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High pressure phase transformations in α -AlPO₄: an x-ray diffraction investigation

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Abstract. We have re-investigated the high pressure behaviour of berlinite AlPO₄ (α -AlPO₄) with x-ray diffraction using a powerful synchrotron x-ray source SPring-8. Our results show that it transforms to a crystalline phase beyond \sim 13 GPa. Our data seem to be consistent with a CrVO₄ type of structure in the *Cmcm* space group, similar to the high pressure phase observed in some isostructural phosphate compounds. The persistence of the diffraction pattern up to 40 GPa establishes that the previously accepted amorphization of AlPO₄ around 12–18 GPa is incorrect. Experimental results suggest that the so-called memory glass effect observed earlier may in fact be the reversibility of the α -phase \leftrightarrow crystalline phase transformation. Comparisons of our experimental and theoretical results raise serious doubts about the theoretical understanding of the high pressure behaviour of α -AlPO₄.

1. Introduction

High pressure studies of corner-linked tetrahedral α -quartz-like compounds have been of considerable interest due to their geophysical importance. Since the tetrahedra cannot be close packed, this set of compounds has also been the subject of intense investigations in the context of pressure induced amorphization of materials [1]. In particular, the high pressure behaviour of α -AlPO₄ (berlinite) has been of special interest. Berlinite, AlPO₄ (space group *P*3₁21), is related to the α -quartz structure with AlO₄ replacing one SiO₄ and PO₄ the other one with its *c*-axis double than that of quartz. It has been claimed to exhibit a memory glass effect [2] near 15 GPa. The term memory glass refers to the reverse transformation of the high pressure amorphous phase to the original single crystal with the same orientations as the starting crystal [2]. Occurrence of the high pressure amorphous phase was demonstrated by the loss of sharp x-ray diffraction peaks [2, 3] around 12–18 GPa. This also found support from the precipitous decline of intensities of its Raman peaks [4] near this pressure. In addition, IR absorption studies showed that beyond \sim 15 GPa, the 1025 cm⁻¹ band due to anti-symmetric tetrahedral P–O vibrations broadened substantially and the tetrahedral Al–O vibration at 780 cm⁻¹ vanished altogether [2]. Subsequent Brillouin scattering experiments by Polian *et al* [5] also supported these findings as they showed a complete reversal of sound velocities on decompression from the high pressure phase. These authors also found that the high pressure phase (>15 GPa) was not elastically isotropic and instead was an anisotropic glass. Observations of amorphous phase from the samples after non-hydrostatic compression in the ungasketed diamond anvil cell [6] as well as in the recovered samples after shock loading [7] further supported the idea of the high pressure phase being the amorphous phase.

These experimental results on AlPO_4 inspired several theoretical investigations. As in α -quartz, energy minimization and lattice dynamical calculations [8, 9] were used to show that 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 at the k point $(1/3, 1/3, 0)$ along with a part of the acoustic branch softens at ~ 30 GPa [8, 10]. This was proposed to be the dynamical mechanism of pressure induced amorphization in this material. Classical molecular dynamics (MD) calculations [10–12] showed that AlPO_4 amorphizes above 30 GPa in contrast to the experimental values of 12–18 GPa. Moreover, the high pressure amorphous phase was found to be anisotropic, supporting the Brillouin scattering results. These MD investigations attributed [12] the memory glass effect to the reversion of octahedrally coordinated AlO_6 at $P > 30$ GPa to the tetrahedrally coordinated AlO_4 on decompression. This was conjectured to be due to the relatively less deformability of the PO_4 tetrahedra in the disordered phase at high pressures [12].

