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Abstract. Constant-pressure molecular dynamics calculations were used to study the pressure-induced transformation of the α-cristobalite form of GaPO$_4$. A crystal → crystal transformation was found at about 4 GPa. The transformed structure is orthorhombic *Cmcm* and consists of six-coordinated gallium and four-coordinated phosphorus. The calculations confirm the structure observed in a recent high-pressure experiment. The analytically calculated pressure dependence of the elastic properties of the α-cristobalite form of GaPO$_4$ revealed the mechanism of this phase transition.

1. Introduction

Gallium phosphate is an isoelectronic analogue of SiO$_2$ and forms structures homotypical to those of silica [1]. Pressure-induced phase transitions of silica polymorphs hold the attention of many scientists due to involvement of these transformations in processes occurring in the Earth's mantle. Tsuneyuki *et al* [2] using molecular dynamics (MD) simulation predicted a phase transition of α-cristobalite to a new crystalline phase with Si equally occupying four- and six-coordinated sites at 16.5 GPa. The structure was described as orthorhombic with *Cmcm* space group symmetry and with $a = 5.20$ Å, $b = 7.44$ Å, $c = 5.58$ Å unit cell parameters. In contrast, another MD calculation using the SiO$_2$ potential developed by van Beest *et al* [3] predicted a direct transformation into the stishovite form at high pressure [4]. Experimental high-pressure studies revealed the existence of at least three pressure-induced phase transitions (at 1.2 GPa, 10 GPa and 30 GPa) of α-cristobalite SiO$_2$, neither of which gave rise to the formation of the predicted simulated *Cmcm* structure [5,6]. However, interestingly, upon laser annealing, the stishovite form can be recovered from the sample [7].

A general mechanism of pressure-induced phase transformations of the silica structures and their analogues (such as AlPO$_4$) has been described in terms of the folding up of the [TO$_4$] tetrahedra (where T denotes tetrahedral atoms) into the openings of the structure [8–10]. Such deformations are easier to realize in the case of a less covalent and, thus, more flexible T–O–T bonding. Consequently, application in the simulation of SiO$_2$ pair-wise spherical symmetry potentials, which do not properly account for the directionality of the Si–O bonding, resulted in the observation of the Tsuneyuki's phase of silica, which

has not yet been found in nature. This may explain the failure of the two-body potentials in predicting the correct structure for these oxides at high pressure. On the other hand, two-body potentials can mimic less covalent interactions, like Al–O and, particularly, Ga–O much better. This is why Tsuneyuki's type of phase transformation can occur more easily in aluminium and gallium phosphates. This conjecture is apparently supported by the recent experimental observation of a phase transition of the α-cristobalite form of $GaPO_4$ (lc-$GaPO_4$, where lc stands for 'low-cristobalite') into a new-pressure phase [11]. The quality of the powder diffraction data did not allow for the structural refinement of the phase, but the best fit of the experimental diffraction pattern was obtained for the Tsuneyuki-type orthorhombic phase with six-coordinated gallium and four-coordinated phosphorus. The objective of this article is to test the applicability of a newly parameterized $GaPO_4$ potential in the prediction of the structural transformation of the α-cristobalite form of $GaPO_4$ at high pressure.

2. Calculations

Constant-pressure $N\sigma T$ MD simulations [12] of the lc-$GaPO_4$, using potential parameters shown to reproduce the berlinite and α-cristobalite forms of gallium phosphate fairly well [13], have been conducted to study the experimentally observed pressure-induced phase transition. The MD box contained 27 unit cells of the α-cristobalite form (648 atoms). The simulation was started from the experimental ambient crystal structure [14]. The system was subjected to a step-wise pressurization from 0 GPa up to 4.5 GPa with $\Delta P = 0.5$ GPa. During the first 8000 steps of each cycle, particle velocities were scaled to a desired temperature (300 K) and the constant-pressure method of Parinello and Rahman [15] allowed a change of unit cell shape and size. After that, the system was relaxed for 1000 steps. Finally, when equilibrium was established, structural data were collected.

