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Pressure-induced phase transition of quartz-type $GaPO_4$

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A transformation of the quartz-type $GaPO_4$ to a new high-pressure phase has been observed in molecular dynamics simulation at 7 GPa (experimental value is 9 GPa). The phase has a monoclinic $P2_1$ structure and can be viewed as a wafer structure composed of more densely packed layers with six-coordinated Ga separated by less dense layers containing five-coordinated Ga. Phosphorous retains its fourfold coordination. Upon decompression this new monoclinic phase does not convert back to the quartz-type structure, but undergoes structural deformation without a change in the space-group symmetry. Prolonged annealing of this phase at 1000 K recovered the quartz-type structure.

I. INTRODUCTION

Pressure-induced transformations of α-quartz SiO_2 and isostructural berlinite $AlPO_4$ are intensively studied both experimentally[1–7] and theoretically.[8–15] Yet, there are some unexplained phenomena accompanying these transformations, e.g., the nature of the quartz crystalline-crystalline transformation at 21 GPa with possible formation of a superstructure[1] is still unclear. Along with this transformation (or right after it) the formation of an amorphous solid[2] occurs in the pressure range between 20 and 30 GPa. The suggested mechanism of the pressure-induced transformation of quartz-type materials TO_2 (or $TT'O_4$, where T,T' denote tetrahedral atoms such as Si, Al, Ga, P) includes formation initially of a body-centered-cubic sublattice from oxygen atoms.[8] Coupling of the acoustic-transverse vibrations to the strain may induce displacements of T atoms from tetrahedral to octahedral sites. Considering the quartz-type structure as a stack of six- and three-tetrahedra helices expanding along the c axis [see Fig. 1(a)] such displacements correspond to the formation of T-O-T bonds across and along (between the spirals) three-tetrahedra helices. In addition, five-coordinated T atoms are formed when linking bonds are initiated across six-tetrahedra helices.

Opposite to the case of $T,T'=$Si, where random distribution of newly formed bonds can be likely, a presence of the two types of cations with significantly different electronegativities and ionic radii in the quartz-type $AlPO_4$ and $GaPO_4$, viz. $T=$Al, Ga, and $T'=$P, can favor formation of the crosslinking bonds in a regular manner. Experimental investigation of the behavior of the quartz-type $AlPO_4$ subjected to the hydrostatic pressure,[7] as well as simulation studies[13–15] revealed formation of an amorphous phase lacking long-range periodicity when the pressure reaches 15±3 GPa. On the other hand, observation of a "memory effect," i.e., reconstruction of the crystalline structure with an old crystallographic direction upon decompression, strongly suggests conservation of the local order in the amorphous high-pressure phase. It was shown that the driving force of the memory effect is the rigidity of the $[PO]_4$ tetrahedra, which under release of pressure try to restore the equilibrium tetrahedral angles.[14] In the case of $GaPO_4$ with more flexible P-O-Ga bonding[16] and the larger size of Ga ions favoring formation of five- and six-coordinated gallium (for an example of the observation of such coordination in gallium phosphates at ambient conditions, see Ref. 17), such an effect can be expected to play less of a role in the relaxation of a compressed phase. Indeed, recently reported studies of the high-pressure behavior of the quartz-type $GaPO_4$ revealed a

