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Structural properties of α -berlinite (AlPO_4)

Received: 3 January 1997 / Revised, accepted: 16 April 1997

Abstract We present first principles calculations for the structural properties of α -berlinite (AlPO_4) as a function of pressure. The calculations were performed within the local density approximation using *ab initio* pseudopotentials and a plane-wave basis. We determined the lattice parameters, cohesive energy, and bulk modulus by minimizing the enthalpy of the solid with respect to lattice parameters. We find good agreement, within $\sim 2\text{--}3\%$ of the experimentally observed values, for the structural properties as a function of pressure.

Introduction

While amorphous solids are often produced by the thermal quenching of the melt, it is also possible to induce amorphization in solids by the application of pressure. Pressure-induced amorphization was first observed in ice (Mishima et al. 1984). A recent review (Sharma and Sikka 1996) suggests this phenomenon may have been observed a decade earlier. Unlike thermal quenching, the kinetic processes are inhibited in a pressure-induced amorphization, and the relationship between amorphous solids obtained by thermal quenching versus pressure quenching is unclear. Moreover, in both processes, the microscopic details of the amorphization transformation are poorly understood.

One material known to exhibit pressure-induced amorphization is α -quartz (Hemley et al. 1988). Quartz when subjected to a pressure of approximately 15–30 GPa at ambient temperature will undergo a slow amorphization. A related material, berlinite (AlPO_4), which is isostructural with quartz, also undergoes a pressure-induced amorphization at ~ 20 GPa at ambient temperature. However, unlike quartz, berlinite is believed to

behave as a “memory glass” (Kruger and Jeanloz 1990; Tse and Klug 1992; Chaplot and Sikka 1993; Polian et al. 1993). “Memory glass” is a term used to characterize a group of materials which will undergo an amorphous transition when subjected to high pressure, yet will recrystallize with the original crystallographic orientation upon quenching. This is a relatively new phenomenon which has been observed in several materials that are isostructural with quartz since the pioneering experimental work of Kruger and Jeanloz in 1990. In 1992, Tse and Klug used interatomic potentials to perform molecular dynamics in order to investigate the mechanism of the memory effect in berlinite. They found that enhanced oxygen coordination around the aluminum atoms in AlPO_4 at high pressure led to a mechanical instability that caused the transformation from single crystal to an amorphous solid. They concluded that the O-P-O bond angle distribution remains close to the original and the PO_4 tetrahedra remain four-coordinated, even when severely distorted. This gives the structural memory behavior observed. Chaplot and Sikka’s 1993 molecular dynamics simulations were in agreement with Tse and Klug. Recently, this effect has been interpreted to involve a polymorphic crystal-crystal phase transition (Gillet et al. 1995).

While structural properties of quartz at ambient and high pressure have been examined theoretically using both pseudopotentials (Chelikowsky et al. 1990a, b, 1991; Teter et al. 1995, and references therein) and interatomic potentials (Tsuneyuki et al. 1988; Chelikowsky et al. 1990a, b), the only theoretical work that has been done on the structural properties of berlinite involved using interatomic potentials to examine lattice dynamical and elastic instabilities (Keskar et al. 1994 and references therein). To explore theoretically this interesting material, we will use a pseudopotential approach to examine the structure of α -berlinite.

Computational methods

A key difficulty in describing the structural properties for α -berlinite is that the unit cell is large for *ab initio* calcu-

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lations. It contains three molecular units of AlPO_4 and requires the specification of several internal coordinates. Theoretical determination of the structural parameters involves minimizing a multi-parameter total energy function. Numerous evaluations of the forces must be made to ensure that a global minimum of the total energy has been obtained as a function of the structural parameters.

