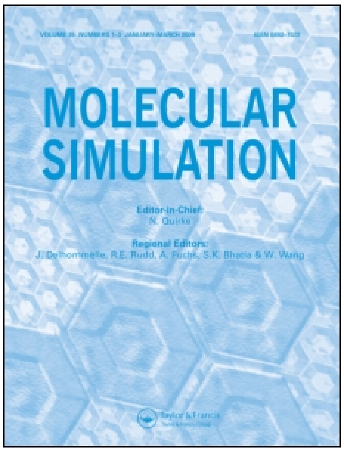

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Molecular Dynamics Simulation of Structural Phase Transition of $AlPO_4$ Induced by Pressure

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MOLECULAR DYNAMICS SIMULATION OF STRUCTURAL PHASE TRANSITION OF AlPO$_4$ INDUCED BY PRESSURE

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The mechanism of pressure-induced phase transition of AlPO$_4$ has been investigated by means of a molecular dynamics method of constant temperature and pressure. A new crystalline phase with space group C2, which has not yet been experimentally found, appears by an instantaneous compression of 60, 70 and 80 GPa at 300 K. At high temperature (2500 K) and pressure (58 GPa), another new phase of AlPo$_4$ (γ-phase), which is composed of PO$_6$ and AlO$_6$ octahedra, has been observed.

KEY WORDS: Molecular dynamics method, aluminophosphate, high pressure, structural phase transition, pressure-induced amorphization.

1 INTRODUCTION

A pressure-induced transition from crystalline to amorphous phase has been observed in several solids. For example, H$_2$O ice I$_h$ below 80 K, and CaAl$_2$Si$_2$O$_8$ anorthite and Fe$_2$SiO$_4$ fayalite at 300 K amorphize at pressures ranging from 5 to 40 GPa and remain in the glassy state like SiO$_2$ even after release of pressure [1]. In contrast, crystalline SnI$_4$, LiKSO$_4$, Ca(OH)$_2$ and AlPO$_4$ all amorphize upon compression above 10 to 15 GPa at 300 K [2]. These materials transform back from the glassy to the stable crystalline state upon decompression to zero pressure.

Kruger and Jeanloz [3] reported that α-berlinite(AlPO$_4$) exhibits a structural memory effect through the compression process of a single crystal. When the pressure is increased above 15 ± 3 GPa, the powder x-ray diffraction pattern of the sample vanishes. Furthermore, although no diffraction pattern is observed to 40 GPa, the x-ray pattern of berlinite reappears upon decompression to below 5 GPa. Similarly, as pressure is increased above 15 ± 3 GPa, the infrared absorption spectra of AlPO$_4$ change in a manner typical of crystals being converted to glass. Specifically, the 1025 cm^{-1} band attributed to antisymmetric tetrahedral P—O vibration broadens significantly, and analogous Al—O vibration at 780 cm^{-1} vanishes altogether. As with the x-ray diffraction pattern, the crystal-like infrared pattern of AlPO$_4$, reappears upon decompression to below $5 \sim 7$ GPa. On the base of these

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experimental results, they conclude that the pressure-induced amorphization is reversible with a hysteresis of about 10 GPa.

The pressure-induced amorphization of $AlPO_4$ has previously studied by molecular dynamics method by Tse and Klug [4], and Chaplot and Sikka [5]. Tse and Klug have concluded that the difference in the structural memory behavior between $AlPO_4$ and α-quartz, for which the pressure-induced amorphized phase is reversible, can be attributed to the presence of the PO_4 units, which remains essentially four-coordinated even when severely distorted. Chaplot and Sikka have obtained the conclusion that crystalline-to-crystalline transition upto 2000 K and up to 35 GPa was not observed. Experimentally, no high-pressure crystalline phase of $AlPO_4$ is known yet. However, it is known that other similar phosphates such as $InPO_4$ and $TlPO_4$ crystallize in the space group Cmcm in which the cations In and Tl have sixfolded coordination.