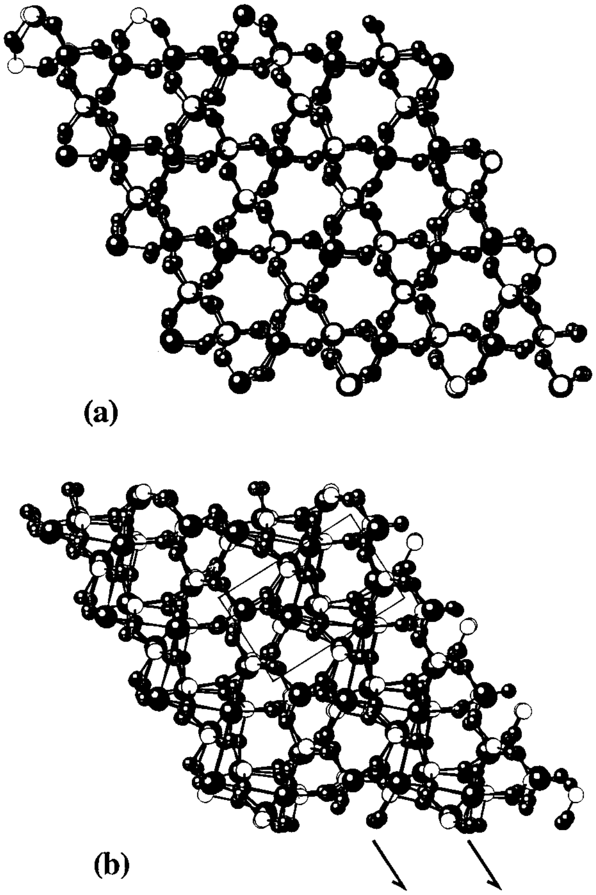

FIG. 1. Projections of the simulated quartz-type (a) and monoclinic (b) $GaPO_4$ structures along the c axis at 300 K and 0.1 GPa. The arrows indicate twofold screw axes in the monoclinic structure. The rectangle represents the monoclinic unit cell. The large solid circles are Ga atoms, the small solid circles are O atoms, and the open circles are P atoms.

nonreversible phase transition at about 9 GPa.[18] Broadness of the powder-diffraction lines has been connected with amorphization of the phase.

Recent *ab initio* calculations on gallium phosphate clusters, which provided force-field parameters for the Ga-O interaction,[16] allows for an investigation of the high-pressure behavior of $GaPO_4$ with the quartz-type structure. Preliminary investigation of the validity of the proposed potential parameters showed reasonable reproduction of gallium phosphate structures,[16] as well as elastic properties of the quartz-type gallium phosphate and the pressure-induced phase transformation of the low-cristobalite form of gallium phosphate.[19]

II. CALCULATIONS AND DISCUSSION OF RESULTS

The constant pressure and constant temperature (NPT) molecular dynamics (MD) simulations (program "MOLDY"[20]) have been undertaken to study the behavior of gallium phosphate in the pressure range from 0 to 30 GPa. The constant-pressure Parinello-Rahman algorithm[21] allowing for a change of unit-cell shape and size was used in these calculations. The pressure was changed by 1 GPa every 10 000 steps (1×10^{11} GPa/s). The molecular-dynamics cell consisted of 96 ($4\times4\times2$ unit cells in the a,b,c directions, respectively), 150 ($5\times5\times2$) and 216 ($6\times6\times2$) units of $GaPO_4$ and had a hexagonal shape (details of the simulation procedure can be found in Ref. 16).

At ambient conditions (300 K, 0.1 GPa) the simulations fairly accurately reproduce the experimentally observed unit cell parameters of the quartz-type $GaPO_4$ (see Table I) and the site distribution. It is necessary to notice one significant discrepancy between the simulated and experimental results: the x coordinate of the O(1) atoms is off by 0.13 Å, which leads to an increase of the Ga-O(1)-P angle by 5% compared to the experimental value[18] (still this difference is not uncommon for this type of simulations). This divergence is most probably due to a deficiency of the employed spherical pairwise potential model, which neglects directionality of T-O bonding. Therefore, the results discussed below need to be considered cautiously. MD simulation being a powerful tool in the investigation of the macroscopic properties of solids by means of modeling at microscopic level, still remains an approximate method, which depends strongly on the employed potential model and can be considered only as a valuable supplement to other experimental and theoretical methods.[22]

The structure of quartz-type materials can be viewed as a net of jagged planes built from three-tetrahedra helices and stretching along twofold screw axes [see Fig. 1(a)]. Spaces between such planes constitute six-tetrahedra helices. As the hydrostatic pressure applied to the simulated system increases, the deformation of the structure initially follows the proposed scheme for quartz compression, viz. six-tetrahedra helices squeeze (the rate of contraction of the a dimension is 2.5 times that of the c dimension), while the oxygen atoms approach a body-centered-cubic configuration.[8] At 7 GPa the $[GaO_4]$ tetrahedra are distorted strongly enough [the O-Ga-O angle distribution shows splitting of a peak corresponding to the tetrahedral angle 109.5° into two peaks centered at about 100° and 115°, see Fig. 2(a)] to allow for a displacement of gallium atoms into six-coordinated sites and formation of bonds across six-tetrahedra helices. In contrast, a valence angle peak on the O-P-O angle distribution does not show splitting, but only broadens at 7 GPa, manifesting much less severe distortion of the $[PO]_4$ units [see Fig. 2(b)]. The slope of the pressure dependence of the unit-cell parameters, as well as the calculated critical pressure correlates fairly well with those observed in the experiment[18] (compare the simulated $a=4.679$ Å, $c=10.855$ Å at 6 GPa with the experimental values $a=4.642$ Å, $c=10.802$ Å at 6.8 GPa and the simulated critical pressure of 7 GPA with the corresponding experimental value of 9 GPa).