Some subsequent investigations have raised doubts about the above accepted picture of the high pressure behaviour of AlPO_4 . A recent Raman scattering study showed that the high pressure phase beyond 14 GPa has sharp Raman lines, typical of a crystalline material [13]. An x-ray diffraction study by Kruger and Meade [14] suggested a crystalline–crystalline phase transformation at ~ 6.5 GPa while a high resolution single crystal x-ray diffraction investigation by Sun *et al* [15] indicated the existence of a disordered crystalline phase at ~ 12 GPa. These experimental results prompted an extensive MD simulation of this compound using a much larger MD cell [16] than used in the earlier calculations. These simulations showed that the high pressure phase ($P > 30$ GPa) though disordered is not x-ray amorphous. These also showed that the translational order persists along the crystallographic $[10\bar{1}2]$ and $[10\bar{1}4]$ 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 also demonstrated that, with the pair potentials of van Beest *et al* [17], the transformation of the berlinite phase to the orthorhombic phase is kinetically suppressed. These and other contradictory results from various studies mentioned above motivated us to undertake a careful re-investigation of this material through high resolution powder x-ray diffraction experiments.

2. Experiment

Angle dispersive x-ray diffraction experiments were performed on a dedicated high pressure undulator beamline BL10XU of the third generation synchrotron SPring8. A monochromatic x-ray beam of 0.7009 \AA , collimated to $50 \mu\text{m}$ was utilized. Diffraction data were recorded for 1 h at low pressures and for 2 h from 9 GPa onwards on an imaging plate kept at a distance of ~ 245 mm from the sample. Steel gaskets pre-indented to a thickness of $\sim 60 \mu\text{m}$ with a hole of diameter $\sim 100 \mu\text{m}$ were used in a Mao-Bell [18] kind of diamond anvil cell. A coarsely powdered α - AlPO_4 sample, a tiny ruby chip and 4:1 methanol–ethanol mixture were loaded in the gasket hole. The material was deliberately not finely powdered. This was to avoid any accidental amorphization due to grinding seen in other materials [1] and also to observe unambiguous signatures of a complete amorphization of berlinite, as the grainy diffraction lines would then evolve to smooth and broad features in the diffraction pattern. Two experiments were done, one to a maximum pressure of 30 GPa and the other one to 40 GPa. Pressure was monitored using ruby R lines. Observed variation in R_1 – R_2 splitting [19] and the broadening of R lines indicated the presence of non-hydrostatic stresses beyond 20 GPa in the first experiment while in the second experiment pressure was seen to be almost quasi-hydrostatic up to ~ 40 GPa.

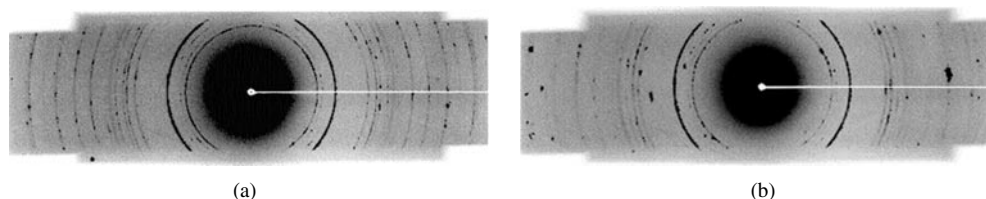


Figure 1. Imaging plate records of the diffraction pattern of α -AlPO₄ at 2 and 13 GPa.

Two dimensional IP records were transformed to one dimensional diffraction patterns by radial integration of the diffraction lines.

3. Results and discussion

Imaging plate records show that granular diffraction lines persist up to the highest pressures in both the experiments. Two diffraction patterns, at 2 and 13 GPa, are shown in figure 1. Figure 2 shows some of the one dimensional diffraction profiles obtained at various pressures. It is seen that sharp Bragg diffraction peaks exist even at 25 GPa. The persistence of diffraction peaks up to the highest pressures (40 GPa) is contrary to earlier experimental results that the sharp Bragg diffraction peaks are lost at \sim 12–18 GPa, which was taken as the evidence for the transformation to the amorphous phase. At \sim 13 GPa, in both the experiments, new diffraction lines emerged in addition to those of the α -phase. This result implies the existence of a phase transformation to another crystalline phase between 11 and 13 GPa. In figure 2, these new lines are marked with arrows at 15 and 25 GPa. On release of pressure in each run, all the new diffraction lines disappeared and the diffraction pattern of only the α -phase remained.