Our calculations are based on *ab initio*, norm-conserving pseudopotentials constructed to be rapidly convergent with a plane-wave basis (Troullier and Martins 1990, 1991a, b). The oxygen pseudopotential was generated from the $2s^2 2p^4$ non-spin-polarized oxygen atomic valence ground state configuration, using a core radius cutoff of 1.79 a.u. for both the *s* and *p* pseudopotential components. The non-local *d* component was neglected owing to the high energy of the *d* state relative to the 2*s* and 2*p* atomic valence states. The aluminum pseudopotential was generated from the $3s^2 3p^1 3d^0$ aluminum atomic valence ground state configuration, using a core radius cutoff of 2.14 a.u. for all the pseudopotential components. Similarly for phosphorus, the pseudopotential was generated from the $3s^2 3p^3 3d^0$ phosphorus atomic valence ground state configuration, using a core radius cutoff of 1.70 a.u. for all the pseudopotential components. The pseudopotentials were transformed into the computationally efficient Kleinman-Bylander separable form (Kleinman and Bylander 1982), using the *p* component as the local component for all elements. The local density formalism of Ceperley and Alder (1980) for exchange and correlation was used. The one-electron Schrödinger equation was solved using an iterative diagonalization technique (Martins and Cohen 1988; Troullier and Martins 1991a, b). Plane waves up to an energy cutoff of 49 Ry were included in the basis set. Typically, 7200 and 9000 plane waves were used in the basis for the smallest volumes and largest volumes, respectively. Increasing from 49 to 64 Ry decreased the total energy per unit cell by less than 35 mRy. Self-consistency was reached in less than 10 iterations with the Fourier components of the potential differing by less than 0.2 mRy from the previous iteration. Two reduced *k*-points in the Brillouin zone were used to construct the charge density for self-consistency in the potential for all calculations.

Equation of state

The hexagonal unit cell of α -berlinite contains three molecular units of AlPO_4 (Fig. 1). The levo- (dextro-) form has $P3_121$ ($P3_221$) symmetry (Wyckoff 1964), and is defined by the lattice constants (*c*, *a*) and eight internal parameters ($u_1, u_2, x_1, y_1, z_1, x_2, y_2, z_2$). The parameters u_1 and u_2 define the Al and P atom positions in the unit cell, respectively. The set of parameters (*x*, *y*, *z*) define O atom positions for two non-equivalent sites. The atom coordinates are explicitly given in terms of these parameters in Thong and Schwarzenbach 1979.

We examined nine different volumes and determined the optimum internal structure for each case; i.e., we op-

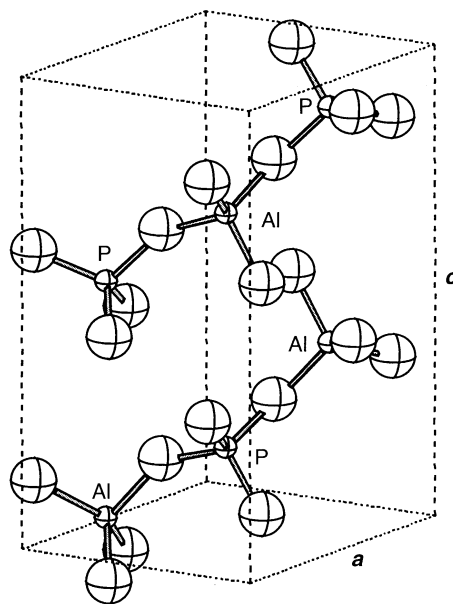


Fig. 1 Structure of α -berlinite (AlPO_4)

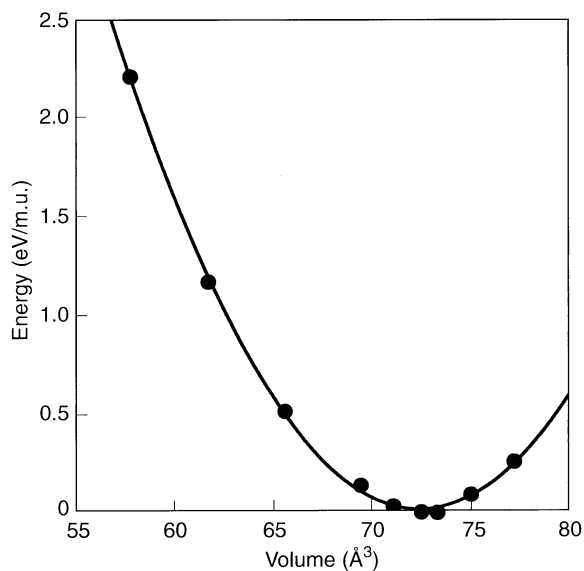


Fig. 2 Calculated total energy per molecular unit for α -berlinite as a function of volume. The energy is referenced to the equilibrium energy. The volume is per molecular unit. The curve is a Murnaghan fit to the calculated points

