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Theoretical Study of P_2O_5 Polymorphs at High Pressure: Hexacoordinated Phosphorus

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Binary oxides of elements belonging to groups 13−15 are of special relevance from a fundamental point of view as well as because of their technological applications as a basis in zeotypes, glasses, or semiconductors. Aluminum oxide, Al_2O_3, crystallizes in the corundum structure, which is stable at low and high pressures, with the Al showing octahedral coordination. Silicon oxide, SiO_2, crystallizes in phases with tetrahedral Si coordination at low pressures as α-quartz, but at high pressures, octahedral coordination is stable in the stishovite polymorph. The only known binary phosphorus(V) oxides have tetrahedral P coordination. We have studied the stability of different phases of P_2O_5 at high pressure, applying density functional theory methodology within the local density and generalized gradient approximations and a plane-wave basis set. Our results indicate that the most stable form of P_2O_5 at high pressure could be one with hexacoordinated phosphorus. All of the high-pressure phases of Al, Si, and P can be described as a different linking of the same rutile-type blocks.

Introduction

Phosphorus(V) oxides are the simplest compounds that feature the tetrahedral PO_4 group as a structural unit, the group that dominates most of phosphate chemistry. Al and Si also participate in similar tetrahedral units in their compounds. Al has the greater tendency to choose 6-fold oxygen coordination. Si atoms are usually found in tetrahedral coordination in oxides at ambient conditions but not always, e.g., SiP_2O_7.[1] At high pressures, SiO_2 converts to the octahedral stishovite phase,[2] a dense silicate structure of primary geophysical importance. There is no known octahedral PO_6 in an inorganic compound at ambient conditions. Phosphorus pentoxide is the commonest and most important phosphorus oxide.[3] Until now, P_2O_5 has not been studied at high pressures. However, experimental evidence of 6-fold oxygen-coordinated phosphorus has been reported very recently, when incorporated as a minor element in SiO_2 stishovite[4] and in $AlPO_4$ under high pressure.[5]

Under normal conditions of temperature and pressure, three different forms of crystalline P_2O_5 have been isolated so far: the so-called h form, belonging to the hexagonal crystal family though to the trigonal crystal system, contains discrete P_4O_{10} molecules;[6] the metastable orthorhombic (o-P_2O_5) form;[7] and the stable orthorhombic (o′-P_2O_5) form.[8] Binary oxides of other group 15 elements (As and Sb) show some degree of 6-fold coordination in their structures. For arsenic(V) oxide, As_2O_5, the orthorhombic form (o-As_2O_5)[9] and the tetragonal high-temperature form (t-As_2O_5)[10] are now known to consist of equal numbers of AsO_6 octahedra and AsO_4 tetrahedra. The crystal structure of Sb_2O_5 was solved[11] as isostructural with B−Nb_2O_5 and consists of distorted corner- and edge-sharing SbO_6 octahedra. Oxides with a similar formula of elements belonging to the same group are good candidates for possible high-pressure polymorphs.

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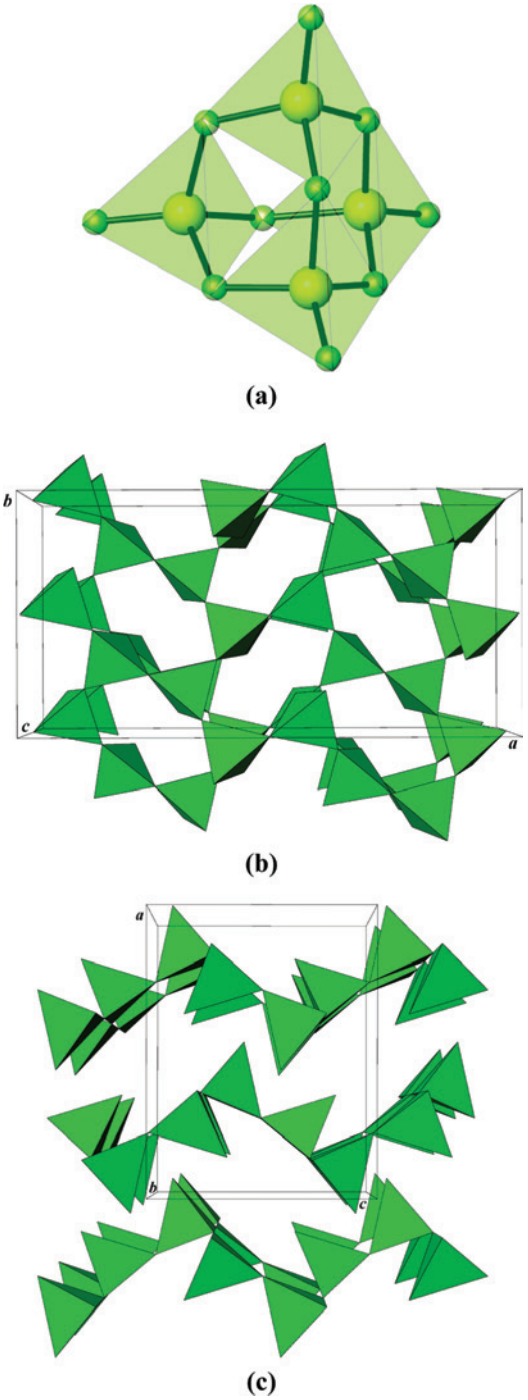