Due to very strong texture effects in the present x-ray diffraction data (as evidenced by the granular diffraction patterns), we could not employ the Rietveld method for determining the crystallographic parameters. Therefore, we have used profile fitting to evaluate the cell parameters only. Unit cell lengths of α -AlPO₄ as a function of pressure are shown in figure 3 along with those from MD simulations [16, 20]. These display a smooth and monotonic behaviour. Quantitatively, these agree well with our recent MD results (a_α within 5% and c_α within 2.5%). Qualitatively, beyond \sim 10 GPa, theoretical values of a_α show a deviation away from the experimental results. In figure 4 we compare the observed variation in $(c/a)_\alpha$ with that from an earlier x-ray diffraction study [21] and also from MD simulations [16]. Up to \sim 9 GPa, where the earlier experimental data are available, these agree very well. Again the absolute values of observed and our MD calculated c/a ratio of the berlinite phase compare favourably (within 2%) up to 30 GPa. However, unlike MD predictions, the experimental results do not show a plateau of c/a beyond \sim 12 GPa. We shall discuss below more about this disagreement with MD results.

We found that the additional diffraction lines can be indexed on a structure of CrVO₄ type in the $Cmcm$ space group. However, as in many high pressure x-ray diffraction studies, the uniqueness of structure is hard to establish due to paucity of data. In particular, in this case, a lower symmetry structure cannot be ruled out due to the small number of diffraction lines (seven) available for the high pressure phase. However, since this structure has been earlier found at high pressures in isostructural compounds like GaPO₄ [22] and FePO₄ [23] it is more likely that the new structure belongs to the $Cmcm$ space group. In this structure Al atoms have octahedral coordination with oxygen atoms while P continues to be tetrahedrally bonded to oxygens. Thus the proposed $Cmcm$ phase is consistent with the general result that at high

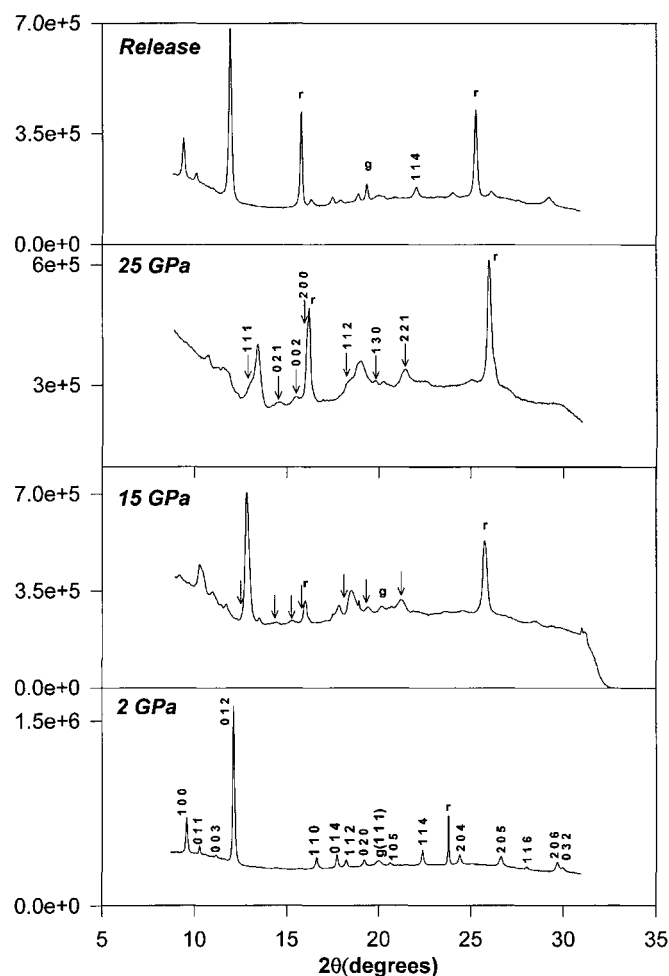


Figure 2. One dimensional diffraction profiles of AlPO_4 at various pressures. Arrows at 15 and 25 GPa indicate the new diffraction peaks. At 25 GPa, given hkl indices refer to the unit cell of CrVO_4 type structure in the $Cmcm$ space group. The gasket and the ruby diffraction lines are marked as g and r respectively.