The main aim of the present work is to investigate a high-pressure crystalline phase of $AlPO_4$ over a wider range of pressure (from 0.1 MPa to 80 GPa) and temperature (from 300 K to 2500 K) by means of molecular dynamics method.

2 SIMULATION METHOD

The isothermal-isobaric molecular dynamics method proposed by Nose [6], and Parrinello and Rahman [7] was employed. The Hamiltonian of virtual system is expressed by

$$H = \sum_{i=1}^{N} \frac{\pi_i^t G^{-1} \pi_i}{2m_i f^2} + \Phi(r_1, r_2, \ldots. N) + \frac{Tr(\Pi^t \Pi)}{2Wf^2} + P_{ex}\Omega + \frac{1}{2} Tr(\Gamma G) + \frac{P_f^2}{2M} + gk_B T_{ex} \ln f \tag{1}$$

where π_i is the conjugate momentum of coordinate S_i; G is the metric tensor: $h^t h$; h is the molecular dynamics cell size matrix; Π is the conjugate momentum of h; W is a virtual mass for volume motion; P_{ex} is the externally set pressure; Ω is a volume of molecular dynamics cell; Γ is the symmetric tensor related to the stress tensor; P_f is the conjugate momentum of f, M is a parameter with dimension of energy•(time)^2 and behaves a mass for the motion of f; f is a scale variable between real system and virtual system; g is a number of freedom given by $3N + 9$; N is a number of atoms included in molecular dynamics cell, T_{ex} is the externally set temperature. The original equation is modified in that in the third term of the right-hand side the factor $1/f^2$ is multiplied. The equations of motion for the NTP ensemble are derived as follows:

$$m_i \frac{d^2 s_i}{dt^2} = \sum_{i=1}^{N} \chi_{ij} s_{ij} - m_i(\dot{f}/f + G^{-1}\dot{G})\dot{s}_i \tag{2}$$

$$W \frac{d^2 h}{dt^2} = \Omega(\Lambda - P_{ex}) h^{t-1} - h\Gamma - W\dot{f}\dot{h}/f \tag{3}$$

$$M \frac{d^2 f}{dt^2} = \left[\sum_{i=1}^{N} m_i (h\dot{s}_i)^t (h\dot{s}_i) + WTr(\dot{h}^t \dot{h}) - gk_B T_{ex} \right] f + M \left(\frac{\dot{f}}{f} \right)^2 \tag{4}$$

where $\chi_{ij} = -(1/r_{ij})(d\phi_{ij}/dr_{ij})$; ϕ_{ij} is a pair potential function; Λ is a virial. Equation (2) is the equation of motion of coordinate s_i of atom i; Equation (3) is the equation of motion of cell size matrix h; Equation (4) is the equation of motion of scale variable of time f.

The following three simulations using the isothermal-isobaric molecular dynamics method as a function of pressure and temperature have been carried.

Case 1: At 300 K, the pressure is increased from 0.1 MPa to 80 GPa with a rate of 0.2 GPa/ps, and decreased from 80 GPa to 0.1 MPa with the same rate.
Case 2: At 300 K, the pressure is increased instantaneously from 0.1 MPa to 60 GPa, 70 GPa, and 80 GPa.
Case 3: At 2500 K, the pressure is increased from 40 GPa to 80 GPa with a rate of 0.267 GPa/ps.

Available interatomic potential proposed by Kramer *et al.* [8] based on a combination of ab intio calculations using 6–31G ** basis set and empirical data have been used:

$$\Phi = \begin{cases} \sum\sum_{i<j} \left[\dfrac{z_i z_j}{r_{ij}} + A_{ij}\exp(-b_{ij}) - \dfrac{C_{ij}}{r_{ij}^6} \right] & \text{for T—O, O—O (T = P, Al)} \\ \sum\sum_{i<j} \dfrac{z_i z_j}{r_{ij}} & \text{for T—T (T = P, Al)} \end{cases} \tag{5}$$

The value of charge z_i of Aluminum, Phosphorus, and Oxygen ions and other potential parameters (A_{ij}, B_{ij}, and C_{ij}) are given in Table 1.

