

Prediction of Phase Transition and Ignition Sensitivity of Ammonium Periodate

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ABSTRACT: The ammonium periodate (NH₄IO₄, API) was theoretically investigated to understand the influence of the crystalline structure on mechanical ignition sensitivity. Density functional theory (DFT) calculations predicted polymorphism of API, showing a phase change from tetragonal (API_T) to monoclinic (API_M) starting at an external pressure of ~3 GPa. During this transformation, isolated IO₄⁻⁻ ions are linked to form a chain structure. Theoretically predicted optimal phase change temperature is ~450 K, where calculated enthalpy of phase transition ΔH_{phase} reaches a minimum of 4.6 kJ/mol. The API_M has properties correlated with ignition sensitivity, including low resistance to shear, with Young's modulus of 16.27 GPa compared with 25.99 GPa of API_T, and smaller electronic band gap, 3.51 eV compared with 4.46 eV



of API_T. The ΔH_{phase} is reduced from 7.3 kJ/mol at 0 K to 4.62 kJ/mol at 450 K, indicating that heat should facilitate the phase transition. The calculated enthalpy of decomposition (ΔH_{dec}) of -12 and -17 kJ/mol for API_T and API_M indicates a relatively small difference, suggesting that phase transition does not affect combustion performance. Therefore, the polymorphism induced by shear and facilitated by higher temperatures may be a powerful mechanism of ignition for API.

1. INTRODUCTION

Advancing material synthesis strategies to develop solid oxidizers is needed for power generation, such as in hypersonic applications. Halogenated compounds offer good potential because halogens act as aggressive oxidizers when combined with metal fuels, such as aluminum.¹ Halogenated oxidizers can also be formulated with a high oxygen content. One candidate material is ammonium periodate (NH₄IO₄, API), with an oxygen balance of +15%. API could be an alternative to ammonium perchlorate (NH₄ClO₄, APC) which has an oxygen balance of +27%, and both API and APC form ionic crystals from NH_4^+ and XO_4^- ions. However, there are hazards associated with API,^{2,3} particularly with respect to impact and friction² that limit its safe handling. Understanding the mechanisms responsible for API heightened ignition sensitivity is a goal of this study and will inform future material synthesis efforts.

Advancing new solid oxidizers based on halogenated compounds can be safely accomplished only if chemical properties responsible for heightened ignition sensitivity can be realized. Material stability leading to ignition sensitivity can be examined by analyzing the molecular lattice structure. The lattice structure of API is crystallized in a tetragonal system,⁴ while APC is in orthorhombic.⁵ However, despite structural similarities, these materials display different behavior with respect to mechanical stability, as shown in previous work.⁶ The oxygen balance, density, and heat of combustion for APC and API make them favorable candidates as a solid propellant

oxidizer,^{7,8} but the instability of API limits its functionality in power generation applications.

One of the main factors to define the properties of solid materials is the lattice structure, and crystalline phase transitions can have a deep influence on the macroscopic behavior. Probably the most recognized example is the allotropy of iron, which undergoes different crystallographic phases at different temperatures and pressures, resulting in different mechanical, thermal, and magnetic properties.9,10 Similarly, SnTe and SnSe were found to experience several crystallographic phase transitions at different pressures, and the geometric changes have a great effect on the electronic structure.¹¹ The insulator SnTe becomes a semiconductor and then metallic after phase transitions at 5.8 and 12 GPa, respectively. The semiconductor SnSe becomes semimetal at 6.2 GPa and metallic at 12.9 GPa, after phase transitions.¹¹ Another example of the influence of phase transition over the electronic structure is in the work of Wang et al.¹² on carbonized polymer dots. The authors found that the amorphous-to-crystalline phase transition influences the π -

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states and can be used to tune the room temperature luminescence. $^{\rm 12}$

Crystalline phase transition as a reactivity enhancer was studied by Maksimov et al.¹³ on different ferrovanadium alloys in a nitrogen atmosphere, and significant influence over burning rates was observed. The authors found that the alloy containing the phase σ -FeV burns 1.5 to 2 times faster than α -FeV and attributed that to the $\sigma \rightarrow \alpha$ phase transition at 1150 °C. In another study,¹⁴ it was found that the optimum burn of Ti-Cr alloys in a nitrogen atmosphere happens at 66% wt Cr. According to the authors, this concentration is in an interval of homogeneity of the λ -phase, and the combustion temperature is higher than the $\lambda \rightarrow \beta$ transition temperature. Therefore, the phase transition is the reason for the higher burning rate. In both cases, the crystalline transformation increases the reactivity by accelerating the decomposition reaction, producing higher burning processes. However, modifying the performance of energetic materials in a posterior combustion reaction is not the only possible effect.