TABLE I. The calculated structural data for the quartz-type and the monoclinic form of gallium phosphate. Structural parameters are given for phases at ambient conditions (300 K, 0.1 GPa).

Atom	Site	x	y	z
Berlinite form:				
Space group $P3_121$				
Cell parameters $a=4.908(1)$ Å, $c=11.05(1)$ Å[a]				
Density $\rho=3.56$ g/cm^3				
Ga(1)	$3a$	0.455(0.4565)	0	1/3
P(1)	$3b$	0.447(0.4565)	0	5/6
O(1)	$6c$	0.434(0.4069)	0.316(0.3169)	0.398(0.3928)
O(2)	$6c$	0.409(0.4087)	0.263(0.2714)	0.882(0.8723)
Monoclinic (high-pressure) form:				
Space group $P2_1$				
Cell parameters $a=7.373(3)$ Å, $b=4.717(2)$ Å, $c=11.01(2)$ Å, $\beta=88.8(5)°$				
Density $\rho=4.29$ g/cm^3				
Ga(1)	$2a$	0.094	0.747	0.305
Ga(2)	$2a$	0.309	0.527	0.029
Ga(3)	$2a$	0.486	0.897	0.631
P(1)	$2a$	0.537	0.372	0.815
P(2)	$2a$	0.030	0.782	0.841
P(3)	$2a$	0.238	0.424	0.525
O(1)	$2a$	0.277	0.726	0.173
O(2)	$2a$	0.801	0.172	0.100
O(3)	$2a$	0.555	0.660	0.764
O(4)	$2a$	0.057	0.073	0.794
O(5)	$2a$	0.389	0.201	0.505
O(6)	$2a$	0.931	0.773	0.439
O(7)	$2a$	0.288	0.658	0.609
O(8)	$2a$	0.741	0.051	0.603
O(9)	$2a$	0.568	0.685	0.268
O(10)	$2a$	0.043	0.104	0.262
O(11)	$2a$	0.481	0.333	0.948
O(12)	$2a$	0.875	0.786	0.935

[a] Experimental parameters are $a=4.899(1)$ Å, $c=11.034(2)$ Å. Experimental atomic positions in the unit cell of the quartz-type $GaPO_4$ are given in the brackets after calculated values (Ref. 23).

Investigation of the recovered structure (for $4\times4\times2$ and $6\times6\times2$ sizes of MD boxes) revealed its highly crystalline character in contrast to the amorphous phases observed in the simulations of α-quartz and berlinite. The structural transformation can be described as an establishment of linking bonds across three-tetrahedra helices, regularly, in every other zigzag plane of three-tetrahedra helices and between spirals of three-tetrahedra helices along their axes [see Fig. 1(b)].

