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High-pressure x-ray-diffraction study of α-AlPO$_4$

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Our high-pressure x-ray diffraction experiments on berlinite AlPO$_4$ (α-AlPO$_4$) show that it transforms to a crystalline *Cmcm* phase beyond 13 GPa. The persistence of diffraction pattern up to 40 GPa does not confirm the previous conclusions of high-pressure amorphization of AlPO$_4$ around 12–18 GPa. Our experimental results, in agreement with earlier Raman scattering results, suggest that the so called memory glass effect observed earlier may in fact be due to the reversibility of α-phase$\Leftrightarrow$*Cmcm* phase transformation. These new experimental observations raise serious doubts about the theoretical understanding of the high-pressure behavior of α-AlPO$_4$.

Tetrahedral framework structures have been extensively investigated under high pressures due to their geophysical relevance. Also as the tetrahedra cannot be close packed, this set of compounds have been at the center of activity related to pressure induced amorphization of materials.[1] Of these, the high-pressure behavior of α-AlPO$_4$ (berlinite) has been hailed as unique and extraordinary[2] due to what in the literature has been termed as memory glass effect. Memory glass nature refers to the reversion of high pressure amorphous phase to the original single crystal with the same orientations as the starting crystal.[2] The existence of high-pressure amorphous phase (for $P > 12–18$ GPa) was proven with the help of x-ray-diffraction studies[2,3] and supported by Raman[4] and infrared absorption studies.[2] Memory glass nature was established with the help of resurgence of original optical birefringence on decompression from optically isotropic amorphous phase.[2] Subsequent Brillouin scattering experiments by Polian, Grimsditch, and Philippot[5] supported these results through the demonstration of complete reversal of sound velocities on decompression from the high-pressure phase. These authors also noted that the high pressure phase (>15 GPa) was not elastically isotropic and instead was an anisotropic glass.

These experimental results on AlPO$_4$ encouraged several theoretical investigations. Energy minimization and lattice dynamical calculations[6,7] suggested that, as in quartz, the oxygen atoms in α-AlPO$_4$ too have a tendency to approach the bcc lattice. These calculations also showed that a zone boundary phonon mode along with a part of acoustic branch softens at $\sim$30 GPa. The softening of these modes was suggested to be responsible for pressure induced amorphization. Classical molecular dynamics (MD) calculations[8–10] showed that AlPO$_4$ amorphizes for $P > 30$ GPa in contrast to the experimental values of 12–18 GPa. These studies also showed the high-pressure amorphous phase to be anisotropic. These MD investigations ascribed the memory glass effect to the reversibility of six coordinated AlO$_6$ octahedra to the four coordinated AlO$_4$ tetrahedra due to the retention of four coordination in the PO$_4$ tetrahedra in the disordered phase at high pressures.[9]

Recently a few more investigations have been carried out. An x-ray-diffraction study by Kruger and Meade[11] suggested a crystalline-crystalline phase transformation at $\sim$6.5 GPa while a high resolution single crystal x-ray-diffraction investigation by Sun *et al.*[12] indicated the existence of a disordered crystalline phase at $\sim$12 GPa. In addition, a recent extensive Raman scattering study showed several interesting aspects related to the high-pressure behavior of the berlinite.[13] Under the quasihydrostatic pressures, using alcohol and alcohol water mixtures, beyond $\sim$14 GPa, the sharp α-berlinite Raman peaks are lost and weak Raman bands appeared. This was interpreted in terms of a phase transformation of α-berlinite to a disordered crystalline phase.[13] With a less soft pressure transmitter like KBr, the emergence of the same disordered crystalline phase was noted, however, this new phase seemed to progressively transform to an amorphous phase at higher pressures. On decompression while the samples with liquid transmitters transformed back to α-phase, the high-pressure phase, under relatively nonhydrostatic compression transformed partly to an amorphous phase.[13]

To understand some of these experimental results another detailed MD simulation of this compound was carried out using a much larger cell than used in previous calculations.[14] These simulations showed that the high-pressure phase ($P > 30$ GPa) though disordered is not x-ray amorphous. In particular, these simulations demonstrated that the translational order persists along the crystallographic $(10\,\overline{1}\overline{2})$ and $(10\,\overline{1}\overline{4})$ directions. In addition, these calculations predicted a disorder in the oxygen sublattice beyond 15 GPa. These computations also showed that beyond 12 GPa, a CrVO$_4$ structure type in the orthorhombic *Cmcm* space group has a lower total energy than the α-phase, in agreement with earlier enthalpy calculations.[10] Further, these MD calculations demonstrated that, with the pair potentials of van Beest, Kramer, and van Santen,[15] the transformation of the berlinite phase to the orthorhombic phase is kinetically hindered. These and other contradictory results from various studies mentioned above motivated us to undertake a careful reinvestigation of this material through x-ray-diffraction experiments at high flux SPring8 synchrotron facility in Japan.