Typically, solid-state reactions start with the loosening of the crystal lattices, ¹⁵ which often makes phase transitions a trigger of reactivity due to the accumulation of lattice defects. From a macroscopic perspective, the loosening of the crystal lattice increases the effective diffusivity, facilitating the transport of atoms in the reactants to rearrange and form products. This was observed by Alizadeh et al.¹⁶ on calcium silicate hydrates (C–S–H) reacting with silver nitrate (AgNO₃). They found that the reaction between these materials happens when the system is heated above the temperature at which AgNO₃ undergoes a phase change (~190 °C). According to the authors, the phase transition activates the reactivity of AgNO₃, and the reaction starts as soon as polymorphism occurs. Therefore, a phase transition may work as a reaction trigger.

If a given phase transition reduces the ignition temperature (T_{ign}) of a material to the current system temperature, this would promote its immediate ignition, as recently demonstrated by Yan et al.¹⁷ Their research found that some Al-, Mg-, lanthanide-, Fe-, Zr-, Ti-, Ni-, and Cu-based amorphous alloys can self-ignite upon exothermic crystallization. This happens because T_{ign} of the crystalline phase coincides with the crystallization temperature, regardless of the heating rate. This effect is not observed in pure metals because their $T_{\rm ign}$ values are normally much higher than the melting point. It is not the case with APC, which undergoes a crystallographic phase transition at the temperature of ~240 °C, changing from orthorhombic to cubic phase without experiencing peaks of reactivity.⁷ Moreover, an opposite behavior was observed, the rate of decomposition of APC decreased during the phase transition.⁷ APC can also change phase under pressure, as demonstrated by Kroonblawd et al.¹⁸ They found a phase transition at 4.5 GPa, where the lattice vectors of the initial orthorhombic cell (Phase I) vary substantially, with $a \rightarrow a'$ axis decreased by 14.2%, $c \rightarrow b'$ axis increased by 14.5%, and only b \rightarrow c' axis variation remaining constant in Phase II. The study by Hunter et al.¹⁹ classified Phase II as the Pnma space group. The pressure-induced phase transition was seen not to facilitate the decomposition, explaining the observed resistance to mechanical shock.

Differently from APC, the API is extremely sensitive to mechanical inputs, particularly friction. Ignition sensitivity indicates a possible low-pressure phase transition. The present work used density functional theory (DFT) calculations to predict and investigate the polymorphism and phase transformation of the known tetragonal API structure (API_T) . The crystalline structure, mechanical and thermal properties, and electronic structure were analyzed for the original API_T and newly discovered monoclinic phase to provide an understanding of API reactivity with respect to a phase transformation at the molecular level.

2. COMPUTATIONAL METHODS

Calculations were performed by using the Vienna ab initio simulation package (VASP), $^{20-23}$ which included structural relaxations, and the calculation of mechanical and electronic properties of API structures. The method used for electron exchange-correlation correction was the generalized gradient approximation method applying Perdew-Burke-Ernzerhof (PBE)²⁴ functional and D3 dispersion correction scheme by Grimme²⁵ (PBE-D3). The electronic structure was refined by performing single-point calculation on the PBE-D3 optimized structures by using more accurate screened hybrid functional of Heyd-Scuseria-Ernzerhof (HSE06).²⁶ Projector-augmented wave^{27,28} pseudopotentials were used for all atoms. The plane wave basis set cutoff was set to 600 eV, with the energy convergence limit of 10^{-7} eV. The geometry optimization was performed using the Gadget tool²⁹ with convergence criteria of 10^{-5} Hartree for energy and 4×10^{-5} Hartree/Bohr for energy gradient. The Brillouin zone was integrated with the Monkhorst–Pack³⁰ method in a $4 \times 6 \times 6$ k-points grid for the optimization of the crystallographic unit cell. In the case of optimization of supercells (used in an isostatic volume compression), $4 \times 4 \times 4$ k-point mesh was selected.

The thermal corrections were calculated by using the program Phonopy.³¹ In addition, rotational and translational contributions for molecules in the gas phase were obtained from calculations performed using the Gaussian package.³² To keep consistency within VASP calculations and ensure direct comparison among all data, the Gaussian calculations were performed with the same DFT functional (PBE-D3) and by taking the large atomic basis set of the def2-TZVP^{33,34} quality.