(a)

(b)

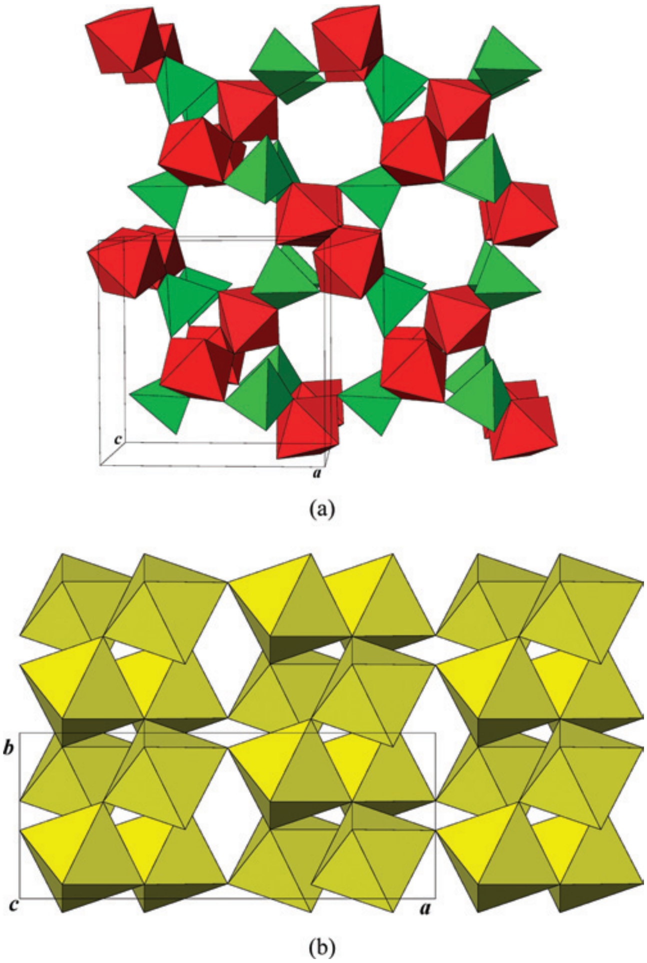
(c)

Figure 1. Crystal structures of (a) h-P_2O_5, (b) o-P_2O_5, and (c) o′-P_2O_5.

In this paper, we present a theoretical study of the relative stability at high pressures of the three known P_2O_5 phases and two hypothetical structures with the mixed octahedral−tetrahedral framework of As_2O_5 and the octahedral Sb_2O_5 net.

Experimental Section

Computational Details. We performed a series of first-principles calculations, including full structural optimizations, in order to study the stability and properties of the proposed phases up to 60 GPa. Density functional theory (DFT) calculations were carried out within the local density approximation (LDA) and Perdew−Burke−Ernzerhof generalized gradient approximation (GGA) using the ABINIT v4.6.5 code,[12] which implements plane-wave basis sets. We used nonlocal pseudopotentials (*s*, *p*, and *d* angular momentum projections) of the Troullier−Martins type.[13] The *k* point grids used to perform integrations in the Brillouin zone were selected with a smallest real-space vector larger than 20 bohr and, from among these grids, the one that reduces to the smallest number of *k* points when full symmetry is taken into account. A 50 Ha plane-wave cutoff was found to be sufficient for the relative enthalpy difference between phases, pressure, and bond length to converge better than 1 meV/molecule, 4×10^{-4} GPa, and 1×10^{-3} Å, respectively.