Gear's algorithm was used for the numerical integration. Time step size was 1.0 fs. The molecular dynamics cell was composed of 4 × 4 × 2 unit cells. The atomic structure obtained by x-ray diffraction [9] was used for initial configuration.

3 RESULTS AND DISCUSSION

3.1 *Case-1*

The time evaluation of volume, pressure, temperature, molecular dynamics cell-length and angles in the case of Case-1 is shown in Figure 1. As pressure is increased above 30 GPa, the structural phase transition from α to β-phase is observed. No further structural phase transition is observed up to the highest pressure of this simulation (80GPa). Structural phase transition from amorphous β-phase to α-phase occurs upon decompression to below 20 GPa, and the α-phase reappears. The reversibility of the amorphous transformation is in agreement with experimental result, although, the transition pressure is 10 GPa higher in molecular dynamics simulation than in experiment. The calculated lattice constant and the c/2a as a function of pressure are in good agreement with the experimental results [9] as shown in the Table 2.

The atomic structure perpendicular to the c-axis of the β-phase at 80 GPa and 300 K are shown in Figure 2. The atomic configurations perpendicular to the c-axis is amorphous.

Table 1 Potential parameters of $AlPO_4$[5].

	A_{ij}[eV]	b_{ij}[$Å^{-1}$]	c_{ij}[$eVÅ^6$]	*charge Z*
O—O	1388.7730	2.76000	175.0000	$Z_o = -1.2$
Al—O	16008.5345	4.79667	130.5659	$Z_{Al} = 1.4$
P—O	9034.2080	5.19098	19.8793	$Z_P = 3.4$

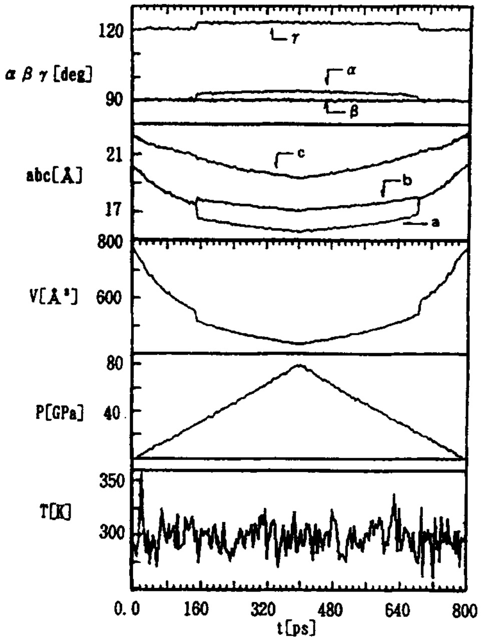

Figure 1 Time evaluation of angle ($\alpha\beta\gamma$) and box length(abc) of molecular dynamics cell, temperature (a), pressure (P), and volume (V) for the Case-1 simulation.

To clarify the structure of the β-phase perpendicular to the a-axis, the atomic structures of P—O network and Al—O network respectively are shown in Figure 3. Aluminum atoms acquire a sixfold coordination (partly a fourfold coordination), while PO_4 tetrahedra remain essentially intact. A typical stereoscopic view of PO_4(tetrahedron)-PO_4 connection and AlO_6(octahedron)-AlO_6 connection are shown in Figure 4. The recovery of the pressure-induced amorphized phase is caused by presence of the PO_4 tetrahedron unit which remains up to 80 GPa.

3.2 *Case-2*

The pressure is increased instantaneously from 0.1 MPa to 60 GPa, 70 GPa, and 80 GPa at 300 K, where a crystalline-to-crystalline phase transition is observed. Figure 5 gives the atomic structure after the transition. This crystalline has space group C2. The phase transition from α-$AlPO_4$ to C2-$AlPO_4$, which is not achieved

Table 2 Structural parameters of the new polymorphs of AlPO$_4$ obtained here. Comparison is also made with an experiment data [9] for α-phase. N$_c$ is the coordination number of cations (Al and P).