As API is a highly energetic material (such as APC) the reaction energy and enthalpy of the overall decomposition process were calculated according to eq 1, where X = Cl, I. The electronic energies of gaseous molecules (N₂, O₂, H₂O, I₂, and Cl₂) were calculated by VASP on an isolated molecule inserted in a 40 × 40 × 40 Å periodic box with Γ -point sampling.

$$NH_4 X O_4(s) \rightarrow 0.5 X_2(g) + 0.5 N_2(g) + O_2(g)$$

+ $2H_2 O(g)$ (1)

The overall decomposition energy (ΔE_{dec}) is calculated according to eq 2 as

$$\Delta E_{\rm dec} = \sum E(\rm products) - \sum E(\rm reactants)$$
(2)

To obtain the enthalpy of thermal decomposition (ΔH_{dec}) , calculations were performed for all of the species in eq 1. ΔH_{dec} (eq 3) is defined as a sum of ΔE_{dec} and the net enthalpy correction $(\Delta H_c, \text{ eq } 4)$, which includes the *pV* term for molecules in the gas phase. The enthalpy correction (H_c) was calculated using the software package Phonopy³¹ for crystals, and the Gaussian program suite was used for gaseous molecules to include rotational and translational contributions. Reactions were calculated in a temperature range of 100–1000 K.

$$\Delta H_{\rm dec} = \Delta E_{\rm dec} + \Delta H_c \tag{3}$$

$$\Delta H_c = \sum H_c(\text{products}) - \sum H_c(\text{reactants})] + \Sigma nRT$$
(4)

where $\sum nRT$ is a volume correction term with $\sum n$ being a sum of moles of gaseous products.

Further, elastic constants (C_{ij}) were calculated by VASP using the stress-strain approach.^{35,36} For tetragonal API_T phase, relevant C_{ij} are C_{11} , C_{33} , C_{44} , C_{66} , C_{12} , and C_{13} , while for the monoclinic API_M phase, C_{11} , C_{22} , C_{33} , C_{44} , C_{55} , C_{66} , C_{12} , C_{13} , C_{23} , C_{15} , C_{25} , C_{35} , and C_{46} are relevant. The elastic moduli equations and mechanical stability evaluation followed the work by Wu et al.³⁷ Using the Voigt-Reuss-Hill (VRH) average method^{38,39} using C_{ij} , corresponding bulk (K), shear (G), and Young's (Y) moduli, and Poisson's ratio (ν) were obtained as the arithmetic averages of Voigt (K_{V} , G_{V} , Y_{V} , and ν_{V}) and Reuss (K_{R} , G_{R} , Y_{R} , and ν_{R}) methods. To obtain moduli and ν for the new API_M phase, equations were used according to the work by Watt⁴⁰ suggested for polycrystals with monoclinic symmetry. The effect of the pressure on the structural changes of API was investigated by using the isostatic compression of the 1 × 2 × 2 supercell up to 30% volume reduction for both API phases.

In order to understand the thermodynamics of the structural transformation, the enthalpy of phase transition (ΔH_{phase}), corresponding to the previously known crystallographic tetragonal (API_T) to the predicted monoclinic (API_M), is calculated through eq 5.

$$\Delta H_{\text{phase}} = [E(\text{API}_{\text{M}}) + E_{\text{hp}}(\text{API}_{\text{M}})] - [E(\text{API}_{\text{T}}) + E_{\text{hp}}(\text{API}_{\text{T}})]$$
(5)

The electronic band gap (Δ_g) and its changes with respect to pressure were analyzed for the compression series. Furthermore, the detailed analysis of electronic structure of both API structures was performed through density of electronic states (DOS) and partial DOS (PDOS), band gap (Δ_g) , electronic electron affinity (EA), ionization potential (IP), electronic hardness (η) and softness (S), chemical potential (μ), and electrophilicity index (ω). Corresponding formulas are given in eqs S1–S6 in the Supporting Information (SI).