Elastic constants were calculated analytically by differentiation of the Helmholtz free energy with respect to the strains [16]. At every pressure the crystal structure was allowed to relax to achieve a minimum-energy state. The isothermal compressibility, k_T, was estimated as a sum over all nine coefficients of the upper left-hand corner of the elastic compliance matrix [17], i.e.

$$k_T = \sum_{i,j=1}^{3} S_{ij}.$$

Young's moduli along the principal directions of the crystal were found as $E_{ii} = 1/S_{ii}$ [18].

3. Discussion

As a first step of this research a test of the reliability of the force-field parameters for $GaPO_4$ in the reproduction of dynamic properties has been undertaken. Comparison of the calculated and experimentally available data on the elastic constants of the quartz form of $GaPO_4$ (table 1) shows reasonable agreement.

In the case of SiO_2 with only one type of tetrahedral atom (Si) and tetragonal symmetry of the cristobalite, inward folding of the $[TO_4]$ tetrahedra chains gives rise to lateral contraction (along both of the a-axes of the tetragonal unit cell) of the α-cristobalite when compressed along the c-axis [20]. Such behaviour is reflected by a positive value of the off-diagonal element of the elastic compliance matrix $S_{13} = 0.0017 \times 10^{-9}$ m^2 N^{-1}. In the α-cristobalite form of $AlPO_4$ and $GaPO_4$ the chains are composed of alternating

Table 1. Elastic constants of the quartz and α-cristobalite forms of $GaPO_4$.

ij	Quartz[a] C_{calc} (10^9 N m^{-2})	C_{exp} (10^9 N m^{-2})	α-cristobalite[b] C_{calc} (10^9 N m^{-2})	S_{calc} (10^{-9} m^2 N^{-1})
11	70.48	66.58(37)	69.95	0.017 30
12	19.72	21.81(70)	15.13	−0.008 19
13	22.59	24.87(60)	14.89	−0.005 78
22			32.48	0.034 68
23			−0.77	0.003 25
14	7.46	3.91(33)		
33	130.33	102.13(55)	45.68	0.023 83
44	39.81	37.66(27)	52.70	0.018 96
55			55.75	0.017 94
66	25.38	22.38(32)	17.02	0.058 74

[a] Experimental data on elastic stiffness constants are from [19].
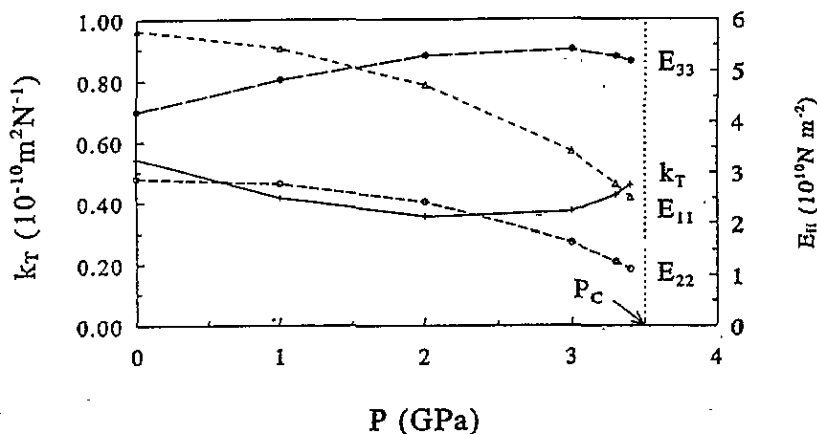[b] Experimental data on elastic properties of the α-cristobalite form of $GaPO_4$ are unavailable.

Figure 1. The calculated pressure dependence of the Young's moduli and isothermal compressibility of the lc-GaPO₄.

[TO₄] tetrahedra: more rigid tetrahedra with T = P and pliant ones with T = Al, Ga. Such alternation gives rise to a lowering of the symmetry of the unit cell from tetragonal to orthorhombic. A positive value of the elastic compliance constant $S_{23} = 0.003\,25 \times 10^{-9}$ m^2 N^{-1} calculated for the α-cristobalite $GaPO_4$ (table 1) indicates lateral contraction (along the b-axis) of a crystal of this phase when subjected to stress along the c-axis. This distortion of the unit cell corresponds to the deformation of the [GaO₄] tetrahedra and their movement toward each other in the ⟨010⟩ direction, while the [PO₄] tetrahedra remain essentially unchanged. These observations are in accordance with the pressure dependence of the Young's moduli, viz. the Young's modulus along the y-axis is particularly small and decreases further upon compression, suggesting possible collapse of the structure along the b-direction (figure 1). The Young's modulus along the c-axis also shows a negative slope in its pressure dependence curve. The other Young's modulus, along the a-direction, reaches a maximum at about 3 GPa, while the isothermal compressibility, k_T, of the lc-GaPO₄ goes through a minimum at 2 GPa (figure 1). All three moduli fall rapidly while the pressure approaches a critical value, indicating thermodynamic instability of the