(a)

(b)

Figure 2. Crystal structures of (a) t-P_2O_5 and (b) m-P_2O_5.

Six phases were used as the starting point for structural optimization at zero pressure: the three known P_2O_5 phases (h, o, and o′), the o- and t-As_2O_5 structures changing As to P (hereinafter called o″- and t-P_2O_5, respectively), and the m-Sb_2O_5 phase changing Sb to P (hereinafter called m-P_2O_5). In the case of h-P_2O_5, optimization at zero pressure with the GGA functional leads to a divergent cell volume, whereas optimization at 1 GPa was successful and was subsequently used for the sake of comparison. For all of the phases, successive optimizations were performed at 5,

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Table 1. Cell Parameters at Room Pressure of Studied Phases

	h-P_2O_5	o-P_2O_5	o′-P_2O_5	t-P_2O_5	m-P_2O_5
cryst syst	trigonal	orthorhombic	orthorhombic	tetragonal	monoclinic
space group	*R*3*c* (No. 161)	*Fdd*2 (No. 43)	*Pnma* (No. 62)	$P4_12_12$ (No. 92)	*C*2/*c* (No. 15)
a (Å)	10.3035(9)[a]	16.314(2)[b]	9.193(9)[c]	8.572(4)[d]	12.646(1)[e]
LDA	9.9207	16.189	9.017	7.956	11.676
GGA	10.3495[†]	16.616	9.719	8.095	11.848
b (Å)		8.115(3)	4.890(4)		4.7820(4)
LDA		8.048	4.861		5.232
GGA		8.108	4.939		5.642
c (Å)	13.510(2)	5.265(9)	7.162(7)	4.636(3)	5.4247(5)
LDA	13.179	5.152	7.082	4.313	5.0342
GGA	13.653[†]	5.682	7.415	4.392	5.0932
β (deg)					103.91(1)
LDA					114.73
GGA					114.99

[a] Experimental data from ref 6. [b] Experimental data from ref 7. [c] Experimental data from ref 8. [d] Data of As_2O_5 at 538 K.[10] [e] Data of Sb_2O_5.[11] [†] Data at 1 GPa.

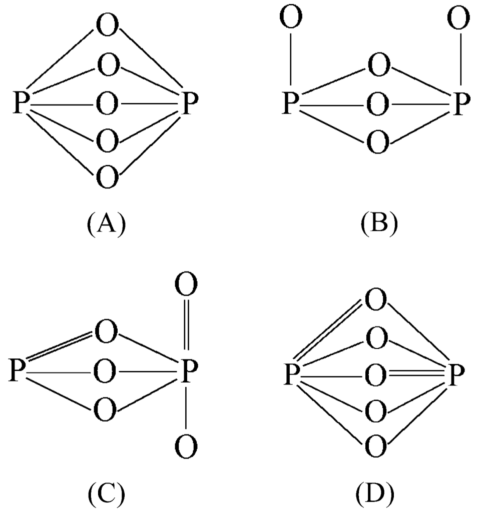

Figure 3. Four possible bond graphs for the P_2O_5 formula.

10, 20, 30, 40, 50, and 60 GPa. Bond-valence-sum (BVS) calculations[14] were carried out using the program *VaList*.[15]

Crystal Structures. The crystal structures of the three known P_2O_5 polymorphs are shown in Figure 1 (using coordinates from LDA optimization at zero pressure) and the hypothetical structures in Figure 2 [using coordinates from LDA optimization at zero pressure (part a) and 50 GPa (part b)].