3. RESULTS AND DISCUSSION

3.1. Pressure-Induced Phase Transition. The known experimental crystallographic system of API is tetragonal (API_T, Figure 1 top). In our previous work, the API_T structure was fully relaxed (including cell parameters) at the PBE-D3 level.⁶ The optimized API_T unit cell was then used to generate a $1 \times 2 \times 2$ supercell with 16 formula units (Z), which was taken for further calculations under isostatic compression (using $4 \times 4 \times 4$ k-point mesh). In these calculations, atoms and a cell shape (at fixed cell volume) were relaxed using 12 isostatic compression steps evenly distributed from 0 to 30% compression ratio (CR), plus two additional steps around the observed local energetic minimum. CR is defined as the volume decrease as a percentage of initial volume, according to eq S7 in SI. The change of the electronic energy and pressure with respect to the isostatic compression is presented in Figure 2. As observed in Figure 2a, the electronic energy of the API_T (blue curve) monotonically increased up to CR ${\sim}23\%$. Then, it dropped down, starting to increase again up to the last compression step (CR = 28%). The external pressure (Figure 2b) follows a similar trend as the energy dependence. The unit

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Figure 1. Two different views of optimized unit cells of API_T and API_M . Iodine (purple), oxygen (red), nitrogen (blue), and hydrogen (white).

cell vectors and angles keep the tetragonal shape up to CR ~20%, and then angle β shifts down, turning the unit cell into a monoclinic structure. The lengths of *b* and *c* diverge while *a* is decreased. The evidence of a local minimum in both electronic energy and pressure and the significant changes in the lattice parameters indicate that there is a phase transition to a new monoclinic API structure (API_M). The structure achieved at the CR 25% is shown in Figure S1 (top) in the Supporting Information (SI). The most important structural change under pressure is the linking of the isolated tetragonal IO₄⁻ ions and formation of double chain with 6-fold coordination of iodine atoms as visible in Figures 1 (bottom) and S1. More details about the structural changes will be discussed later.

Achieving the phase change, the new monoclinic API supercell structure achieved at a CR of 25% was used to create a new monoclinic unit cell (Z = 4) comparable to the original unit cell of the API_T structure. This new API_M structure was again fully relaxed without any geometric constraints under the same conditions as the original API_T structure. The result of this geometry relaxation is visualized in Figure 1 (bottom). The comparison of optimized cell vectors and volume with the original API_T structure (Table 1) showed that the unit cell (UC) volume of the monoclinic phase is about 2.5% larger than that of the API_T, meaning that API_M has a slightly lower density (Table 1). The difference in energy between API_T to API_M is only 5.13 kJ/mol per structural formula, showing that the newly discovered phase could also be stable at the normal pressure being only slightly less stable than the original API_T.

Comparison of the optimized cell parameters (Table 1) shows that fully relaxed API_M does not follow all trends observed in the compression of API_T. Initially, vectors *a* and *b* were shortened while vector *b* was elongated during compression (Figure 2). However, the relaxed API_M structure (zero pressure) has shorter *c* (due to the formation of IO₄⁻ chains) but elongated *a* and *b* (Table 1). The monoclinic configuration of the unit cell is kept after optimization with β = 82.77° in the direction of the chains.

The bonding scheme of API_T is presented in Figure 3. Isolated IO_4^- units have a tetrahedral symmetry with all I–O bonds of the same length (1.796 Å). The hydrogen bonds in API_T between IO_4^- and neighboring NH_4^+ ions are also of the same length, 1.830 Å (Figure 3a). The bonding in API_{MP} on



Figure 2. Changes in energy, pressure, and lattice parameters of API_T and API_M under different CRs: (a) energy curves are relative to the energy of relaxed API_T , (b) external pressures (API_T and API_M), (c) lattice vectors (API_T), and (d) unit cell angles (API_T), (e) lattice vectors (API_M), and (f) unit cell angles (API_M).

the other hand, has a more complex structure (Figures 3b,c and 1 bottom). In the formed double IO_4^- chain, the tetrahedral coordination of the I atom changed to 6-fold coordination having different I–O bond lengths. The terminal oxygen atoms of the IO_4^- chains hold I–O bonds of 1.787 and 1827 Å, respectively (Figure 3b). The bridging oxygen atoms in the I–O–I chains show I–O bonds ranging from 1.960 to 2.053 Å. The hydrogen bonding also changed in API_M comparing to API_T (Figure 3c). Several shorter hydrogen bonds are formed between IO_4^- chains and surrounding NH₄⁺ ions in a range of 1.713–1.822 Å. Complex and asymmetric geometry of API_M leads to more complex structural and electronic configurations, as discussed later.