timized *c/a*, $u_1, u_2, x_1, y_1, z_1, x_2, y_2, z_2$ for each volume. The optimization of these coordinates was based on a steepest descent procedure using the quantum interatomic forces. The resulting energy-volume relationship is illustrated in Fig. 2 where we show the energy as a function of molecular volume. A Murnaghan equation of state (Murnaghan 1944) was fit to these points, and was used to determine the equilibrium energy, equilibrium volume, and the bulk modulus. These values are compared to the experiment in Table 1.

Our cohesive energy exceeds experiment by $\sim 30\%$. This fairly large difference is typical for the local density

Table 1 Equation-of-state parameters for α -berlinite. The experimental value of the cohesive energy is from CRC handbook of chemistry and physics (1983). The structural parameters are from Sowa et al. (1990). The volume is per molecular unit of AlPO_4

	Equilibrium volume ($\text{\AA}^3$)	Cohesive energy (eV/atom)	Bulk modulus (GPa)
Theory	73.2	7.7	36.3
Experiment	77.2	5.8	36

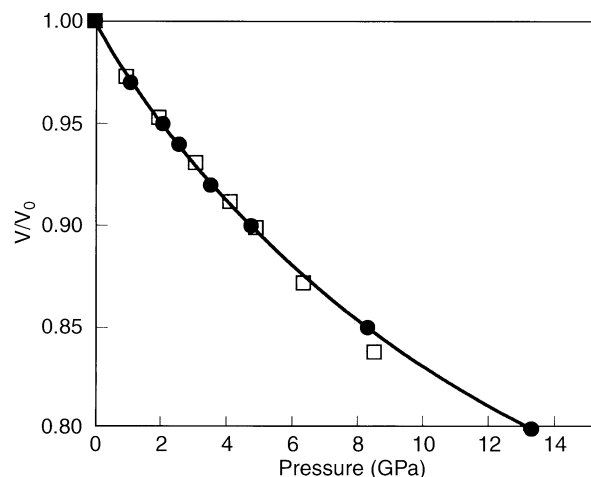


Fig. 3 Equation of state for α -berlinite. The volume is normalized to the ambient experimental volume, $77.2 \text{ \AA}^3$ per molecular unit. The experimental data points (*open squares*) are from Sowa et al. 1990. The *solid curve* is the theoretical Murnaghan equation of state from the fit in Fig. 2

approximation (LDA) (see e.g., Hamann 1996). In general, the cohesive energy is a good test of the basis. If the cohesive energy is less than indicated by experiment, the basis may be poorly converged.

We have included spin-polarization corrections in the cohesive-energy calculation (Gunnarsson et al. 1974). For aluminum the energy of the pseudoatom is -53.1 eV , including a correction of 0.18 eV for spin polarization. For phosphorus the energy of the pseudoatom is -175.8 eV , including a correction of 1.73 eV for spin polarization. For oxygen the energy of the pseudoatom is -424.9 eV , including a correction of -1.51 eV for spin polarization. To arrive at the binding energy in Table 1, we used a heat of formation for α -berlinite of -414.4 kcal/mol , a cohesive energy for aluminum of -78.0 kcal/mol , a cohesive energy for phosphorus of -75.2 kcal/mol , and a dissociation energy for O_2 of 238.2 kcal/mol (CRC Handbook 1983). We have adjusted the experimental cohesive energies for zero temperature, but not the heats of formation. The inherent errors in the local density theory probably exceed any errors present in ignoring the role of temperature. This may not be true for the structural properties. However, we are not in a position at this stage to include changes in structure as a function of temperature. The structural properties de-

termined by local density theory are expected to be more accurate than the cohesive energy as the cancellation of errors is expected to be more complete.