Angle dispersive x-ray-diffraction experiments were carried out at the undulator beamline BL10XU of SPring8 using a monochromatic x-ray beam of 0.7 Å and 50 μm diameter. The diffraction pattern was recorded using an imaging plate

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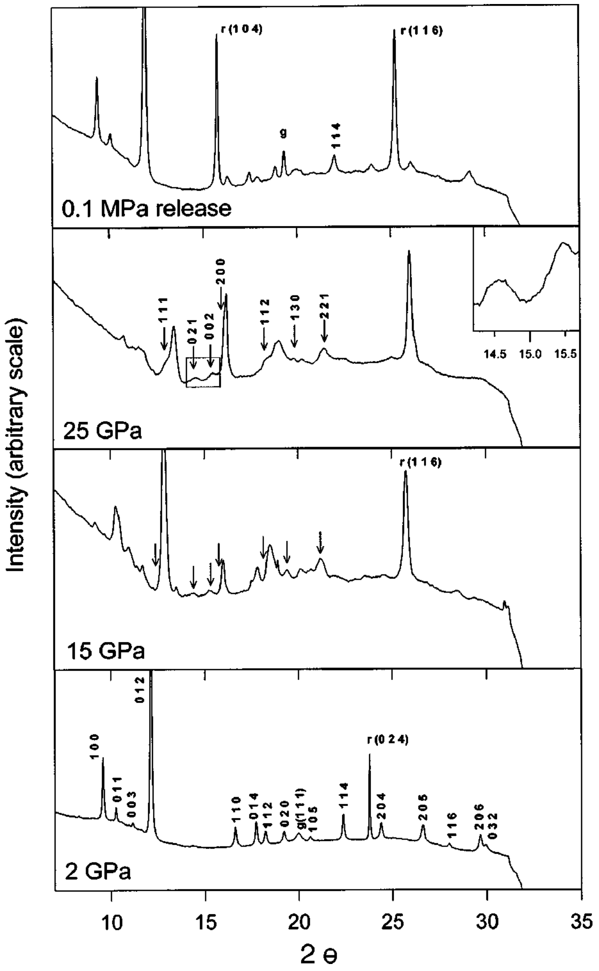

FIG. 1. One dimensional diffraction profiles of AlPO$_4$ at various pressures. Arrows at 15 and 25 GPa indicate the new diffraction peaks. At 25 GPa, hkl indices refer to the unit cell of CrVO$_4$ type structure in the *Cmcm* space group. The ruby and gasket diffraction lines are labeled as **r** and **g**. Inset at 25 GPa shows that the diffraction peaks of the new phase are broader.

kept at a distance of ~25 cm from the diamond anvil cell. Coarsely powdered α-AlPO$_4$ sample was loaded in a steel gasket hole (diam~100 μm) of a diamond anvil cell. Material was not finely powdered partly to avoid any accidental amorphization due to griding seen in other materials.[16] Two experiments were carried out. The first experiment was terminated at ~30 GPa while in the second one pressure was released from 40 GPa. In the first experiment, the pressure transmitter (4:1 methanol-ethanol) was less than the sample. In the second experiment, the gasket was less than half filled with the sample to provide better quasihydrostatic pressures. A tiny ruby chip (~10 μm) was loaded along with the sample to measure pressure by monitoring R-line shifts. A variation in the R_1-R_2 splitting and broadening indicated that beyond ~20 GPa pressure became nonhydrostatic in the first experiment while in the second experiment pressure was seen to remain quasihydrostatic up to ~40 GPa.