The theoretical X-ray powder diffraction (XRD) plots obtained by using the VESTA software⁴¹ for both API phases are presented in Figure S2 (SI). An evident difference in the peak positions is observed with the phase transition, particularly the (1,1,0) and (1,0,1) peaks at $2\theta = 16^{\circ}$, and (2,1,1) at $2\theta = 25^{\circ}$, replaced by (1,1,0) and (2,0,0) at $2\theta = 14^{\circ}$, without other major peaks.

The relaxed API_M structure was then used for the isostatic compression in the same way as for the API_T structure– compressing a $1 \times 2 \times 2$ supercell with each compressing point relaxed at the constant volume in the $4 \times 4 \times 4$ *k*-point

scheme. The results are presented in Figure 2. The relative energy of the API_M structure increases with the increasing CR being above the relative energy of the API_T structure up to a CR \sim 10%. At this point, the energy and pressure curves of the new API_M phase show a certain break in the trend (Figure 2a,b), indicating a pressure-induced phase transformation of the monoclinic structure (\sim 3 GPa pressure). The breaks in energy and pressure observed at a CR of ~10% correspond to structural modifications of the API_M unit cell, evidenced by visible breaks on lines representing a and c vectors (Figure 2e) and the β angle (Figure 2f). Inspection of the structure at this point showed that the phase transformation is due to reorientation of the IO₄⁻ chains. They changed from the alternate disposition along the *ab* plane (Figure 1, bottom) to a side-by-side configuration along the b direction (Figure S1, bottom). The energy curves of both API phases crossed at CR of ~10%, and the new API_M phase formed at this point became energetically more stable than the original API_T structure. This is also displayed by the energy difference between the API_M and API_T phases (ΔE_{phase}) presented in Figure 4.

3.2. Mechanical Properties. PBE-D3 calculated elastic constants C_{ij} for both API phases are collected in Tables S1 (API_T) and S2 (API_M) of the SM, respectively. Corresponding mechanical parameters calculated from C_{ii} constants, partic-

Table 1. Structural Data of API_T (Experimental⁴ and Theoretical⁶) and New API_M Phase (Theoretical, This Work)^{*a*}

	$API_T (exp.)^4$	$API_T (DFT)^6$	API_M
a (Å)	12.574	12.146	12.621
b (Å)	5.993	6.065	7.389
c (Å)	5.993	6.103	4.984
α (°)	90.00	89.99	90.11
β (°)	90.00	90.00	82.77
γ (°)	90.00	90.00	90.04
vol. (Å ³)	451.5	449.9	461.1
ho (g/cm ³)	3.07	3.09	3.01
ΔE per Z (kJ/mol)		0.00	5.13
bond length (Å)			
I–O	1.772	1.796	1.787
			1.827
			1.960
			2.053
hydrogen bond length	(Å)		
О…Н		1.830	1.713
			1.804

"Bonds and hydrogen bonds of both API phases are displayed in Figure 3.

ularly bulk (K, K_V , K_R), shear (G, G_V , G_R) and Young's (Y, Y_V , Y_R) moduli, Poisson (ν , ν_V , ν_R) and Pugh (K/G) ratios, and Cauchy pressure ($C_{12}-C_{44}$), are presented in Table 2. The API_M has considerably lower resistance to shear, with G = 5.89 GPa for API_M against 9.75 GPa for API_T. The main contribution to reduced shear resistance is from a C_{55} of only 1.1 GPa in the *ac*-plane (Table S2). The C_{55} corresponds to the shear around the angle β , in the direction of the IO₄⁻ chains, implying that the API_M crystalline structure can easily shear in this direction (shear is typically referred to as a reactive behavior in crystalline solids^{42,43}).

Analysis of the values of *K* and *Y* presented in Table 2 showed a relatively small reduction in *K* from API_T to API_M (25.87 \rightarrow 22.80 GPa) but a significant reduction in *Y*, changing from 25.99 to 16.27 GPa. As *K* is related to volumetric strain while *Y* is related to unidirectional strain, the phase change has a more negative impact on the ability of API to keep its shape than to keep its volume. The *K/G* (Pugh's) ratio reveals a more ductile behavior of the new API_M phase with *K/G* = 3.87 against 2.65 for API_T. Although slightly smaller, the Cauchy pressure $C_{12}-C_{14}$ of API_M is still high, with 10.1 GPa, compared to the 13.1 GPa of API_T. Therefore, phase transition does not significantly affect the ductility of API. Since localization of energy due to plastic shear is seen to be an important ignition mechanism,^{42,43} a smaller *Y* naturally contributes to the sensitivity to friction. As a sample of API_T



Figure 4. Energy difference between API_T and API_M for different compression rates.