	α-phase (*at 300* K, *0.1* Mpa)		*α-phase* (*at 300* K, *15* GPa)		*β-phase* (*at 300* K, *30* GPa)	*γ-phase* (*at 2500* K, *80* Gpa)	*C2-phase* (*at 300* K, *80* Gpa)
	This work	*Exp.*	*This work*	*Exp.*	*This work*	*This work*	*This work*
a[Å]	5.05	4.93	4.64	4.49	4.18	4.09	4.41
b[Å]	5.05	4.93	4.64	4.49	4.47	3.91	4.41
c[Å]	11.2	10.9	10.9	10.5	10.4	9.78	10.74
c/2a	1.10	1.11	1.17	1.17	1.25	1.20	1.21
α[deg.]	90.0	90.0	90.0	90.0	86.0	81.0	71.0
β[deg.]	90.0	90.0	90.0	90.0	90.0	90.0	110.0
γ[deg.]	120.0	120.0	120.0	120.0	123.0	122.0	137.0
V[cm^3/mol]	49.2		39.1		33.28	26.1	26.89
N_c(Al)	4		4		5.5	6	6
N_c(P)	4		4		4	6	6

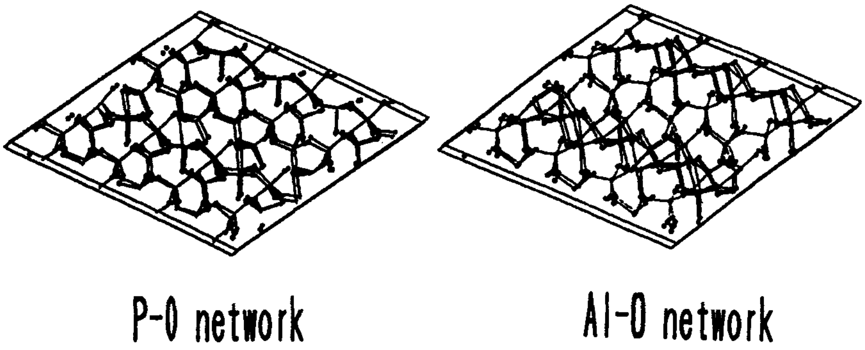

Figure 2 The atomic structure of the β-phase at 80 GPa and 300 K. The view is along $AlPO_4$ c-axis. The left-hand picture and the right-hand one indicate the P — O network and Al — O network, respectively.

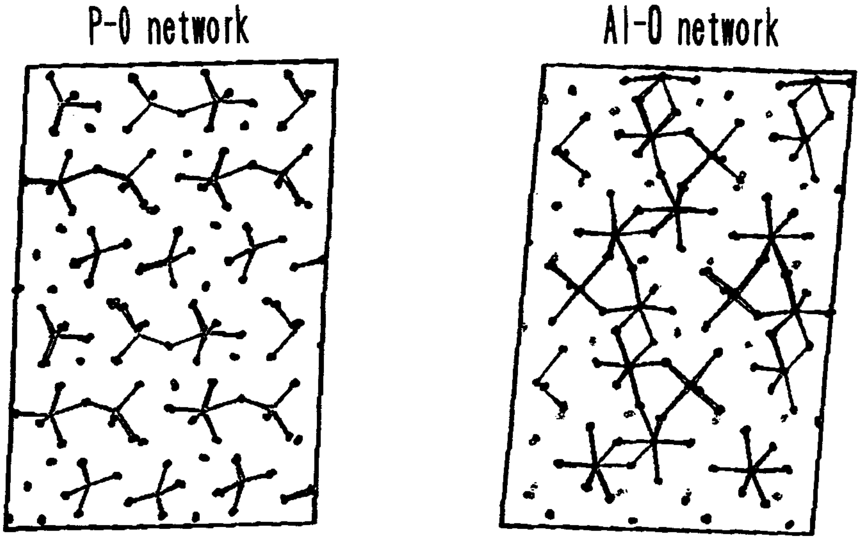

Figure 3 The atomic structure of the β-phase at 80 GPa and 300 K. The view is along $AlPo_4$ a-axis. The left-hand picture and the right-hand one indicate the P — O network, respectively.

