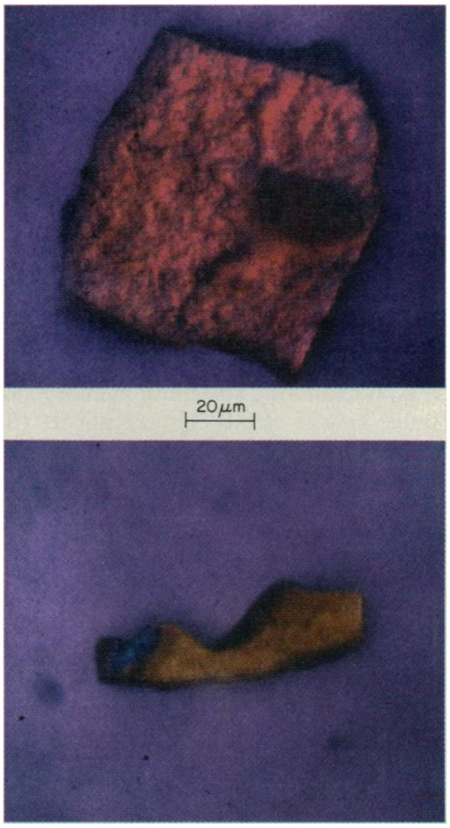

Fig. 2. Photographs of an $AlPO_4$ berlinite sample taken between crossed polarizers (white transmitted light with gypsum plate) before compression (top) and after decompression from 28 GPa (bottom). After quenching, except for the left end where part of the sample flaked off (hence is thinner), the interference color is uniform, implying that the sample is a single crystal with uniform orientation across its entire width. The apparent difference in the color of the crystal before compression and after decompression is an artifact of the photography. The scale bar is 20 μm long.

the multi-unit cell dimensions sampled by x-ray diffraction. Therefore, we have shown that a state lacking long-range structural order can be created such that it reverts spontaneously back to the original state of crystallographic order (including crystallographic orientation) from which the glass was formed. In this sense, the glass that we have formed retains a memory of its structurally ordered precursor.

Our interpretation of how this comes about is simple. The originally crystalline sample is compressed far beyond its limit of thermodynamic stability, metastability resulting from the kinetically low temperature of the experiment. At pressures above 15 GPa the crystal structure becomes unstable relative to the amorphous state, possibly through a dynamical instability (*19*). Because of the low temperatures, however, the ions cannot move far from their positions in the original crystal structure. In particular, diffusive motion is precluded and it is likely that the ions are located within a fraction of an atomic dimension of their crystallographic sites. Thus, although long-range order is lost, we infer that the ions within the glass are displaced by small but random amounts away from their positions in the ordered state. On decompression, it is therefore possible for the ions to slip back into the state of lowest free energy: the original, structurally ordered state with the same crystallographic orientation as before. Unlike the thermal randomization that precedes the formation of glass by conventional means, pressure-induced amorphization apparently allows the "memory glass" to retain a memory of its structurally ordered precursory state.