pressures the structures evolve to the one having higher cation–anion coordination. It is also interesting to note that the Raman lines observed by Gillet *et al* [13] at $P > 14$ GPa are very similar to that of CuCrO_4 which exists in the $Cmcm$ phase at ambient conditions [24]. Table 1 summarizes the observed and calculated d_{hkl} values for both α as well as the new phase indexed to the CrVO_4 structure at 15 GPa. Figure 5 shows the variations of a , b and c as deduced from the profile fitting of the experimental data with respect to CrVO_4 structure. It may also be noted that the observed $a:b:c$ ratios are 0.716:1:0.732 and these compare very well with the experimental data for other compounds of CrVO_4 structure type [25]. Pressure–volume data for the α -phase are displayed in figure 6 along with corresponding MD results [16, 26]. The volume reduction at the first order phase transformation at ~ 13 GPa for AlPO_4 is found to be $\sim 27.3\%$. It may be compared with the value of $\sim 21\%$ for FePO_4 [23]. P – V data of the α -phase were fitted to the Birch–Murnaghan equation [27], *viz.*,

$$P = (3/2)K[(V_0/V)^{7/3} - (V_0/V)^{5/3}]\{1 - (3/4)(4 - K')[V_0/V]^{2/3} - 1\}. \quad (1)$$

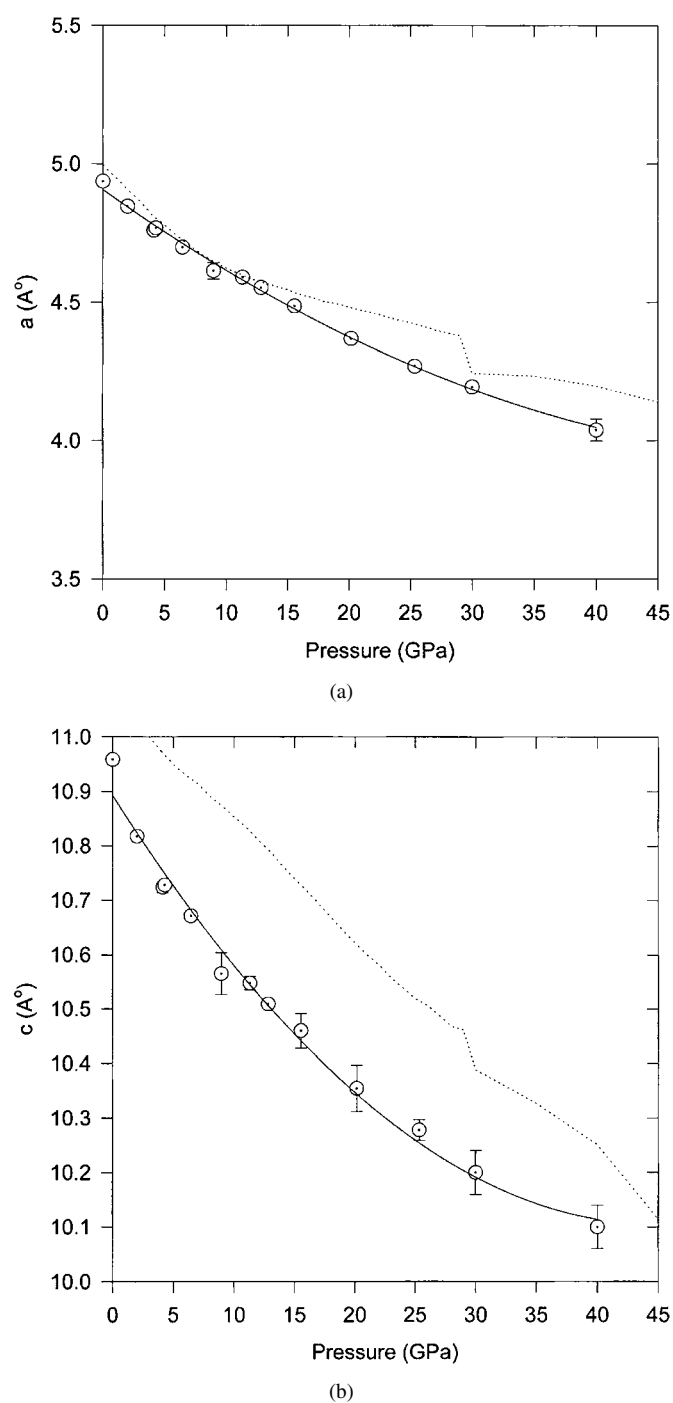


Figure 3. Variation of unit cell parameters (a) a_α and (b) c_α of α -AlPO₄ with pressure. Dotted lines represent the results of recent MD calculations [16].