Table 2. Calculated Mechanical Parameters: Bulk (K), Shear (G), and Young's (Y) Moduli, Poisson's (ν) and Pugh's (K/G)⁴⁴ Ratios, and Cauchy Pressure⁴⁵ (C₁₂-C₄₄) for API_T and API_M^a

feature	API_T	API_M	feature	API_T	API_M
K [GPa]	25.87	22.80	Y [GPa]	25.99	16.27
K _V [GPa]	26.23	22.87	Y _V [GPa]	27.92	23.92
$K_{\rm R}$ [GPa]	25.51	22.73	$Y_{\rm R}$ [GPa]	24.03	7.96
G [GPa]	9.75	5.89	ν	0.33	0.38
$G_{\rm V}$ [GPa]	10.56	9.02	$ u_{ m V}$	0.323	0.326
$G_{\rm R}$ [GPa]	8.94	2.76	$ u_{ m R}$	0.343	0.442
K/G	2.65	3.87	$C_{12} - C_{44} [{ m GPa}]$	13.1	10.1
^a Values for API _T were taken from previous work. ⁶					

is subject to shear, the spots of concentration should change to $API_{M\nu}$ which causes the shear strain to be intensified (smaller *Y*), easily yielding to plastic deformation, increasing the temperature, and finally igniting. The slight increase in Poisson's ratio (ν , Table 2), from 0.33 (API_T) to 0.38 (API_M), also points to a less stable strain behavior of $API_{M\nu}$ with more lateral deformation.

3.3. Electronic Structure. The pressure dependences of the PBE-D3-calculated Δ_g of the isostatically compressed API_T and API_M phases are presented in Figure 5 (HSE06 results for the optimized API_T and API_M structures are discussed later). The value of Δ_g for API_T is slightly upshifted at the first step and then kept practically constant until CR ~22%. After the phase transition point, the band gap significantly dropped, achieving a similar value as the API_M. Starting with the fully relaxed new API_T phase, the Δ_g value decreases and is always below the Δ_g values of the API_M structure until the transition point, after which both curves cross.

The single-point calculated HSE06 orbital contributions to the electronic density of states (PDOS) of the fully relaxed



Figure 3. Calculated (a) I-O and O···H bonds of API_T and (b) I-O and (c) O···H bonds of API_M.



Figure 5. Trends of PBE-D3-calculated $\Delta_{\rm g}$ with respect to increasing compression for $\rm API_T$ and $\rm API_M$ phases.

 $\mbox{\rm API}_{\rm T}$ and $\mbox{\rm API}_{\rm M}$ structures are compared in Figure 6. The greater complexity of the oxygen states of the new API_M phase reflects the changes in I–O bonding (Figure 3). Moreover, the crystalline phase transition resulted in the smoothening of the sharp oxygen peak below the Fermi level, and a more scattered distribution of oxygen states between -8 and -1 eV, and fewer electrons in the highest occupied orbitals. These features indicate that API_M could be less reactive. However, API_M has a smaller Δ_g of 3.51 eV compared to 4.46 eV for API_T (Table 3), implying an overall higher API_M reactivity. As discussed in the literature,46-48 a small band gap is strongly associated with ignition sensitivity, and the smaller Δ_g of API_T is in contrast to APC and was used to explain API sensitivity in previous work.⁶ The analysis of the PDOS indicates that API_M tends to be even more sensitive to mechanical stimuli than API_T, and therefore, the phase transition favors its spontaneous ignition.

The calculated (HSE06) electronic parameters, particularly IP, EA, ω , η , μ , and S, are presented in Table 3. Following the trend seen in the DOS, API_M is more electronically active, with electronic indexes associated with easier excitation and more sensitivity to charge changes. Beyond the smaller Δ_{g} , the higher IP indicates a more energetic state of the highest occupied orbitals of API_M. The greater S and lower η indicate more sensitivity to changes in the electronic charge of the system.