The theoretical results in Table 1 underestimate the equilibrium volume by $\sim 5\%$. This is consistent with the trends and accuracy generally obtained with LDA calculations. For example, in quartz a similar trend has been observed; the theoretical volume is about 5% less than the experimental equilibrium volume (Chelikowsky et al. 1991). The bulk modulus, B_0 , is in excellent agreement with experimental data. Our volume-versus-pressure curve (Fig. 3) represents the calculated pressures using the semi-empirical Murnaghan expression (Murnaghan 1944)

$$P = \frac{B_0}{B'_0} \left[\left(\frac{V_0}{V} \right)^{B'_0} - 1 \right] \quad (1)$$

with the theoretical B_0 in Table 1 and B'_0 set equal to 4. We did not allow B'_0 to vary in our fitting procedure owing to the relatively small pressure range over which the Murnaghan expression is expected to be valid. Our calculations are in good agreement with the experimental data points in Fig. 3 which were used to calculate the experimental B_0 (Sowa et al. 1990) in Table 1. The experimental B_0 was calculated by Sowa from a Birch-Murnaghan equation of state with B'_0 set equal to 4 also.

Structural properties as a function of pressure

In Table 2, we give the optimized structural parameters for each volume we have investigated. In this table we present a normalized volume, V/V_0 , where we have normalized to the experimental equilibrium volume. This is a common practice in comparing internal parameters with experiment when the equilibrium volumes determined by experiment and by theory are not in registry. In Fig. 4 we illustrate the (c, a) parameters as a function of the *normalized* volume and compare them to experiment (Sowa et al. 1990). The behavior of (c, a) is essentially linear as a function of volume. Experimentally, this ratio changes by $\sim 4\%$ from 2.21 at ambient pressure (or $V/V_0=1.0$) to 2.29 at 8.5 GPa (or $V/V_0=0.838$). Theoretically, the change is less than 5% with the c/a ratio being about 2.22 at $V/V_0=1.0$ and about 2.32 at $V/V_0=0.80$.

In Fig. 5 we present the variation of the aluminum parameter, u_1 , and phosphorus parameter, u_2 , with volume and compare them to experiment (Sowa et al. 1990). Similar to the (c, a) parameters, the internal parameters exhibit a near-linear behavior. The primary difference between experiment and theory is in the phosphorus parameter, u_2 , as seen in Fig. 5. At ambient pressure, experiment and theory agree perfectly. At smaller volumes, there is a deviation between the two. This deviation is still less than 3% by the smallest volumes, with an experimental value of 0.434 at $V/V_0=0.838$ and a theoretical value of 0.4466 at $V/V_0=0.85$. The aluminum parameter, u_1 , is in excellent agreement with experiment, the largest variation being less than 1%.

Table 2 Theoretical structural parameters for α -berlinite as for a given molecular unit volume. The parameters have been determined on the basis of a self-consistent pseudopotential calculation using the local density approximation. The normalized volume, V/V_0 , is determined using the experimental equilibrium volume

Volume ($\text{\AA}^3$)	77.16	75.00	72.50	71.09	69.45	65.59	61.73
V/V_0	1.000	0.972	0.940	0.921	0.900	0.850	0.800
a ($\text{\AA}$)	4.9414	4.8955	4.8335	4.7962	4.7463	4.6314	4.5191
c ($\text{\AA}$)	10.947	10.841	10.750	10.705	10.679	10.593	10.471
u_1 (Al)	0.4663	0.4630	0.4596	0.4585	0.4556	0.4451	0.4412
u_2 (P)	0.4665	0.4635	0.4607	0.4584	0.4556	0.4466	0.4373
x_1 (O)	0.4170	0.4145	0.4100	0.4084	0.4066	0.4017	0.3982
y_1 (O)	0.2920	0.2975	0.3027	0.3060	0.3093	0.3207	0.3326
z_1 (O)	0.0640	0.0616	0.0592	0.0581	0.0572	0.0547	0.0522
x_2 (O)	0.4160	0.4135	0.4119	0.4101	0.4067	0.3986	0.3892
y_2 (O)	0.2590	0.2640	0.2708	0.2742	0.2780	0.2883	0.2979
z_2 (O)	0.5507	0.5482	0.5450	0.5435	0.5421	0.5387	0.5354