α-cristobalite structure [21]. The calculated pressure dependence of the elastic stiffness tensor shows that from 3.5 GPa onwards, the form of the elastic stiffness matrix suggests significant deviation of the atomic positions from orthorhombic toward lower symmetry.

Investigation of the evolution of the frequency of elastic waves propagating in a crystal can provide information on the lattice vibrational mode(s) associated with a phase transition. In this case at an isotropic hydrostatic pressure, P, diagonal elements of the matrix of wave propagation coefficients $A_{ii} = C_{ii} - P$ [18] are proportional to the squares of the frequencies of lattice vibrations with wavevectors close to the centre of the first Brillouin zone: $A_{ii} \propto \omega_{ii}^2$ ($i = 1, 2, 3$)—longitudinal acoustic waves, propagating in the $\langle 100 \rangle$, $\langle 010 \rangle$ and $\langle 001 \rangle$ directions (for $i = 1, 2$ and 3, respectively); $A_{ii} \propto \omega_{jk}^2$ ($i = 4, 5, 6$; $j, k = 1, 2, 3$; $i \neq j \neq k$)—transverse acoustic waves, propagating in the $\langle 100 \rangle$, $\langle 010 \rangle$ and $\langle 001 \rangle$ directions (for $i = 4, 5$ and 6, respectively). Pressure dependence of the frequency of the longitudinal wave propagating along the y-axis demonstrates a maximum at about 2 GPa (see figure 2), while the other acoustic mode frequencies gradually rise upon pressurization (up to 3.5 GPa). Such behaviour of lattice vibrations may be interpreted as 'softening' [22] and can suggest connection of the instability of the lc-GaPO$_4$ at high pressures with longitudinal acoustic vibrations with the wavevector aligned along the $\langle 010 \rangle$ direction.
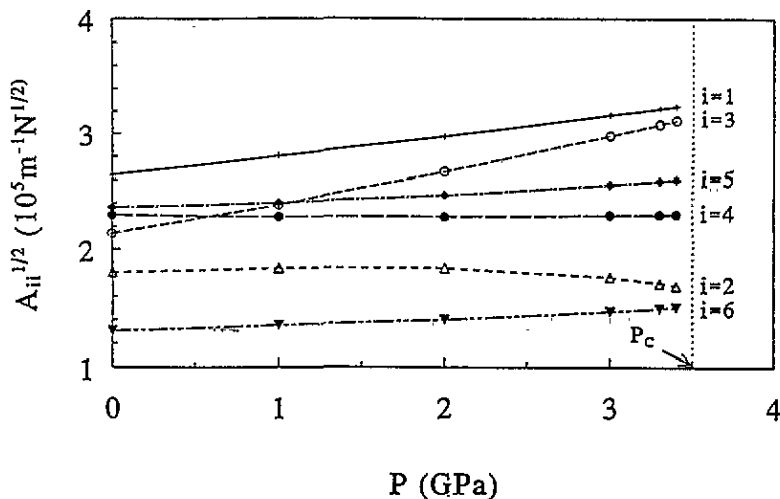

Figure 2. The calculated pressure dependence of $A_{ii}^{1/2} \propto \omega_{jk}$ of the lc-GaPO$_4$.