h-P_2O_5. The hexagonal form is composed of discrete P_4O_{10} molecules (Figure 1a). These molecules can be thought of as being built of P_4 in tetrahedral form, with a P atom at each vertex of the tetrahedron. Six bridging O atoms are added after P−P bonding is turned off, with each O atom bridging two adjacent P atoms. The coordination of the P atoms is completed by adding a terminal oxygen, O(t), to each P atom to form PO_4 tetrahedra. The bridging P−O bonds, P−O(b), should have a valence close to 1.0 vu,[16] leaving the terminal bond with a valence of 2.0 vu. Accordingly, the P−O(t) bond is longer than P−O(b). These distances are respectively 1.429 and 1.562 Å[17] in the gas phase. Because there are two independent P atoms in the hexagonal solid, there are thus two P−O(t) distances: 1.431 and 1.434 Å.[6] The P−O(b) distances lie within the interval 1.588−1.597 Å.

o-P_2O_5 and o′-P_2O_5. This first orthorhombic polymorph is composed of 6-fold helices of PO_4 tetrahedra running along the *c* axis. Each PO_4 tetrahedron shares three corners with three adjacent helices forming a three-dimensional network (Figure 1b). The second polymorph, on the other hand, is composed of infinite two-dimensional sheets, running approximately parallel to the *bc* plane, of three corner-linked PO_4 tetrahedra forming six-membered rings (Figure 1c). In both cases, one O atom of each PO_4 group remains as terminal, with a P−O bond length shorter than that of the bridging bonds.

o-As_2O_5 and t-As_2O_5. As_2O_5 crystallizes into two pure crystalline varieties (orthorhombic and tetragonal). In both phases, the structural units consist of AsO_4 tetrahedra and AsO_6 octahedra linked together only by O corners (Figure 2a shows the isostructural tetragonal P compound), giving rise to cross-linked strands that define tubular cavities along the *c* axis. The tetragonal−orthorhombic phase transition in arsenic pentoxide has been found to be a proper ferroelastic transition.[18]

m-Sb_2O_5. Sb_2O_5 is known in a monoclinic form that is isostructural with B−Nb_2O_5 and consists of distorted corner- and edge-sharing octahedra. The structure can be described as being built up from rutile-like slabs of edge-sharing SbO_6 octahedra, two octahedra wide, and linked by corner sharing (Figure 2b shows the isostructural P compound). The O atoms are arranged in a slightly distorted hexagonally close-packed array.

Results and Discussion

Cell parameters of the P_2O_5 phases at zero pressure were collected and compared with the experimental values in Table 1. In the case of the three known phases, h-, o-, and o′-P_2O_5, as is usually observed, the LDA underestimates the lattice constants, whereas the GGA overestimates them. For the two hypothetical structures, the LDA values are still below those of the GGA, although the two sets of values are more similar. The analysis of the results showed that starting from the o-As_2O_5 cell and coordinates the optimized o″-P_2O_5 structure had a higher tetragonal symmetry and was identified as being identical with the t-P_2O_5 structure (analogous to the As_2O_5 high-temperature phase). On the other hand, analysis of the optimized m-P_2O_5 structure

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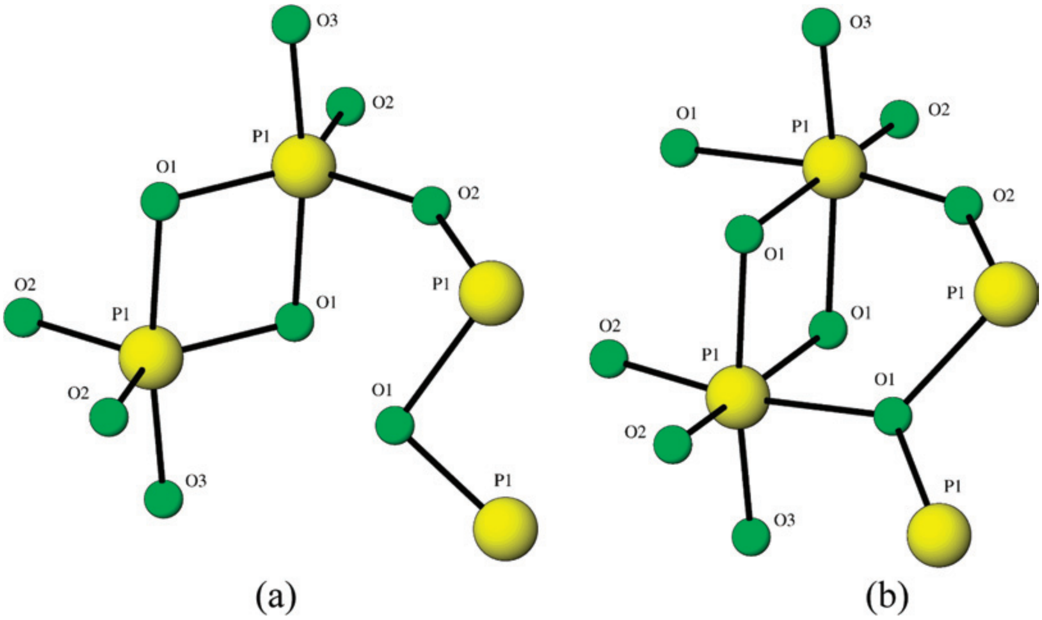