kinetically at room temperature, occurs presumably because of instantaneous high temperature state generated by the instantaneous compression. Experimentally, C2-crystalline phase of $AlPO_4$ is unknown yet. For comparison, for SiO_2 C2-structure was observed at 50 GPa using molecular dynamics simulation by Tuneyuki *et al.* [10].

3.3 Case-3

The time evaluation of volume, pressure, temperature, molecular dynamics cell-length and angle in the case of Case-3 is shown in Figure 6. As pressure is increased

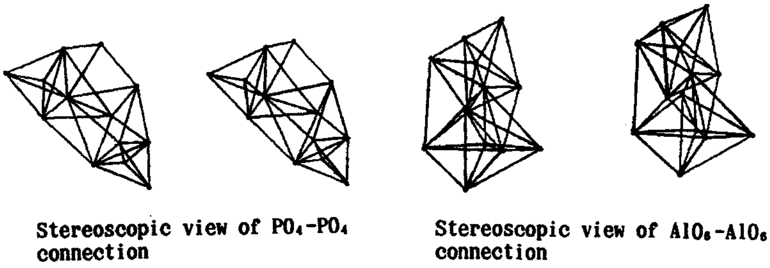

Figure 4 The stereoscopic view of unit structures in the β-phase at 80 GPa and 300 K. The left-hand picture and the right-hand one indicate the PO$_4$-PO$_4$ connection and AlO$_6$-AlO$_6$ connection, respectively.

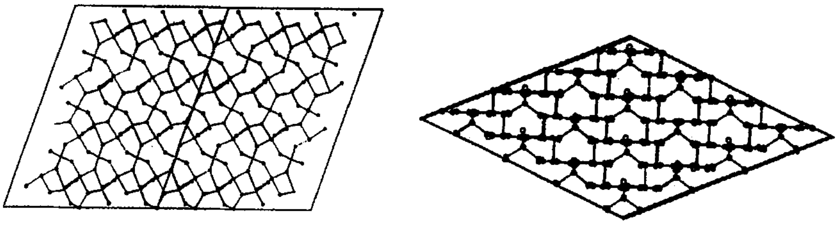

Figure 5 The atomic structure of C2-phase obtained by molecular dynamics simulation of instantaneous compression at 80 GPa and 300 K. The left-hand picture and the right-hand one indicate the view along c-axis and the view along [110] direction, respectively.

above 30 GPa, a structural phase transition from α to β-phase is observed like in Case-1. No structural phase transition is observed upto 58 GPa and 2500 K. A structural phase transition from the amorphous β to a new amorphous γ-phase occures at 58 GPa and 2500 K. The γ-phase remains upto 80 GPa.

The atomic structure perpendicular to the c-axis of γ-phase at 80 GPa and 2500 K is shown in Figure 7. Atomic configurations of the P—O and Al—O networks perpendicular to the c-axis are disordered like in the β-phase. To clarify the structure of the γ-phase perpendicular to the a-axis, the atomic structure of P—O network and Al—O network is shown in Figure 8. Both Al and P atoms have a sixfold coordination. A typical stereoscopic view of PO$_6$(octahedron)-PO$_6$ connection is shown in Figure 9. The PO$_6$ octahedron structure, which can not be attained kinetically up to 80 GPa at 300K, are formed by high temperature of 2500 K.

3.4 Radial Distribution Function

The radial distribution functions of α and C2-phase are shown in Figure 10. The first peaks of the P—O, Al—O, O—O pairs do not appreciably change with pressure. On the other hand, the first peaks of the Al—Al, P—P, Al—P pairs show large change between α and C2-phase. This decrease is caused by the change of Al coordination from tetrahedral to octahedral.