Fitting the full P - V data gives $K = 34$ GPa ($K' = 4$). However, restricting the fitted data to less than 10 GPa (before the solidification of the methanol-ethanol mixture) we obtain

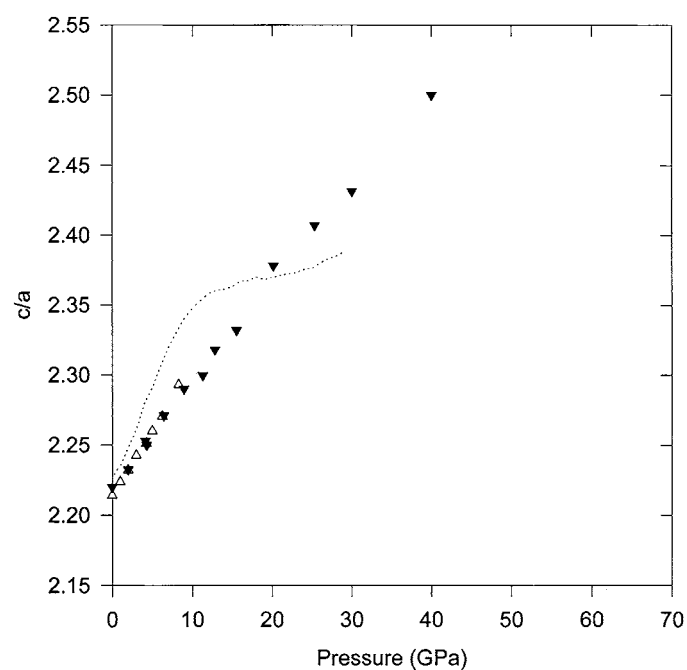


Figure 4. c/a of α -AlPO₄ at high pressures. Open triangles refer to the earlier experimental data [21] while the dotted line represents the results of MD calculation [16].

Table 1. Observed and calculated d_{hkl} spacings for the α -phase and the high pressure $Cmcm$ phase at 15 GPa. The cell parameters for the alpha phase are $a = 4.486(9)$ Å and $c = 10.46(3)$ Å and for the $Cmcm$ phase are $a = 5.06(4)$ Å, $b = 6.77(6)$ Å and $c = 5.19(4)$ Å.

d_{hkl} observed	d_{hkl} calculated			
	α phase		$Cmcm$ phase	
	hkl	d_{hkl}	hkl	d_{hkl}
3.90	1 0 0	3.88		
3.66	1 0 1	3.64		
3.17			1 1 1	3.19
3.12	0 1 2	3.11		
2.80 ^a			0 2 1	2.84
2.62 ^a			0 0 2	2.59
2.52			2 0 0	2.52
2.24	1 1 0	2.24		
2.17			1 1 2	2.18
2.17	0 1 4	2.16		
2.07			1 3 0	2.06
2.06	1 1 2	2.06		
1.94	0 2 0	1.94		
1.90			2 2 1	1.89

^a Weak broad lines.

$K = 37.88$ GPa ($K' = 4$). These values agree quite well with both MD [16] (34.7 GPa) and earlier low pressure experimental data [21] (36 GPa). In contrast, the $Cmcm$ phase was found