Figure 4. Representation of m-P_2O_5 (a) at room pressure and (b) at 30 GPa. Coordinates were taken from LDA optimizations.

Table 2. BVS Analysis of Hypothetical Phases at Room Pressure

		t-P_2O_5	m-P_2O_5
P(1)	LDA	5.06	5.02
	GGA	4.65	4.68
P(2)	LDA	5.13	
	GGA	4.83	
O(1)	LDA	1.89	1.87
	GGA	1.78	1.73
O(2)	LDA	2.10	2.16
	GGA	1.95	2.01
O(3)	LDA	2.05	2.00
	GGA	1.90	1.88

showed that, although symmetry was conserved, coordination around P atoms was 5- instead of 6-fold, being described by the bond graph[14] A of Figure 3, the simplest X_2O_5 bond graph that can be drawn. All known phases (h, o, and o′) of P_2O_5 show the bond graph B. The o″- and t-P_2O_5 phases belong to bond graph C, and m-P_2O_5 belongs to bond graph D.

Bond distances of known phases are very similar in the LDA theoretical calculation and the more recent experimental data. The P−O distances of nonbridging P−O bonds are longer than those of bridging P−O bonds, with these distances being within the intervals 1.56−1.59 and 1.43−1.45 Å, respectively, in the three phases. Subtle variations in these distances between compounds found experimentally are also confirmed by our theoretical calculations: h-P_2O_5 has the longest P−O(b) and the shortest P−O(t), 1.590 and 1.432 Å on average, respectively, while in o-P_2O_5, one of the P−O(b) distances (1.558 Å) is appreciably shorter than the other two (1.580 and 1.578 Å).

The optimization of the hypothetical o″- and t-P_2O_5 and m-P_2O_5 polymorphs from the structures of the As and Sb phases, respectively, produces important changes in cell dimensions and bond distances, as can be expected from the large differences in atomic radii. The cell volume (Table 1) is reduced 19.9% for t-P_2O_5 and 12.3% for m-P_2O_5. In the case of t-P_2O_5, this reduction is isotropic, around 7% on each axis. However, the situation is different for the m-P_2O_5 phase; whereas the a and c axes are reduced by 7.7 and 7.2%, respectively, the b axis increases by 9.4% and the β angle increases by 10.8°. This may be related to the fact that m-P_2O_5 optimized at zero pressure is formed by pentacoordinated phosphorus (Figure 4), as opposed to hexacoordinated phosphorus, thus changing the topology of the structure. In the logical absence of experimental data for these hypothetical compounds to compare our results with, we checked their validity using BVSs[14] around P and O atoms. The results are shown in Table 2. In the case of LDA, the BVSs are in good agreement with the theoretical valences of P (+5) and O (−2), whereas the performance of GGA is slightly worse. It should be borne in mind that bond parameters for P−O were obtained from an empirical fitting to P−O distances in tetrahedral phosphorus (because no other possibilities were available).