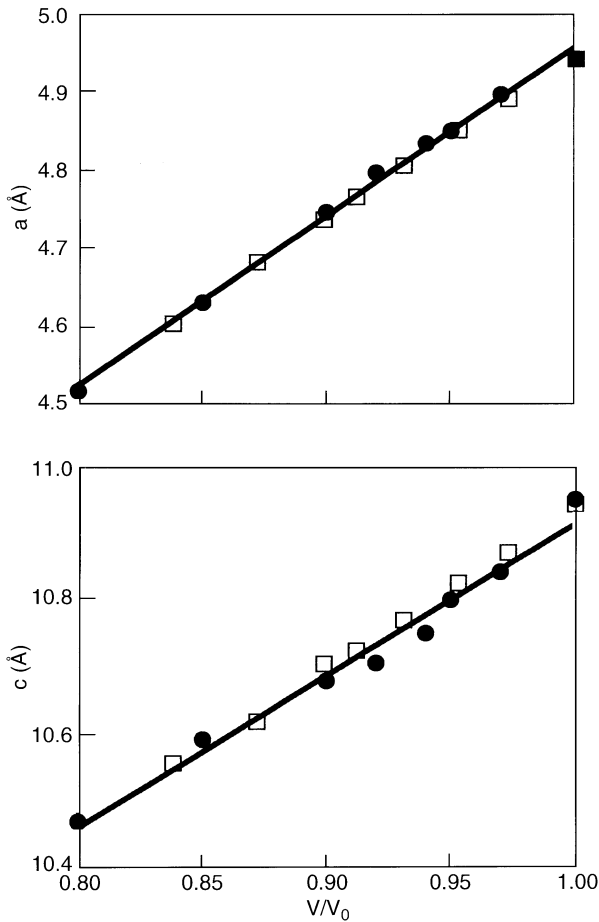


Fig. 4 Theoretical (solid circles) structural parameters for (c , a) versus the molecular volume for α -berlinite and comparison to experiment (open squares) (Sowa et al. 1990). The volume has been normalized to the ambient experimental volume, $77.2 \text{ \AA}^3$ per molecular unit

The remaining internal parameters x_1 , y_1 , z_1 , x_2 , y_2 , and z_2 refer to two non-equivalent oxygens. These are compared to experiment (Sowa et al. 1990) in Fig. 6 as a function of volume. The deviation between experiment and theory varies from less than 0.5% for the z_2 parameter to $\sim 5.0\%$ for the z_1 parameter. Considering the inherent difficulties in our calculations and experiment, the agreement between theory and experiment is very good.

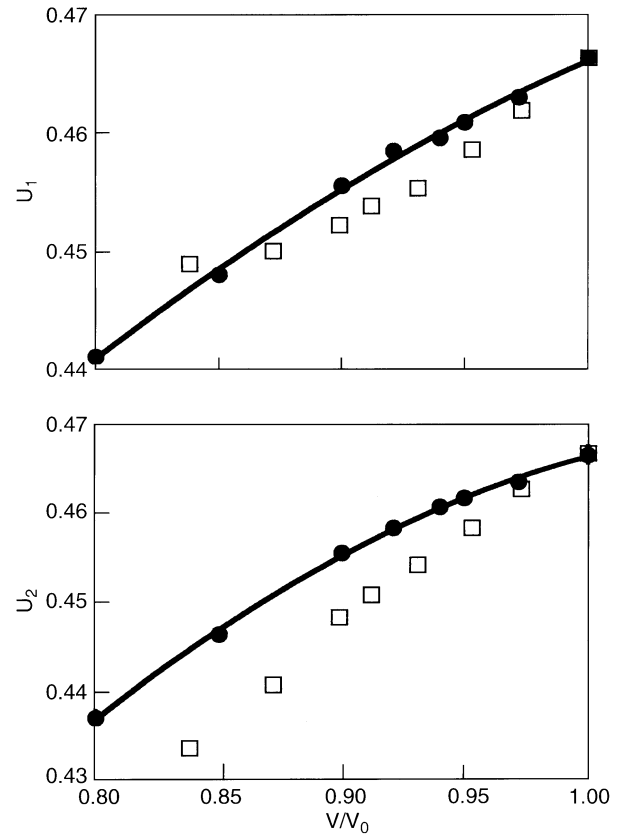


Fig. 5 Theoretical (solid circles) aluminum and phosphorus structural parameters, u_1 and u_2 respectively, versus the molecular volume for α -berlinite and comparison to experiment (open squares) (Sowa et al. 1990). The volume has been normalized to the ambient experimental volume, $77.2 \text{ \AA}^3$ per molecular unit