In Figure 11, the radial distribution functions of the β and γ-phase are shown. The first peak of P—O, Al—O, O—O pair shows small change ($-2.8 \sim 4.0\%$)

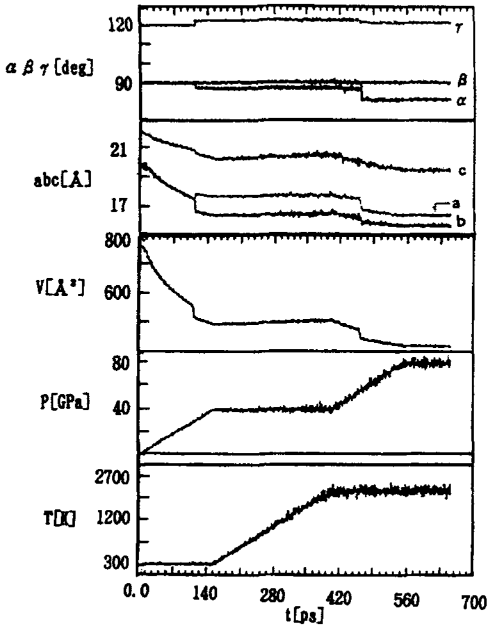

Figure 6 Time evaluation of angle $(\alpha\beta\gamma)$ and box length(abc) of molecular dynamics cell, temperature (T), pressure (P), and volume (V) for the Case-3 simulation.

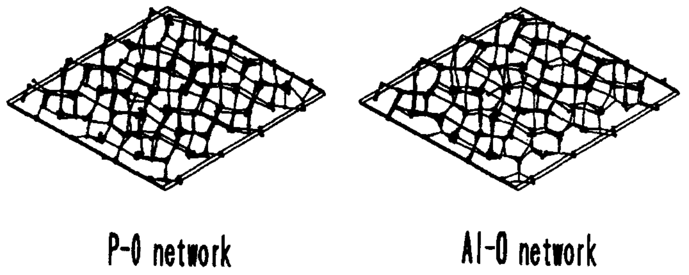

Figure 7 The atomic structure of the γ-phase at 80 GPa and 2500 K. The view is along $AlPO_4$ c-axis. The left-hand picture and the right-hand one indicate the P—O network and Al—O network, respectively.

between the β and γ-phase, while the first peak of P—P pair shows large change (−26.8%). This reduction is caused by the change of P coordination from tetrahedral to octahedral.

The nearest-neighbor distance of each ionpair are listed in Table 3. The calculated nearest-neighbor distances of α-$AlPo_4$ are in good agreement with the experimental data [9]. The P—O, Al—O, O—O distances do not change (1.3 ~ 2.9%) from phase to phase, whereas the Al—Al, P—P, Al—P distances largely decrease

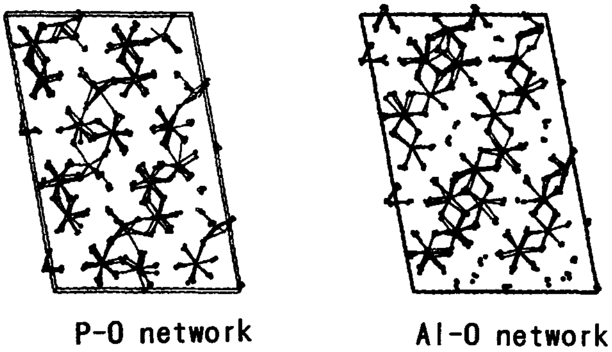

Figure 8 The atomic structure of the γ-phase at 80 GPa and 2500 K. The view is along AlPO$_4$ a axis. The left-hand picture and the right-hand one indicate the P—O network and Al—O network, respectively.