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4. Polycrystalline samples of $AlPO_4$ berlinite were loaded in a gasketted Mao-Bell–type diamond cell. The starting material was a fragment from the single crystal used by Jayaraman *et al.* (*8*), part of which was ground to a grain size less than 3 μm. Pressure was determined using the ruby fluorescence technique [H. K. Mao, P. M. Bell, J. W. Shaner, D. J. Steinberg, *J. Appl. Phys.* **49**, 3276 (1978)].
5. X-ray diffraction at pressure was carried out with monochromatized Mo K_α radiation from a rotating-anode generator, with the pattern being collected on film in a Debye-Scherrer geometry; see E. Knittle and R. Jeanloz, *Science* **223**, 53 (1984); *ibid.* **235**, 668 (1987). For the x-ray diffraction runs at high pressure, ~10% by volume Au powder (99.99% purity, grain size less than 5 μm, obtained from Alpha Ventron Corp., Danvers, MA) was mixed into the sample. This served as a calibration standard for the diffraction intensities of the sample, and no other pressure medium was used.
6. Samples of $AlPO_4$ (8% by weight) mixed in CsI were compressed between anvils of type II diamond. Absorption spectra were collected between 300 cm^{-1} and 3700 cm^{-1} (4 cm^{-1} resolution) with a Bomem DA 3.02 Fourier transform spectrometer equipped with a liquid helium–cooled Ge:Cu detector; see Q. Williams and R. Jeanloz, *Science* **239**, 902 (1988).
7. The difference between infrared absorption spectra of crystals and corresponding glasses is illustrated in and discussed by R. Zallen [in (*2*)]. The interpretation of the infrared absorption spectrum of $AlPO_4$ berlinite is discussed by E. Z. Aldridge, V. C. Farmer, B. D. Mitchell, W. A. Mitchell, *J. Appl. Chem.* **13**, 17 (1963). The spectrum of our sample at ambient conditions is in good agreement with theirs.
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14. The single crystal samples were compressed as described above (*4*), except that a hydrous 4:1 mixture of methanol:ethanol was used as a pressure medium; see G. J. Piermarini, S. Block, J. D. Barnett, *J. Appl. Phys.* **44**, 5377 (1973). This pressure medium becomes nonhydrostatic at pressures above ~14 GPa.
15. The apparent birefringence is the observed optical retardation divided by the sample thickness. Thus, δ depends on the crystallographic orientation of the sample. It was determined by means of white, cross-polarized transmitted light (*16*).
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18. The magnitude of shear stress varies from one experimental run to the next and is quantified by measuring the pressure gradients across the sample [see C. Meade and R. Jeanloz, *J. Geophys. Res.* **93**, 3261 (1988); *ibid.*, p. 3270; *Science* **241**, 1072 (1988)].
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Water and Solutions at Negative Pressure: Raman Spectroscopic Study to −80 Megapascals

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Microscopic inclusions of aqueous fluids trapped in interstices in quartz and other crystals provide novel systems for the deliberate study of liquids under tension. Liquids under tension should differ in interesting ways from those at ambient pressure or compressed liquids because attractive, rather than repulsive, forces should dominate their behavior. Static tensions in excess of 100 megapascals (~1000 atmospheres) have been obtained reproducibly. Video-recorded observations of the final liquid rupture process, coupled with extrapolations of data at positive pressure, suggest that the homogeneous vapor nucleation point was reached in two of the cases studied. Raman spectra of the fluids at −80 megapascals show that an isothermal volume stretch of ~5 percent by volume has only a weak effect on the spectral features and is similar to the effect of isobaric heating.

INTEREST IN THE PROPERTIES OF WATER under tension (that is, at negative pressure) has been stimulated by the conjecture of Speedy (*1*) that the much investigated divergences of thermodynamic properties and relaxation times in supercooled water (*2*) are related to comparable divergences in properties of superheated water (*3*) through a continuous line of mechanical instabilities. For this relation to be possible, the spinodal limit to liquid superheating and stretching, which is predictable for any liquid from reasonable equations of state (EoS) (*1, 4–6*), must behave anomalously in the negative pressure regime in the case of water. The spinodal line for water, obtained from the National Bureau of Standards (NBS) EoS (*5*) where $(\partial P/\partial V)_T = 0$, is shown against the phase diagram for water in Fig. 1. (This contrasts with "normal" behavior predicted by the van der Waals EoS in which the spinodal line moves to ever more negative pressures with decreasing temperature.) Speedy's much simpler (two-parameter) EoS, derived with the assumption of a spinodal limit to the liquid and fit to EoS data from 0° to 100°C and 0 to 100 MPa, yields a somewhat larger tensile limit (dashed line in Fig. 1).

Figure 1 differs from the standard textbook phase diagram for water by inclusion of a gray area for metastable liquid states, most of which falls in the negative pressure domain. At the boundaries of this region, fluctuation correlation lengths diverge, as at the critical point (*4, 6*), and the metastable liquid become mechanically unstable. Anomalous behavior, comparable to the divergence of compressibility, viscosity, and other properties of supercooled water [where an origin in spinodal fluctuations has

Fig. 1. Phase diagram for water showing thermodynamically stable (open) and metastable (shaded) regions. Thin lines are isochores (specific volumes are marked). The spinodal boundary according to the NBS EoS is given as a thick curve commencing at the critical temperature, T_c, whereas the part of the spinodal assessed by Speedy with a (more reliable) two-parameter equation is shown as a thick dashed line. The tension estimated by Roedder for a fluorite inclusion from the observed ice melting point elevation (*11*) is marked as a triangle on the extrapolated melting line, T_m.

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