Concluding statement

The structural properties of α -berlinite (AlPO_4) as a function of pressure via total energy using *ab initio* pseudopotentials have been presented. The equation of state was calculated, yielding the bulk modulus, equilibrium volume, and equilibrium energy. The bulk modulus is in excellent agreement with experiment, differing by less than 1%. The cohesive energy exceeds the experimental energy by $\sim 30\%$ which is consistent with the local density approximation. The volume and the internal structural parameters as a function of pressure are in good agreement with ex-

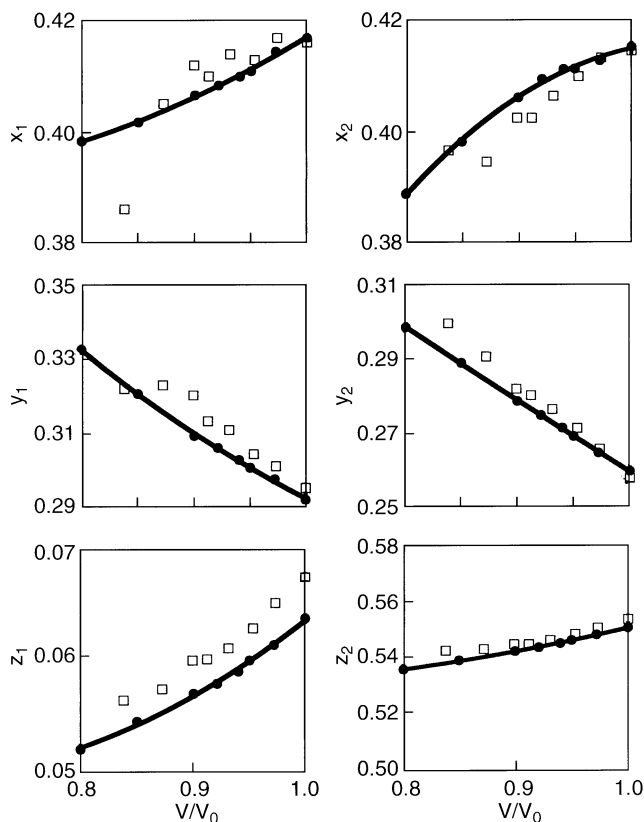


Fig. 6 Theoretical (solid circles) oxygen structural parameters x_1 , y_1 , z_1 , x_2 , y_2 , z_2 versus the molecular volume for α -berlinite and comparison to experiment (open squares) (Sowa et al. 1990). The experimental values of z_1 and z_2 have been changed by 1/3 to agree with Wyckoff's convention (Wyckoff 1964). The volume has been normalized to the ambient experimental volume, 77.2 Å³ per molecular unit

perimental results, differing by $\sim 2\text{--}3\%$. This is consistent with previous *ab initio* pseudopotential work performed on isostructural α -quartz (Chelikowsky et al. 1991).

It is interesting to compare berlinite with quartz in terms of their respective structural properties. Both materials are quite similar in terms of the theoretical calculations and, as such, it is not surprising that both undergo an amorphization transformation. Recently, a new phase of silica has been observed (Kingma et al. 1993) which precedes the amorphization transformation. On the basis of our theoretical work, it would seem natural that berlinite might possess a similar phase, but to date this has not been experimentally confirmed.

Acknowledgements We would like to acknowledge support for this work by the U.S. Department of Energy under Grant No. DE-FG02-89ER45391, and the Minnesota Supercomputer Institute. We also acknowledge helpful conversations with N. Binggeli and R. Wentzcovitch. One of us (J.R.C.) would like to thank the John Simon Guggenheim Foundation for its support.

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