The o- and o′-P_2O_5 phases are very close in terms of energy; experimentally, the enthalpy of the o phase (relative to the P_4O_{10} formula unit) is only 10 kJ mol^{-1} (0.104 eV) less than that of the o′ phase.[3] Bearing in mind that the o′ phase is considered as the thermodynamic stable phase, it may be concluded that its stability at room temperature is driven by entropy. Because the effect of temperature is not contemplated in our calculations, all of the subsequent stability discussions shall refer to enthalpy differences. Furthermore, the results of our DFT calculations should be viewed within the context of the use of approximate functionals. LDA results arrange the phase stability at zero pressure as $t < o' < o < h < m$ for P_2O_5, with the difference between o′ and o being 27.1 kJ mol^{-1} (0.281 eV). GGA results arrange the phase stability as $o < o' < h < t < m$ for P_2O_5, with the difference between o′ and o being −9.9 kJ mol^{-1} (−0.103 eV), close to the experimental value. Quantitative differences with the h-P_2O_5 phase are less significant because of the molecular character of this phase and the

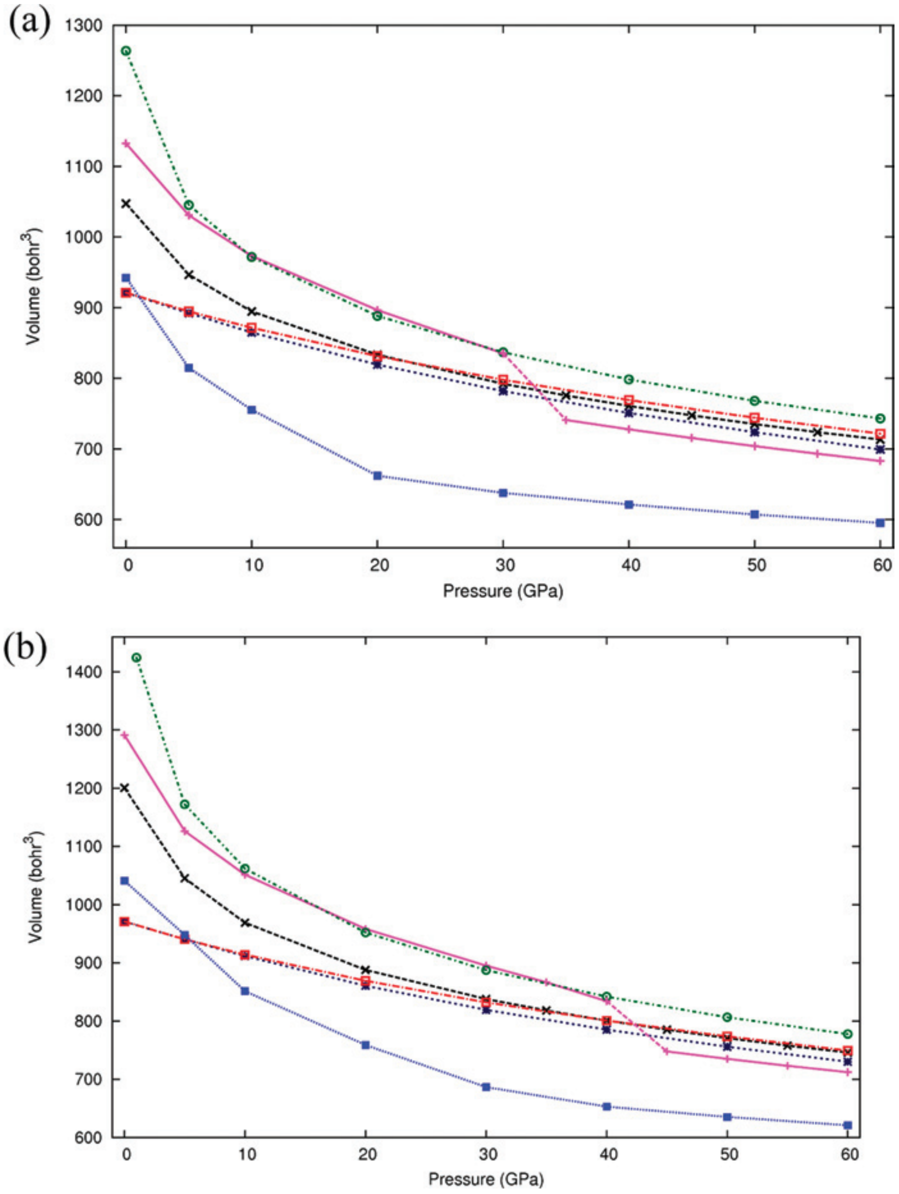

Figure 5. Volume vs pressure: (a) LDA; (b) GGA. Legend: (solid pink line with hash marks) o-P_2O_5, (broken black line with ×) o′-P_2O_5, (broken black line with asterisks) o″-P_2O_5, (dash-dotted red line with dotted ☐) t-P_2O_5, (dotted blue line with ■) m-P_2O_5, (dash-dotted green line with ○) h-P_2O_5.