The calculated Bader charges per species are presented in Table 4. There is not a significant difference in the charge

Table 3. IP, EA	Calculated	Using HSE06	Functional	and
Indexes of ω , η	, S, and μ f	or API _T and A	PI _M ^a	

	API_T	API _M
Δ_{g}	4.4614	3.5099
IP	-1.8422	-1.4814
EA	2.6192	2.0285
ω	0.034	0.021
η	2.231	1.755
S	0.448	0.570
μ	0.389	0.274
^{<i>a</i>} All values are in eV	•	

distributions between both phases. Calculated charges for $IO_4^$ and NH_4^+ ions show the ionic character of both API structures. The main changes in atomic charges are for iodine which goes from 3.032 to 3.165 lel for API_T and API_M, respectively, and for nitrogen which goes from -1.202 (API_T) to -1.330 lel (API_M). While the average charge of all oxygen atoms varies from -0.972 to -1.003 lel for API_M comparing to API_T, the oxygen atoms in the chain (O_{chain}) have more interaction than the terminal ones ($O_{terminal}$) due to the bridging between iodines, with -0.955 and 1.015 lel, respectively. The charges of the hydrogen atoms change from 0.515 lel (API_T) to 0.545 lel (API_M).

3.4. Thermodynamic Properties. The trends of ΔH_{phase} , eq 5, and corresponding $T\Delta S$ with respect to temperature are presented in Figure 7. The ΔH_{phase} curve (Figure 7a) indicates that from 0 K to room temperature the thermal energy difference from the tetragonal to monoclinic phase drops from 7.3 to 4.8 kJ/mol, reaches a minimum at about 450 K, and then slowly increases again, indicating an optimal theoretical temperature of phase transition at ~450 K. The $T\Delta S$ results (Figure 7b) show a smaller entropy contribution for API_M at the whole temperature range, and the difference increases with temperature. Both results indicate that the increase in temperature could contribute to the phase transition.

The total phonon density of states (PhDOS) obtained by Phonopy calculations is presented in Figure 8. Detailed analysis of PhDOS of API_T was done in our previous work.⁶ Here, we compare only the main differences in the PhDOS spectra of the two API phases. In the middle region (1000– 2000 cm⁻¹), a similar pattern is observed for both phases, an



Figure 6. Top: calculated DOS at the HSE06 level per element species for API_T and API_M . Bottom: corresponding PDOS spectra for the O-p orbitals.

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Table 4. Bader Charges Are Given in lel for API_T and API_M



Figure 7. Calculated (a) ΔH_{phase} (eq 5) and (b) $T\Delta S$ for both phases of API. $T\Delta S$ data for API_T from previous work.⁶



Figure 8. PhDOS for (a) API_T and (b) API_M. Data for API_T from previous work.⁶ Calculated using the Phonopy package.³¹

intensive peak near 1450 cm⁻¹, and another one, less intensive, at ~ 1700 cm⁻¹. They correspond to the asymmetric and symmetric bending modes of the NH4+ ion. A different behavior is observed in the high-frequency region (>3000 cm⁻¹) that covers stretching modes of the NH₄⁺ ion. The seemingly single peak observed at $\sim 3200 \text{ cm}^{-1}$ for API_T (Figure 8a) was identified as a mixture of symmetric and asymmetric stretching modes of the highly symmetric NH₄⁺ ion (T_d symmetry). On the other hand, in the monoclinic phase (Figure 8b), the T_d symmetry of the NH_4^+ ion is reduced due to the different hydrogen bonding to IO₄⁻ chain as discussed earlier and shown in Table 1. Thus, the band at 3200 cm^{-1} is split into bands at ~3300 cm⁻¹ (asymmetric N-H stretching) and two bands between 3000 and 3100 cm^{-1} for symmetric stretching. The most significant difference between the tetragonal and monoclinic phases is in the low-frequency region (<1000 cm⁻¹). Both symmetric and asymmetric stretching modes of the IO_4^- ion in API_T are located as a single peak near 800 cm⁻¹, while for the API_M phase, there are two separate peaks in the same region for asymmetric (810 cm⁻¹) and symmetric (720 cm⁻¹) modes. The low-frequency vibrations of API_T are all located below 500 cm⁻¹, with a complex structure of peaks. In this part of the spectrum, various modes are mixed such as hindered rotations and translations of NH4⁺ and IO4⁻ ions and bending modes of IO_4^- ion The monoclinic phase has an even more complex

structure of the low-frequency modes that is broader than that for the API_T (ranging from 0 to 600 cm⁻¹). In this range, hindered rotations and translations of IO₄⁻ ions are converted to the skeletal vibrations of the IO₄⁻ chain such as I–O–I bridging modes. The wider and more spread-out distribution of modes in the low-frequency region indicates a less stable profile of the new API_M phase facilitating its easier ignition compared with the API_T phase.