Imaging plate (IP) records show that granular diffraction lines persist up to the highest pressures in both the experiments. Two dimensional IP records were transformed to one dimensional diffraction patterns by radial integration of the diffraction lines. Some of these one dimensional diffraction profiles are shown in Fig. 1.[17] It was noted that Bragg diffraction peaks persist even at 40 GPa. At ~13 GPa, in both the experiments, new diffraction lines appeared in addition to those of the α phase. In Fig. 1, these new lines are indicated with arrows at 15 and 25 GPa. On release of pressure from 40 GPa, all the new diffraction peaks vanished and the diffraction pattern of only α-phase remained.[18]

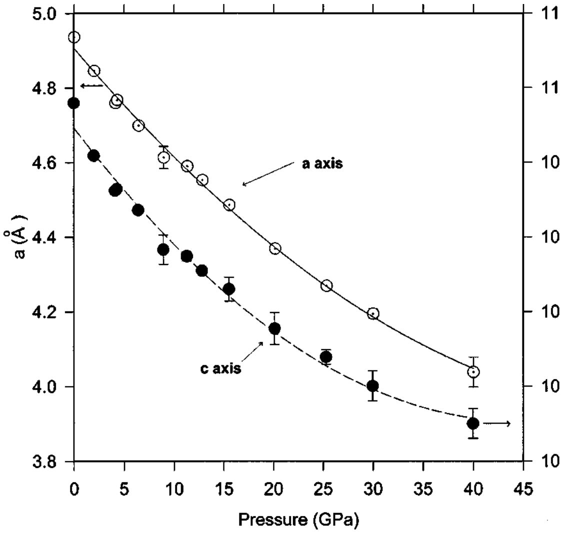

FIG. 2. Variation of unit cell parameters **a** and **c** of α-AlPO$_4$ with pressure.

These x-ray-diffraction results imply the existence of a phase transformation to another crystalline phase between 11 and 13 GPa. In fact some of the diffraction peaks persist up to the highest pressures (40 GPa) and this contradicts the earlier conclusions that the high pressure phase is an amorphous phase.[19] Due to the presence of strong textural effects in the data of the present experiments, Rietveld method could not be used for determining the crystallographic parameters. Therefore, we have employed profile fitting to evaluate the cell parameters only. The cell lengths of α-AlPO$_4$ determined from the present data show a smooth and monotonic behavior as displayed in Fig. 2.[19] In Fig. 3 we compare the observed variation in c/a with that from an earlier x-ray-diffraction study[20] and also from recent MD simulations.[14] Up to ~9 GPa, where the earlier experimental data are available, these agree very well. Though quantitatively the absolute values of observed and MD calculated[14] c/a ratio of the berlinite phase compare reasonably (within 2%) up to ~12 GPa, the rate of change of c/a is distinctly higher for MD results. In addition the experimental results do not show a plateau of c/a beyond ~12 GPa and these disagreements highlight the limitations of the pair potentials used in the MD simulations.

Analysis of additional diffraction lines show that these belong to a structure of CrVO$_4$ type in the *Cmcm* space group. In this context, we should also note that even in the published diffraction pattern of Ref. 2 at 25 GPa, there were weak but new diffraction peaks observed at $d \cong 3.14$, 2.82, 2.72, and 2.21 Å. Probably due to weak intensities, not much attention was paid to these new diffraction lines. With our lattice constants of CrVO$_4$ structure, we could index these new diffraction peaks as (111), (021), (002), and (112), respectively. Figure 4 shows the variations of a, b, and c of the

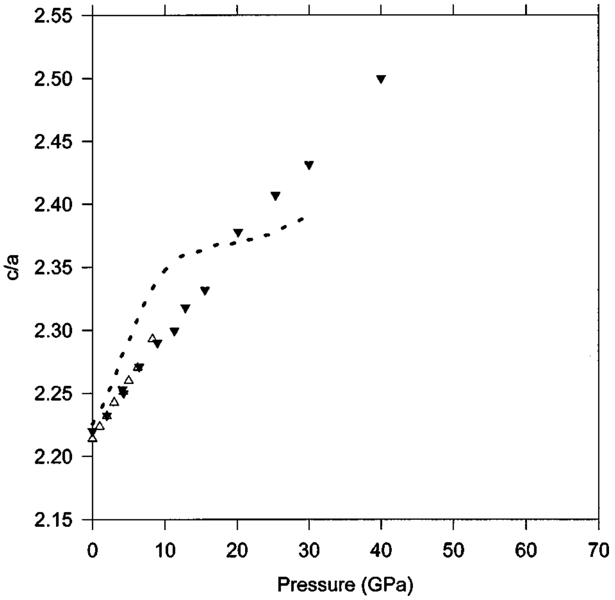

FIG. 3. c/a of α-$AlPO_4$ at high pressures. Open triangles refer to the earlier experimental data (Ref. 20) while the dotted line represents the results of a recent MD calculation (Ref. 14).