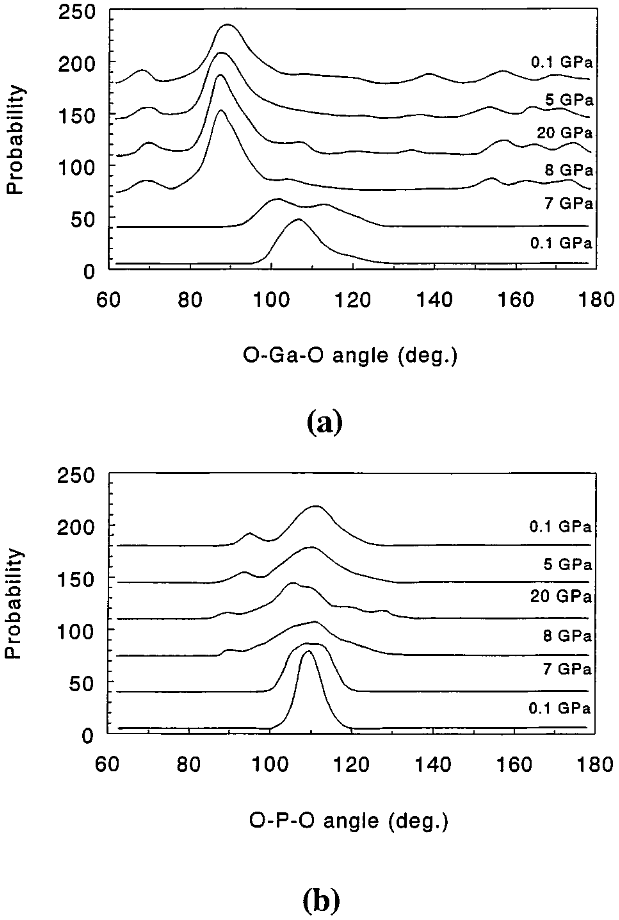

FIG. 2. The calculated O-Ga-O (a) and O-P-O (b) angle distributions in the "pressurization-decompression" cycle proceeding from the bottom to the top.

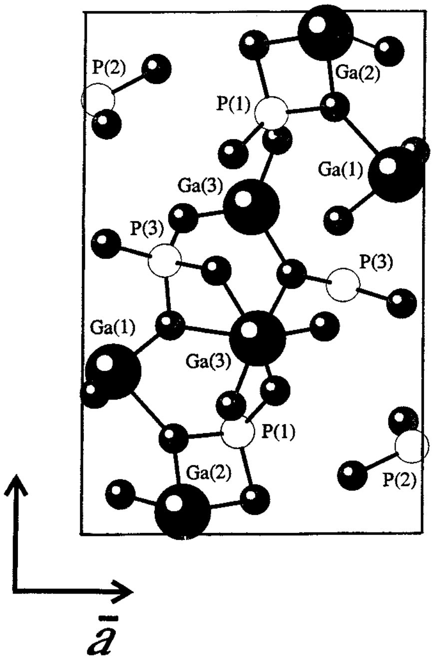

FIG. 3. Projection of the monoclinic unit cell of $GaPO_4$ (300 K, 0.1 GPa) along the *b* axis. The large shaded circles are Ga atoms, the small shaded circles are O atoms, and the open circles are P atoms.

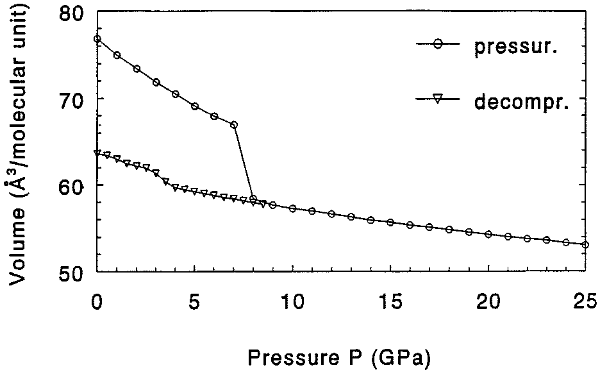

FIG. 4. The calculated pressure dependence of the volume per molecular unit of $GaPO_4$.

Thus, a wafer structure containing highly dense layers of six-coordinated gallium separated by less dense layers of five-coordinated gallium forms [the alignment of the planes corresponds to the direction of arrows in Fig. 1(b)]. Such distortion of the hexagonal quartz-type structure, $P3_121$, destroys the three-order axes, but preserves the twofold screw axes, 2_1, lying in the layers [see Fig. 1(b)], and therefore reduces the space-group symmetry of the structure to a monoclinic, $P2_1$. The unit cell of the structure contains three types of gallium sites, one of which, Ga(1), is five-coordinated and the other two, Ga(2) and Ga(3), are six-coordinated (see Table I and Fig. 3). Phosphorous occupies three sites with fourfold coordination. The appearance of a peak at about 90° after the phase transformation on the O-P-O angle distribution [Fig. 2(b)] shifting toward lower angles upon further compression suggests the presence in the structure of heavily deformed $[PO]_4$ tetrahedra. Such angles can arise from edge sharing by neighboring gallium and phosphorous oxygen polyhedra (e.g., P(1) and Ga(2) in Fig. 3). The transformation to the new structure is accompanied by a volume drop of about 13% (see Fig. 4), which is appreciably larger than the corresponding drop accompanying amorphization of berlinite $AlPO_4$ (5%).[13] Upon further compression to 25 GPa no other phase transformation has been detected.