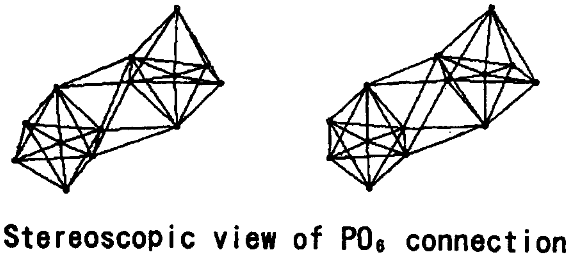

Figure 9 The stereoscopic view of PO$_6$-PO$_6$ connection in the γ-phase of AlPO$_4$ at 80 GPa and 2500 K.

(28 ~ 30%). The decrease in the nearest-neighbor distance is caused by the change of Al and P coordination from tetrahedral to octahedral.

3.5 Phase Diagram

The calculated phase diagram is shown in Figure 12. During the compression process at 300 K, the α-phase is transformed into the amorphous β-phase at 30 GPa. No structural phase transition is observed up to 80 GPa. For the decompression process at 300 K, the amorphous β-phase reverts to the α-phase below 20 GPa and the α-phase reappears. The reversibility of the amorphous transformation is observed. However, the transition pressure is about 10 GPa larger than the experimental one.

For the instantaneous compression process at 300 K, the crystalline-to-crystalline phase transition is observed. The new crystalline has space group C2. For the

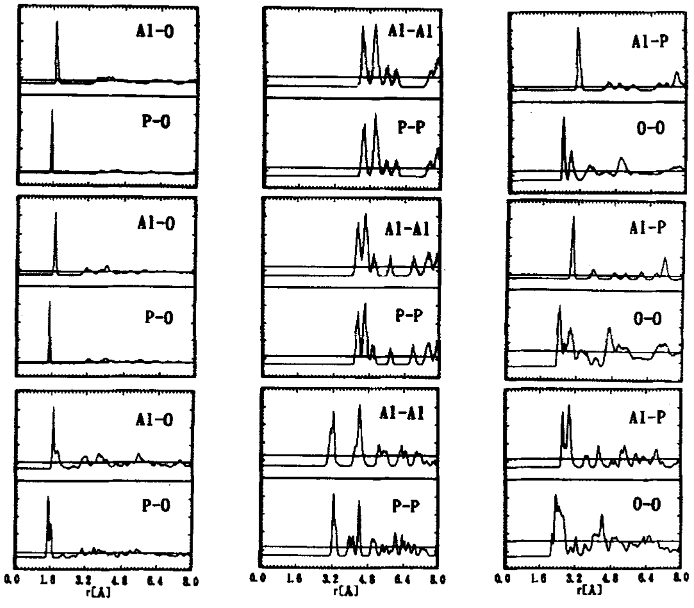

Figure 10 The radial distribution functions of the α (at 0.1 MPa and 300 K), α (at 15 GPa and 300 K) and C2-phases (at 80 GPa and 300 K). The top, middle, and bottom frames correspond to the α (at 0.1 MPa), α (at 15 GPa), and C2-phases, respectively.

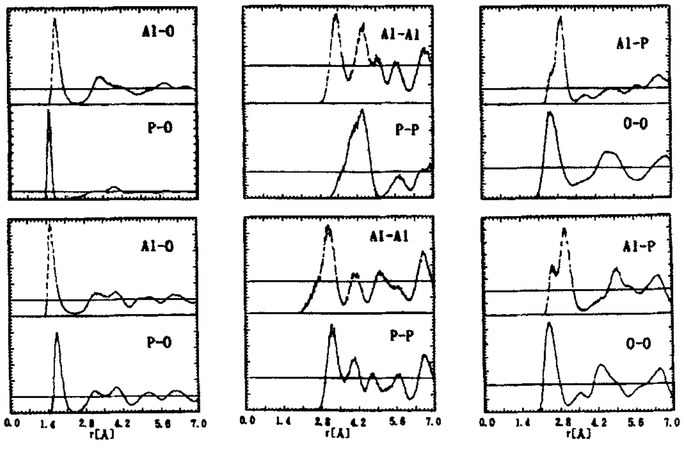

Figure 11 The radial distribution functions of the β (at 40 GPa and 1500 K), and γ-phase (at 80 GPa and 2500 K). The upper and lower frames correspond to the β and γ-phases, respectively.

compression process at 2500 K, the amorphous β-phase obtained at 30 GPa and 300 K is transformed into the new amorphous γ-phase at 58 GPa and 2500 K. The γ-phase remains up to 80 GPa.