MD calculations revealed that an increase of the hydrostatic pressure imposed on the system results in a gradual decrease of $b \approx c$ parameters (see figure 3), while a remains essentially constant. Between 2.5 and 3 GPa a phase transition of the lc-GaPO$_4$ is observed and is accompanied by an abrupt decrease of the unit cell dimension in the $\langle 010 \rangle$ direction. A less dramatic change of the dimension in the $\langle 001 \rangle$ direction destroys the tetragonal relation between unit cell parameters. On the other hand, the unit cell dimension along the x-axis increases sharply. Overall changes in the unit cell dimensions give rise to a denser high-pressure phase ($\Delta V = 24\%$). Analysis of the high-pressure phase revealed that this phase has the orthorhombic space group symmetry *Cmcm* with unit cell parameters $a = 5.11$ Å, $b = 7.47$ Å, $c = 5.97$ Å at ambient conditions, which are very close to the experimentally observed parameters [11] (table 2). Gallium is in 4a positions, phosphorus is in 4c with $y = 0.36$, O1 is in 8f with $y = 0.25$ and $z = 0.05$, O2 is in 8g with $x = 0.24$ and $y = 0.48$. The structure contains rows of [GaO$_6$] octahedra with shared edges. Such

Table 2. Comparison of the experimental and simulated crystal structure data[a] for the low-cristobalite and high-pressure forms of GaPO₄.

Parameter	Low-cristobalite form		High-pressure form	
	Calculated	Experimental [14]	Calculated	Experimental [11]
a (Å)	7.16	6.967	5.11	5.12
b (Å)	6.92	6.967	7.47	7.31
c (Å)	6.83	6.866	5.97	5.92
α	90°	90°	90°	90°
β	90°	90°	90°	90°
γ	90°	90°	90°	90°
Space group		$C222_1$		$Cmcm$

[a] The c-axes of the low-cristobalite and high-pressure forms of GaPO₄ are antiparallel, causing an interchange of the a- and b-axes in these structures.
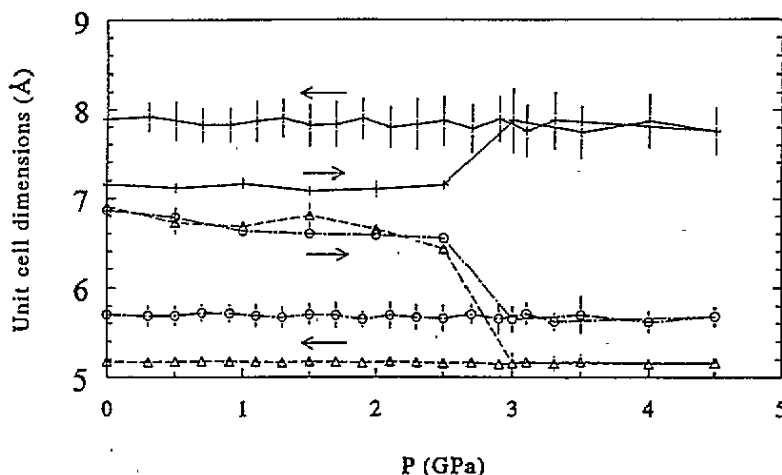

Figure 3. The calculated pressure dependence of the unit cell parameters (arrows show the direction of the 'pressurization–decompression' cycle): +, a-parameter of the lc-GaPO₄ and b-parameter of the high-pressure phase; △, b-parameter of the lc-GaPO₄ and a-parameter of the high-pressure phase; ○, c-parameter.

arrangements of octahedra give rise to a new peak in the radial distribution function (RDF) of Ga–Ga at about 2.8 Å (see figure 4(b)). The radial distribution function P–P also shows dramatic changes associated with formation of the compact structure (see figure 4(c)). The T–O bond lengths do not change appreciably during the phase transition (the Ga–O RDF is given in figure 4(a)). The orthorhombic structure is stable upon decompression, which is in agreement with experiment. It is significant to point out that the high-density orthorhombic form has a lower total energy than the α-cristobalite form even at ambient conditions ($\Delta E = 88$ kJ mol⁻¹). This may help to explain the observed stability of the former structure.