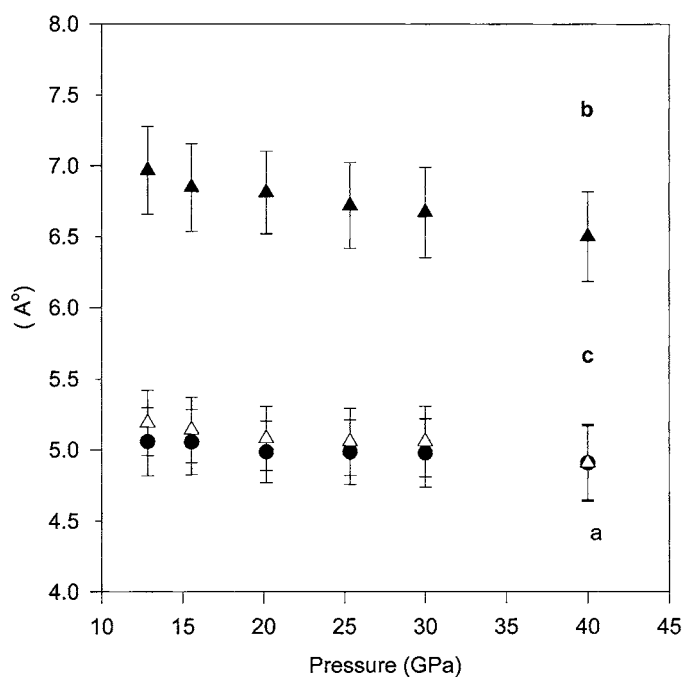


Figure 5. Variation of a , b and c of the $Cmcm$ phase with pressure. The error bars represent the standard deviations from profile fitting.

to be far less compressible with $K = 127$ GPa ($K' = 4.0$). This is expected as an increase in the coordination of a structural unit in this type of compound results in lower compressibility. In GaPO_4 [22, 28] and FePO_4 [23] the K values before and after the transformation are 39.9, 308 and 24, 96 GPa respectively. For subsequent discussion in this section, it may be noted that in figure 6 MD results are shifted away from our experimental data.

From the diffraction patterns beyond 13 GPa, we noted another feature that the diffracted intensities of Bragg peaks of the α -phase reduce gradually, while the intensities of the new peaks grow only marginally. This indicates that though the new phase is crystalline, it may be poorly crystallized [29]. Raman scattering results of Gillet *et al* [13] also lend support to this point of view. The intensities of the new modes are an order of magnitude smaller than those of the α -phase. The existence of poor crystallinity of the new phase also explains why the earlier x-ray diffraction studies done with the laboratory x-ray sources [2, 3] were not able to discover this crystalline–crystalline phase transformation. Instead these studies with low signal to noise ratios had shown a disappearance of the diffraction lines of the α -phase, which was interpreted in terms of pressure induced amorphization. As pointed out above, an $\alpha \rightarrow Cmcm$ phase transformation has also been observed [22, 23] in isostructural materials such as α - GaPO_4 and α - FePO_4 . In particular, Badro *et al* [22] found that in α - GaPO_4 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 [22]. This heating reduced the magnitude of the background hump, which in many cases has been taken to be a signature of the existence of an amorphous phase [23]. This suggests that in many compounds where co-existence of amorphous and crystalline (parent as well as daughter [23]) phases has been proposed (sometimes against the spirit of Gibb's phase rule [30]), the truth may be the poorly crystallized high pressure phase. Thus *in situ* laser heating of the sample may clarify the