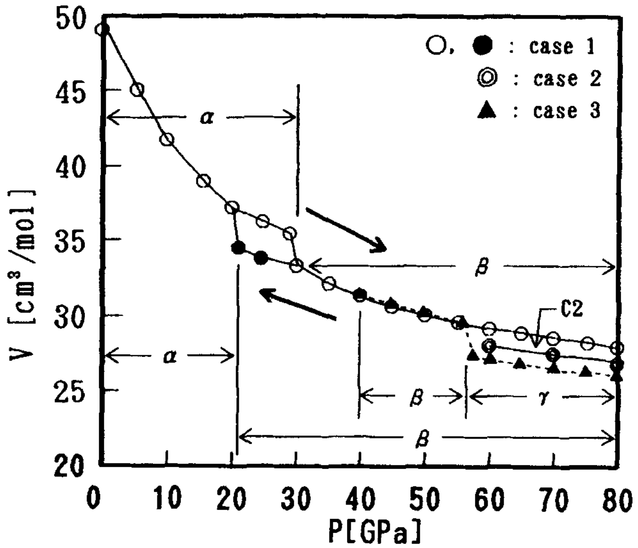

Figure 12 The phase diagram of AlPO$_4$ obtained by this work. A symbol ○ and ● indicate the compression and the decompression process of Case-1 simulation at 300 K, respectively. A symbol ◎ indicates the instantaneous compression process of Case-2 simulation at 300 K. A symbol ▲ indicates the compression process of Case-3 simulation at 2500 K.

Table 3 Frist peak distance [Å] of the radial distribution functions obtained by this work. Comparison is also made with an experiment data [9] given in parentheses.

	P—O	Al—O	O—O	Al—Al	P—P	Al—P
α(T = 300 K, P = 0.1 MPa)	1.50 (1.52)	1.73 (1.73)	2.44, 2.78 (2.48, 2.84)	4.46	4.43	3.12
α(T = 300 K, P = 15 GPa)	1.46	1.67	2.42, 2.89	4.21	4.25	2.94
β(T = 300 K, P = 40 GPa)	1.48	1.73	2.52	3.43	4.37	2.93
γ(T = 2500 K, P = 80 GPa)	1.52	1.78	2.42	3.10	3.20	2.56
C2(T = 300 K, P = 80 GPa)	1.48	1.68	2.30	3.21	3.23	2.60

4 CONCLUSION

The simulation at 300K as a function of pressure on AlPO$_4$ produces a first order transition at about 30 GPa involving partial change of Al coordination from tetrahedral to octahedral. Al atoms acquire a sixfold coordination (partly a fourfold coordination), while the PO$_4$ tetrahedra remain essentially intact. The recovery of the pressure-induced amorphized phase is caused by the presence of the PO$_4$ units, as was previously pointed out by Tes and Klug [4]. We have found that the PO$_4$ units remain up to 80 GPa at 300 K.

For the instantaneous compression process at 300 K, the crystalline-to-crystalline phase transition of $AlPO_4$ is observed. This new crystalline has space group C2. The α-$AlPO_4$ to C2-$AlPO_4$ phase transition, which is kinetically impeded at room temperature, is assumed to occur owing to instantaneous high temperature state generated by the instantaneous compression.

The simulation at 2500 K yields a first order transition of the β-phase to the γ-phase at 58 GPa involving complete change of P coordination from tetrahedral to octahedral. The Al and P atoms acquire a sixfold coordination. The PO_6 otctahedral structure, which is unfavored at the condition up to 80 GPa at 300 K are formed above 58 GPa at high temperature (2500 K).

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