Decompression down to about 4 GPa causes gradual expansion of the monoclinic unit cell (see Fig. 5), but with further release of the pressure a sharp drop of the unique angle of the unit cell, β, and higher expanding rates are ob-

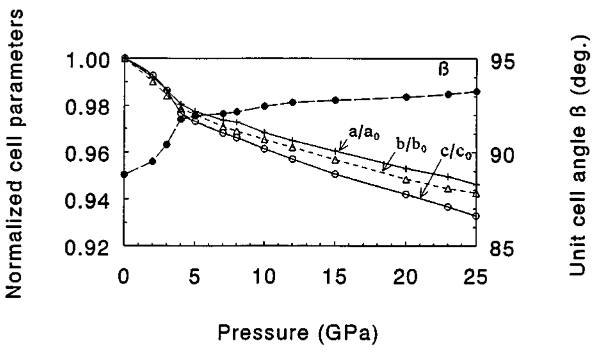

FIG. 5. The calculated pressure dependence of the unit-cell parameters of the monoclinic phase (a_0,b_0,c_0 are the unit-cell dimensions at ambient conditions).

served. This change gives rise to an increase of about 4% in volume (see Fig. 4). The strains in the high-pressure form arising from decompression find their release in termination of the oxygen links between Ga(2) and Ga(3) atoms (that corresponds to the bonding along the axis of the three-tetrahedra helix), thus leading to a reduction of the Ga(2) coordination number to 5. These transformations, which can be viewed as a spreading of helical springs, give rise to a change of the monoclinic unit cell shape, but do not restore the quartz-type structure and do not change essentially the pattern of the structure along the c axis. A slightly higher total energy of the monoclinic phase relative to the quartz-type form (the energy difference is 9 kJ/mol at 300 K and 0.1 GPa) indicates the possible coexistence of the metastable monoclinic and the quartz-type form at ambient conditions. This observation is in agreement with the experimentally discovered stability of the high-pressure $GaPO_4$ phase at ambient conditions.[18] Only prolonged (for 20 ps) annealing at 0.1 GPa and 1000 K restored the quartz-type phase.

A higher rate of decompression of the high-pressure phase ($\sim 5\times 10^{11}$ GPa/s) resulted in the formation of an amorphous solid with a lower density (4.04 g/cm^3) at ambient conditions than that of the monoclinic phase (see Table I), but with essentially the same total energy. This transformation is accompanied by ruptures of some bonds forming the three-tetrahedra helices. On the other hand, new crosslinking bonds in the less dense layers are formed in addition to the few remaining Ga-O-Ga crosslinking bonds in the formerly dense layers. The overall effect leads to a disordered phase with the average coordination number of gallium of 4.7. Under thermal treatment (simulated annealing at 800 K for 15 ps) this phase transformed into the stable quartz-type structure.

The MD box containing $5\times 5\times 2$ unit cells in a, b, and c directions, respectively, does not permit formation of a regular layered monoclinic structure and formation of a disordered phase has been observed. Still this phase bears the principal attributes of the monoclinic phase: alternating zigzag planes of three-tetrahedra helices containing six- and five-coordinated gallium atoms. This observation supports a conjecture that the failure to recover layered monoclinic structures in the previous MD simulations of SiO_2 and $AlPO_4$ might be associated with constraints of a cubic MD box combined with periodic boundary conditions. Other layered structures differing in the pattern of the sequence of the layers can possibly be observed upon compression of quartz-type materials with enlargement of the hexagonal MD box.

III. CONCLUSIONS

In summary, the presented calculations suggest that one can expect formation of the monoclinic layered structure containing five- and six-coordinated gallium and four-coordinated phosphorous on compression of the berlinite form of $GaPO_4$. The experimentally observed ‘‘amorphous’’ phase can be composed of domains of layered structures differing in the sequence of the layers and the orientations of their principal axes giving rise to diffuse lines. An example of such phase can be the structure observed in the simulation of a $5\times 5\times 2$ MD box. Upon decompression the monoclinic phase undergoes structural changes, but retains its main features. A relatively small difference in the total energies of the monoclinic and the quartz-type phases indicates the possible coexistence of both phases at ambient conditions.

It is possible that the experimentally observed crystalline-crystalline phase transition of the α-quartz SiO_2 at 21 GPa is connected with the formation of a layered phase resembling the high-pressure phase of $GaPO_4$ reported here. Alternating layers with an ordered distribution of crosslinking bonds can be responsible for the appearance of signs of a quartz superstructure on the experimental diffraction patterns of the compressed α-quartz SiO_2.[1]

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