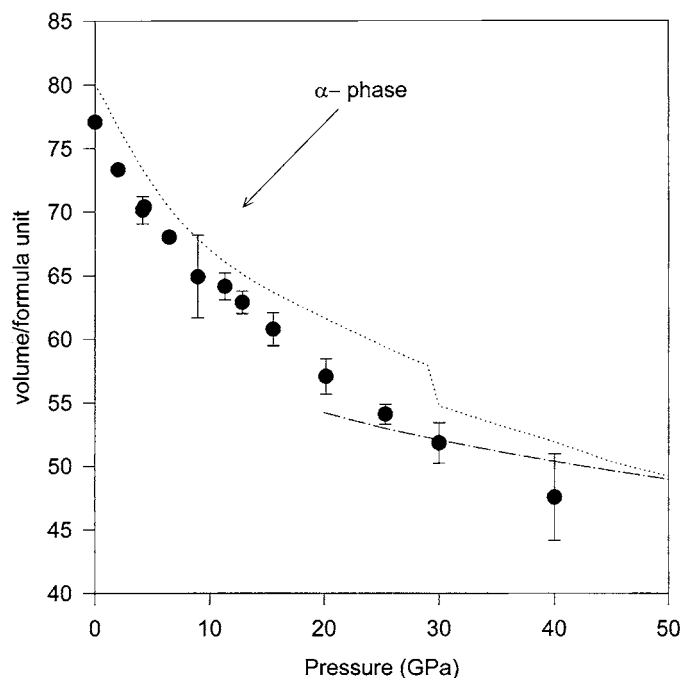


Figure 6. P - V behaviour of AlPO_4 in the α phase. The dotted line represents the computed P - V behaviour of the berlinite phase through MD calculations. The dot-dash line represents corresponding MD results for the $Cmcm$ phase.

physical reality. This would also establish the degree of reversibility of the high pressure phase to the initial α -phase. On decompression, the re-emergence of all the diffraction peaks of the α -phase implies that the poor crystallinity of the high pressure phase does not suppress the reversibility. The fact that the new high pressure phase is poorly crystallized suggests the existence of substantial kinetic hindrance to this transformation. Similar results have earlier been observed in quartz, where it was shown that at high pressures, stishovite poorly crystallizes [31]. We also note here that $\alpha \rightarrow Cmcm$ transformation is reversible in GaPO_4 [22] while in FePO_4 this change is irreversible [23, 32].

It has also been pointed out above that the MD results deviate from the experimental data around 10–12 GPa. In this context we note that the MD computations show that around this pressure the oxygen sublattice is disordered. So the comparison with α -phase ceases beyond this pressure. The fact that experimentally we observe a transformation to a crystalline phase at ~ 13 GPa clearly shows the inadequacies of the pair potentials used. The disordering of oxygen sublattice does indicate some kind of instability of the parent phase, but the present pair potentials are unable to stabilize the $Cmcm$ phase. This is clearly visible in figure 6. Here we see that even up to ~ 12 GPa, MD calculations show the α -phase to be less dense than the experimental results and beyond 10–12 GPa, MD results show less compressibility of the partially disordered phase. Comparison is more dramatic if the new phase is presumed to be the $Cmcm$ phase. Here the volume per formula unit is about 25% higher for the MD results than the experimental values. This huge discrepancy implies that the stabilization energy of the $Cmcm$ phase with respect to the α -phase, as given by the pair potentials of van Beest *et al* [17], may be far smaller than the real value. This may also explain the inability of $\alpha \rightarrow Cmcm$ phase transformation to occur in MD simulations.

4. Conclusion

Based on the results presented above, the following conclusions may now be drawn. Firstly, the present experimental investigation suggests that the so-called memory glass effect is a case of mislabelling. Instead the earlier experimental results on the berlinite AlPO₄ should be re-interpreted as due to the reversibility of the crystalline–crystalline phase transformation. Our results showing a crystalline phase beyond 13 GPa should also resolve the difficulty with the Brillouin scattering results [5], viz., the elastic anisotropy of the high pressure phase. It is interesting to point out here that a similar Brillouin scattering observation in quartz was later reconciled in terms of a crystalline–crystalline transformation preceding amorphization [33–35]. In addition, though the total energy calculations had supported the stability of the *Cmcm* phase at high pressures, this phase has not been reached in any classical MD calculations so far [16]. This and other disagreements between our experimental results and MD computations indicate the inadequacies of presently used pair potentials for these MD and other computations. For more accurate theoretical results, first principles calculations are necessary.