Cmcm phase as deduced from our experimental data. It is interesting to note that our observed $a:b:c::0.716:1:0.732$ compare favorably with the experimental results for other compounds crystallizing in $CrVO_4$ structure.[21] In this structure, Al atoms have octahedral coordination with oxygen atoms while P is tetrahedrally bonded. P-V results for both, α and *Cmcm* phases are shown in Fig. 5. The first-order phase transformation at ~13 GPa is accompanied by a volume reduction of ~27%, which is comparable to (21%) observed in isostructural $FePO_4$.[22] A fit of P-V data of the α phase to Birch-Murnaghan equation gives $K=34$ GPa ($K'=4$). This agrees well with, both, earlier theoretical results[14] (34.7 GPa) and low-pressure experimental data[20] (36 GPa). In contrast, the *Cmcm* phase was found to be relatively incompressible with $K=127$ GPa ($K'=4.0$). This may be compared with the calculated bulk modulus of ~166 GPa from MD simulations.[14] The same relatively incompressible behavior of the *Cmcm* phase is also found in $FePO_4$ where the K values before and after the transformation are 24 and 96 GPa, respectively.[22]

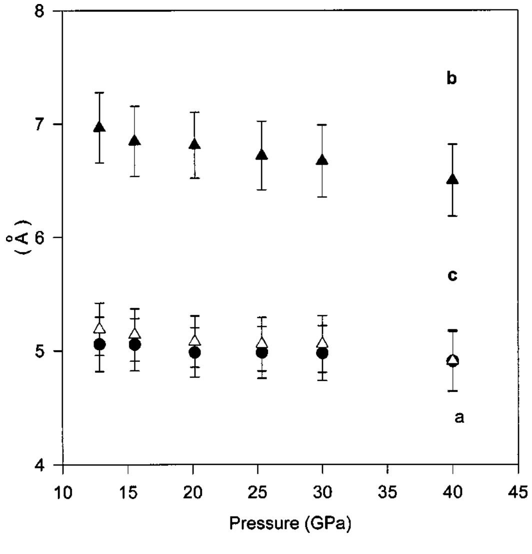

FIG. 4. Variation of *a*, *b*, and *c* of the *Cmcm* phase with pressure. Filled circles represent *a*, filled triangles correspond to *b*, and *c* is represented by the unfilled triangles.

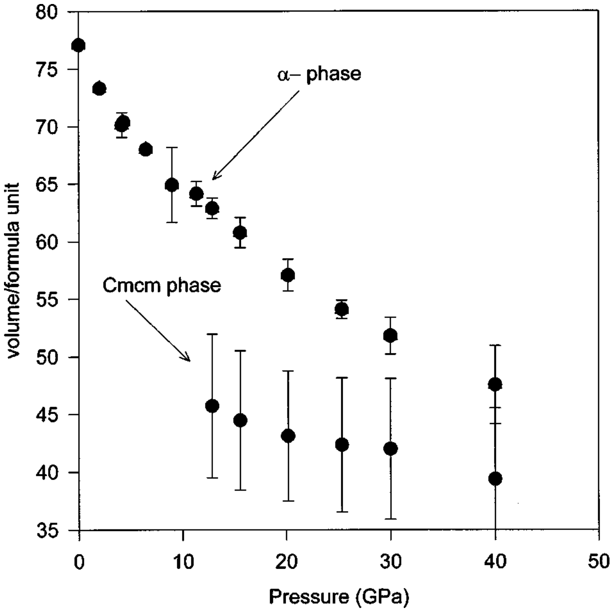

FIG. 5. P-V behavior of $AlPO_4$ in the α as well as *Cmcm* phase.