known difficulties encountered by current DFT functionals in dealing with van der Waals interactions. Thus, GGA gives the correct ordering of known phases at ambient pressure and the expected ordering of hypothetical phases, less stable than known phases, with the dense monoclinic phase being the least stable.

The results of the pressure study are summarized in Figures 5 and 6. In general, although they are quantitatively different, LDA and GGA results show a similar trend, with GGA estimates approximately 10 GPa higher. As can be expected, the molecular form, h-P_2O_5, has the highest compressibility, whereas it is the mixed octahedral and tetrahedral framework of t-P_2O_5 and o″-P_2O_5 that has the highest bulk modulus. Although o″-P_2O_5 is converted to t-P_2O_5 when it is optimized at zero pressure, this is not the case at higher pressures, where o″-P_2O_5 is far from tetragonal symmetry, being capable of achieving a small volume because of its low symmetry. Both phases show PO_4 tetrahedra distorted at high pressures, with this distortion being greater in the case of the tetragonal phase. o′-P_2O_5 maintains its layered structure throughout the range of studied pressures, leading to a volume at 50 GPa similar to that of o″-P_2O_5. The tridimensional o-P_2O_5 phase, however, suffers a change in structure between 30−35 GPa (LDA) when the oxygen terminal joins with neighboring phosphorus to form a full corner-linked structure of distorted square pyramids with a pentacoordinated P atom at its center. This leads to a sudden decrease in the volume (shown in Figure 5 by a discontinuous pink line), thus making the resulting structure the second most compact at high pressures, though far less compact than the monoclinic phase, m-P_2O_5. After the structural change, the volume returns to varying smoothly with pressure. This behavior can be explained by assuming the existence of a new phase, with the same space group but lower enthalpy at high pressure than o-P_2O_5, which could be named o-P_2O_5(HP). The monoclinic phase, m-P_2O_5, changes gradually from pentacoordinated P (distorted trigonal