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References

- [1] Sharma Surinder M and Sikka S K 1996 *Prog. Mater. Sci.* **40** 1
- [2] Kruger M B and Jeanloz R 1990 *Science* **249** 647
- [3] Sankaran H, Sharma Surinder M, Sikka S K and Chidambaram R, Pramana 1990 *J. Phys.* **35** 177
- [4] Jayaraman A, Wood D L and Maines R G 1987 *Phys. Rev. B* **35** 8316
- [5] Polian A, Grimsditch M and Philippot E 1993 *Phys. Rev. Lett.* **71** 3143
- [6] Cordier P, Doukhan J C and Peyronneau J 1993 *Phys. Chem. Miner.* **20** 176
- [7] Cordier P, Gratz A J, Doukhan J C and Nellis W J 1994 *Phys. Chem. Miner.* **21** 133
- [8] Keskar N R, Chelikowsky J R and Wentzcovitch R M 1994 *Phys. Rev. B* **50** 9072
- [9] Watson G W and Parker S C 1995 *Phys. Rev. B* **52** 13 306
- [10] Chaplot S L and Sikka S K 1993 *Phys. Rev. B* **47** 5710
- [11] Vessal B 1991 *Trans. Am. Cryst. Assoc.* **27** 37
- [12] Tse J S and Klug D D 1992 *Science* **255** 1559
- [13] Gillet P, Badro J, Varrel B and McMillan P F 1995 *Phys. Rev. B* **51** 11 262
- [14] Kruger M B and Meade C 1995 *Bull. Am. Phys. Soc.* **40** 667
- [15] Sun T, Herbst C, King H E Jr and Kruger M B 1995 *Bull. Am. Phys. Soc.* **40** 668
- [16] Nandini Garg and Sharma Surinder M 2000 *J. Phys.: Condens. Matter* **11** 375
- [17] van Beest B W H, Kramer G J and van Santen R A 1990 *Phys. Rev. Lett.* **64** 1955
- [18] Vijaykumar V and Meenakshi S *BARC Report*
- [19] Sharma Surinder M and Gupta Y M 1991 *Phys. Rev. B* **43** 879
- [20] Even beyond 15 GPa, the computed diffraction pattern from the averaged atomic coordinates of the MD simulations is completely identified as that of the α -phase. The disorder in the oxygen sublattice reduces only the diffracted intensities, without bringing about any other qualitative change in the diffraction pattern. Therefore, in figures 3 and 4 we continue to refer the MD simulated lattice constants as those of the α -phase.
- [21] Sowa H, Macavej J and Schulz H 1990 *Z. Kristallogr.* **192** 119
- [22] Badro J, Itie J P and Polian A 1998 *Eur. Phys. J. B* **1** 265. It should be noted here that in this paper several *hkl* indices mentioned in table 1 violate the conditions of missing reflections of the space group *Cmcm*. Therefore the inferred *P–V* behaviour of α -GaPO₄ and hence the value of the bulk modulus is likely to be incorrect.
- [23] Pasternak M P, Kh Rozenberg G, Milher E, Amanowicz M, Zhou T, Schwarz V, Syassen K, Taylor R D and Hanfland M 1997 *Phys. Rev. Lett.* **79** 4409

- [24] Baran E J 1994 *Spectrochim. Acta A* **50** 2385
- [25] Sharma Surinder M and Sikka S K 1995 *Phys. Rev. Lett.* **74** 3301
- [26] In MD calculations of [16] α to *Cmcm* phase transformation is kinetically hindered. So the results plotted for the *Cmcm* phase in figure 6 were obtained by a sudden compression of the initial *Cmcm* phase to beyond 20 GPa. This sudden loading completely arrests the decay of this phase.
- [27] Birch F 1978 *J. Geophys. Res.* **83** 1257
- [28] Sowa H 1994 *Z. Kristallogr.* **209** 954
- [29] By a poorly crystallized phase we mean that the particle size of the new phase may be very small. Also due to the heterogeneous nature of growth of the new phase there may be differing amounts of local strains.
- [30] Landau L D and Lifshitz E M 1958 *Statistical Physics* (Oxford: Pergamon)
- [31] Tsuchida Y and Yagi T 1990 *Nature* **347** 267
- [32] Chitra Murali, Sharma Surinder M, Kulshreshtha S K and Sikka S K 1997 *Pramana J. Phys.* **49** 285
- [33] Kingma K J, Hemley R J, Mao H K and Veblen D R 1993 *Phys. Rev. Lett.* **70** 3927
- [34] McNeil L E and Grimsditch M 1994 *Phys. Rev. Lett.* **72** 1301
- [35] Kingma K J, Hemley R J, Mao H K and Veblen D R 1994 *Phys. Rev. Lett.* **72** 1302