The discrepancy between the predicted critical pressure by the MD simulations (between 2.5 and 3.0 GPa) and the elastic property calculations (3.5 GPa) may be due to the neglect of atomic motion (0 K approximation) in the latter study. Both predicted transition pressures seem to support the experimental observation of a continuous phase transition of the lc-GaPO₄ into the high-pressure phase [11], which begins at as low a pressure as
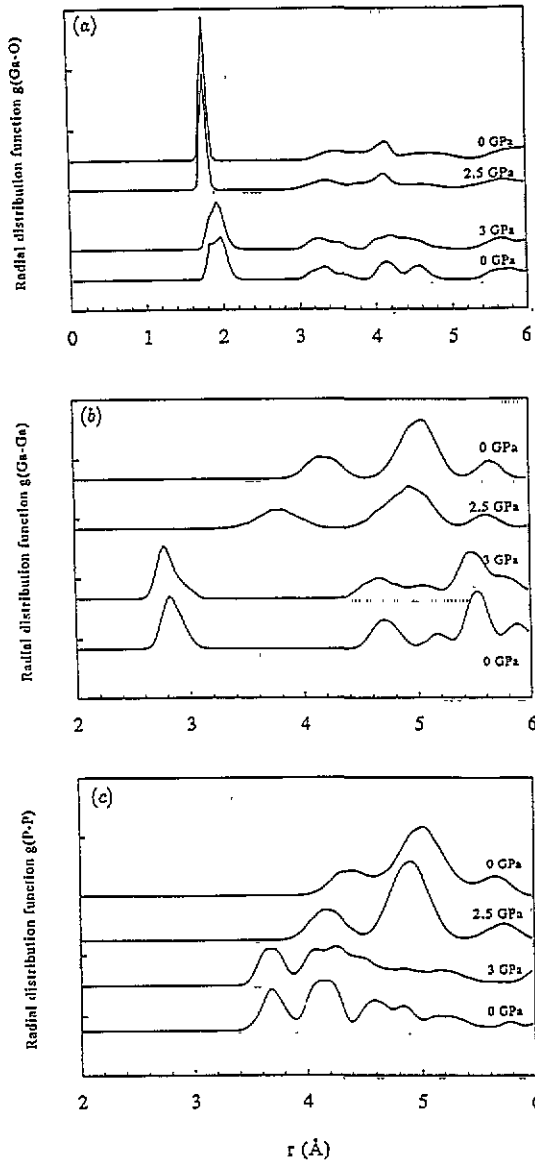
Figure 4. Evolution of the (a) Ga–O, (b) Ga–Ga and (c) P–P radial distribution functions in the 'pressurization–decompression' cycle (from the upper curve to the bottom curve).

4 GPa (or even lower) and is completed at 15.9 GPa. The relatively sharp phase transition obtained in the simulation (viz. compare the range of the simulated $\Delta P = 0.5$ GPa and experimental $\Delta P = 11$ GPa transition pressures) might be connected with the small size of the modelled system. Incidentally, the calculated phase transition pressure is significantly lower than that for the analogous transformation calculated for silica (viz. $P_c = 16.5$ GPa [2]). Greater flexibility of the Ga–O–P bonds compared to the Si–O–Si ones [13], as well as the large ionic radius of Ga, promote the bending of chains of [TO$_4$] tetrahedra and the formation of a six-coordinated Ga at lower pressures.

Still, one has to be cautious of the critical pressure obtained in these calculations. It is

reasonable that the assumption of a non-directional pair-wise potential will underestimate the covalent interactions in the Ga–O bonding and lead to a discrepancy between the theoretical model and experiment. In addition, a very large attractive term of the Buckingham potential for the Ga–O interaction ($C_{Ga-O} = 222.2168$ Å^6 eV [13]) favours formation of dense forms of $GaPO_4$ and can be responsible for the stabilization of high-pressure forms of $GaPO_4$ at relatively low pressures. Tsuneyuki's transformation is accompanied by the development of the higher-order oxygen coordination spheres of Ga at ≈ 3.3 Å, 4.6 Å (see figure 4(a)) and the squeezing of already existing spheres. Therefore, force-field parameters used in this work can promote this phase transition at a lower pressure. In passing, it is important to point out that the $Cmcm$ structure observed for $GaPO_4$ is not a new structural type as indicated earlier [11]. This structure is well documented and is generally known as the 'CrVO₄' structure [23].

4. Conclusions

The calculations performed confirmed the experimentally observed pressure-induced phase transition of the α-cristobalite form of $GaPO_4$. Structural data for the high-pressure phase were recovered from MD simulations. Absence of a substantial change of the volume on the crystal→crystal phase transition suggests that its mechanism is likely to be essentially of the second order, driven by a soft mode. Investigation of the pressure dependence of the elastic properties of $GaPO_4$ revealed that the phase transition might occur through 'softening' of the longitudinal acoustic modes of lattice vibrations propagating in the $\langle 010 \rangle$ direction.

Acknowledgments

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