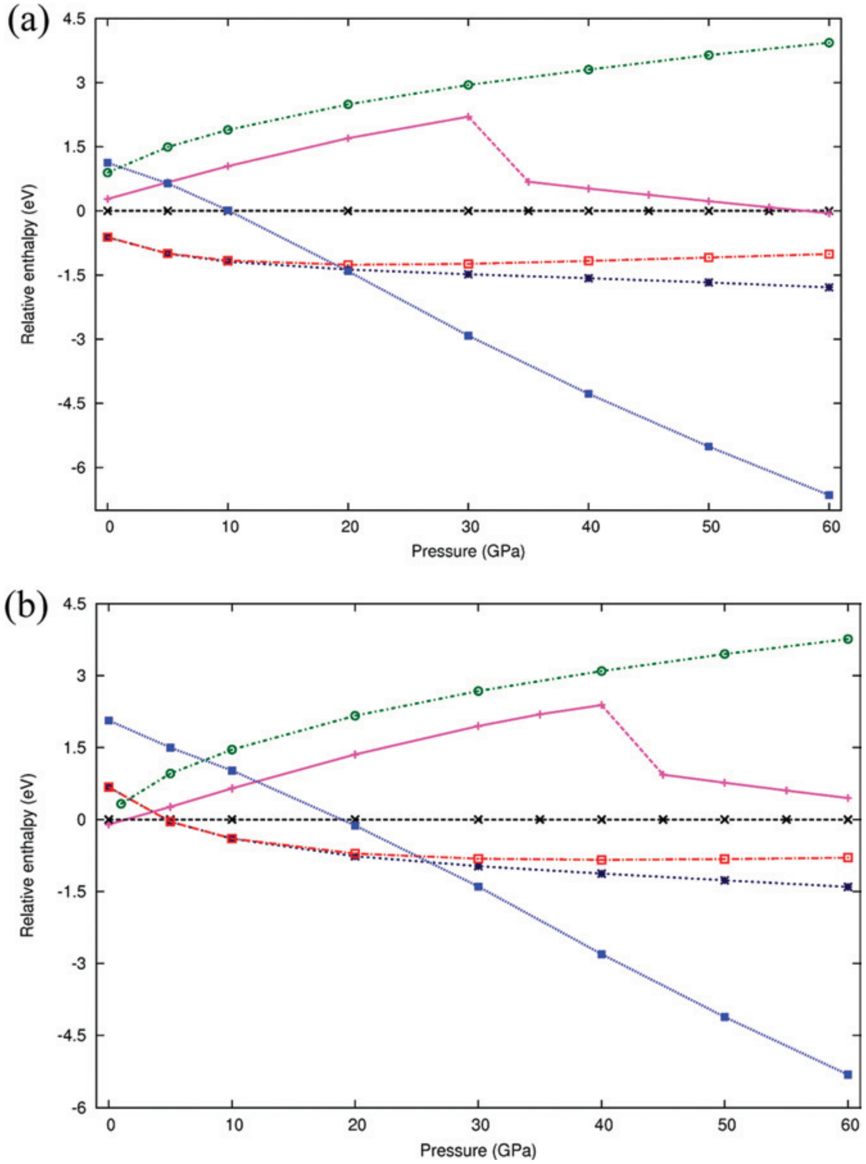

Figure 6. Relative enthalpy vs pressure: (a) LDA; (b) GGA. Legend: (solid pink line with hash marks) o-P_2O_5, (broken black line with ×) o′-P_2O_5, (broken black line with asterisks) o″-P_2O_5, (dash-dotted red line with dotted □) t-P_2O_5, (dotted blue line with ■) m-P_2O_5 (dash-dotted green line with ○) h-P_2O_5.

bipyramid) to hexacoordinated P (distorted octahedra). This change involves the O atoms at the edge-sharing link, which form a third bond with a neighboring P atom. At zero pressure, the P atom can be considered bonded to five O atoms (Figure 4a): two axial bonds (P−O1 1.750 Å; P−O3 1.617 Å) and three equatorial bonds (P−O1* 1.565 Å; P−O2 1.586 Å; P−O2* 1.591 Å) with the next closest contact at 3.020 Å. At 30 GPa (Figure 4b), the axial P−O1 bond is slightly longer (1.767 Å), whereas P−O3 is slightly shorter (1.586 Å). The three equatorial bonds previously described now have the following lengths: 1.681, 1.555, and 1.586 Å, respectively. A fourth equatorial bond appears with a third O(1) atom at a distance of 1.833 Å. The final octahedral topology is analogous to m-Sb_2O_5 and B−Nb_2O_5 and can be derived from rutile slabs[19] joined by corners. It is interesting to show that the same rutile blocks form corundum (Al_2O_3) when joined by face-sharing and TiO_2 rutile, the crystal structure of stishovite, a high-pressure form of SiO_2, when joined by edges. Thus, the high-pressure form of the oxides of Al, Si, and P will be formed by rutile blocks joined in different forms to accomplish the corresponding stoichiometry, from the lower oxygen content, face-sharing Al_2O_3, to the high oxygen content, corner-sharing P_2O_5, passing through edge-sharing SiO_2.

Figure 6 shows the enthalpies of the studied phases relative to that of o′-P_2O_5 as a function of the applied pressure. Although LDA and GGA disagree in terms of quantitative values, several common trends can be observed, with m-P_2O_5 being the most stable phase from 20−25 GPa upward. The o″- and t-P_2O_5 phases have similar enthalpies at low pressure, but o″-P_2O_5 is more stable at high pressure. The h- and o-P_2O_5 phases are destabilized as the pressure is increased, but a sudden relative stabilization of the o phase occurs between 40 and 50 GPa, corresponding to the four to five changes in the phosphorus coordination previously discussed.

In conclusion, our results indicate that the most stable form of P_2O_5 at high pressure (20−25 GPa) could be one with hexacoordinated octahedral phosphorus similar to the occurrence of octahedral silicon in the SiO_2 stishovite high-pressure phase, in agreement with the recent experimental findings in doped SiO_2 and $AlPO_4$.

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