A careful look into the diffraction patterns beyond 13 GPa, shows that the diffraction peaks of α phase gradually lose intensity, while the intensities of the new peaks grow marginally indicating kinetic impedance. Also though the new *Cmcm* phase is crystalline, it seems to be poorly crystallized as suggested by the higher full width at half maximum of the Bragg peaks (inset in Fig. 1).[23] Similar results have earlier been observed in quartz where it was shown that at high pressures, stishovite crystallizes poorly.[24] Raman scattering results of Gillet *et al.* also lend support to this suggestion. First, it should be noted that the Raman bands observed by Gillet *et al.* at $P>14$ GPa are very similar to that of $CuCrO_4$ which exists in the *Cmcm* phase at ambient conditions.[25] Second, the intensity of the new modes is an order of magnitude smaller than that of α phase.[26] Also our data show that beyond 25 GPa, there is an overall decline in the intensities of all the diffraction peaks. This may also indicate that the high-pressure *Cmcm* phase transforms into an amorphous phase under the nonhydrostatic stresses as also noted in the Raman studies.[13] It should also be pointed out that transformation to a disordered *Cmcm* phase has also been seen earlier in isostructural materials such as α-$GaPO_4$ (Refs. 27 and 28) and α-$FePO_4$.[22] Of particular interest is the investigation by Badro, Itie, and Polian[27] on α-$GaPO_4$. In this compound the quality of the diffraction pattern of the daughter *Cmcm* phase improved dramatically on laser heating the material in the stability field of the high-pressure phase.[27] In particular, this heating reduced the amount of background hump which in many cases have been ascribed to the existence of an amorphous phase. In similar situations, laser heating the sample may help reduce the kinetic resistance for crystallization of the new phase. This would also establish the degree of reversibility of the high-pressure phase to α phase. In the present case no quantitative estimate can be made of the back transformation. However, on decompression reemergence of all the diffraction peaks of the α phase indicates that the poor crystallinity of the high-pressure phase does not retard the reversibility.

In conclusion, we shall like to state that the present experimental studies do not confirm the previously observed memory glass effect. Our x-ray-diffraction data show that α-berlinite transforms to a disordered crystalline *Cmcm* phase beyond 13 GPa. These results are in agreement with the earlier Raman work.[13] The presence of a crystalline orthorhombic phase beyond ~13 GPa provides a more easily acceptable rationale for the explanation of the observed elastic anisotropy of the high-pressure phase in Brillouin scattering results.[4] However, for a quantitative explanation of these results, the present results are not adequate and it will be necessary to carry out single crystal diffraction studies. It is interesting to note here that a similar Brillouin scattering result in quartz could be reasoned out in terms of a crystalline-crystalline transformation preceding amorphization.[29–31] Also, though the total energy calculations had supported the stability of *Cmcm* phase at high pressures, this phase could not be dynamically reached in any of the classical MD calculations carried out so far.[14] This failure along with our experimental results may further suggest the possibility of large kinetic resistance for the α phase to *Cmcm* phase transformation and should encourage more experimental and theoretical work.

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[17] So as to provide comparative scale, data shown in Fig. 1 at 0.01 MPa, 15 GPa, and 25 GPa were scaled with (116) ruby diffraction line. Data at 2 GPa were scaled to that of released 0.01 MPa with $(012)_\alpha$ line.

[18] During the release of pressure, our sample did not show any visual signatures of radial partitioning of the sample in two regions as noted in the highly nonhydrostatic Raman investigations of Gillet *et al.* (Ref. 13).

[19] At 40 GPa, only two diffraction peaks of the α-phase, viz. (102) and (104), can be observed. Coincidentally these are the same remnant diffraction peaks as seen in recent MD simulations at ~55 GPa (Ref. 14). Due to several disagreeing features of the experimental results with theoretical predictions, this agreement may be fortuitous. However, the persistence of low-pressure phase well beyond the transformation pressures has also been noted in earlier high-pressure investigations of α-FePO$_4$ (Ref. 22). Corresponding lack of signatures of the coexisting α-phase in the Raman results of Gillet *et al.* may perhaps be due to the reduced transparency of the material as noted across a similar transformation in GaPO$_4$ (Ref. 28). Even in FePO$_4$, Raman results do not provide an unambiguous support to the existence of α phase beyond the transition pressure.

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[23] By a poorly crystallized phase we mean that the particle size of the new phase may be very small as well as that due to the heterogeneous nature of growth of new phase there may be differing amounts of local strains. However, our results cannot rule out the possibility that the new phase is inherently a disordered crystalline phase as suggested by Gillet *et al.* (Ref. 13).

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