Concerning combustion properties, API has 6.7% of nitrogen, 60.7% of iodine, and 30.6% of oxygen by mass; therefore, good oxidation properties are expected, matching the highly reactive behavior observed.^{2,3} However, in our previous work, we showed that all theoretically predicted combustion metrics for API_T are less than for APC,⁶ as presented in Table 5. The same is seen for the API_M phase, as calculated in the current work. API_M performance is very similar to API_T, with ΔQ_v of 89 kJ/mol, T_{det} of 1040 K, V_{gas} of 844 L/kg, p_{det} of 17.8 GPa, and Vel_{det} of 5499 m/s.

The ΔE_{dec} , eq 2) for the overall decomposition of both API phases (eq 1) are also given in Table 5. Clearly, the decomposition reaction is energetically "neutral" as shown by a minimal difference between the energies of reactants and products. The small difference between API_T and API_M corresponds to a slightly higher stability of the API_T phase. To characterize the overall decomposition process, the ΔH_{dec} (eq 3) was calculated for a temperature range of 100–1000 K.

Table 5. PBE-D3 Calculated Energies of Decomposition $(\Delta E_{dec}, \text{Eq 2})$, Heat of Combustion (ΔQ_v) , Detonation Temperature (T_{det}) , Volume of Gaseous Products (V_{gas}) , Detonation Pressure (p_{det}) , and Detonation Velocity (Vel_{det}) Calculated by NASA CEA^{49a}

	API_T	API_M	APC
$\Delta E_{\rm dec} \ ({ m eq} \ 1) \ ({ m kJ/mol})$	5.9	0.8	-77.5
$\Delta Q_{\nu} \ (\mathrm{kJ/mol})$	81	89	139
$T_{\rm det}$ (K)	1020	1040	1050
$V_{\rm gas}~({\rm L/kg})$	844	844	848
p _{det} (GPa)	17.5	17.8	26.3
Vel _{det} (m/s)	5486	5499	7897

 $^a\mathrm{Combustion}$ data for API_T and APC were taken from previous work. 6

The results are displayed in Figure 9. For comparison, ΔH_{dec} of APC is included, as well. Evidently, all decomposition reactions



Figure 9. Calculated ΔH_{dec} for API_T, API_M, and APC.

are exothermic in the whole temperature range, with API releasing considerably less energy, following the trend of calculated ΔQ_v observed in previous work.⁶ Both API phases display the lowest energy release at room temperature (highest $\Delta H_{\rm dec}$), but become more intense between 350 and 400 K, while $\Delta H_{\rm dec}$ of APC starts shifting down only after 450 K.

Summarizing, calculated combustion properties and ΔE_{dec} (Table 5) or ΔH_{dec} (Figure 9) show that the crystallographic phase transition does not significantly affect the overall combustion performance of API, with similar values and trends for all calculated properties. The comparison with APC also shows that while APC and both phases of API have similar combustion properties, API decomposes less exothermically and demonstrates an overall lower heat of combustion. To promote power generation, greater exothermicity is favorable but stability and reduced ignition sensitivity are necessary for safe handling in any application.

4. CONCLUSIONS

DFT calculations were performed on API to investigate its structural, mechanical, electronic, and thermodynamic properties and their implications on API ignition sensitivity. The main discovery of the study was an observation of the new phase upon the application of the isostatic compression, where known tetragonal phase (API_T) was changed to monoclinic phase (API_M). In the new phase, IO_4^- was rearranged by forming double chains bridged by oxygen atoms. Moreover, the 4-fold coordination of the I atom changed to 6-fold coordination. Further, an additional phase transformation of the new API_M phase was observed at a low pressure of ~3 GPa.

This low-pressure phase change was related to the rearrangement of the IO_4^- chains. After that, the new API_M phase becomes energetically more stable than the original tetragonal phase.

The formation of new structural arrangements in the API_M phase affected the electronic density of states, where oxygenoccupied states were more spread than those in API_T . The monoclinic phase also has a smaller band gap (3.51 eV) compared to 4.46 eV of API_T . This indicates higher sensitivity of the monoclinic phase.

The monoclinic phase is predicted to have very similar energy to API_T, with phase transition enthalpy (ΔH_{phase}) of only 4.8 kJ/mol at 300 K. The value of ΔH_{phase} is predicted to have a minimum of 4.6 kJ/mol around 450 K, where API_M is most stable in comparison with API_T. At this temperature, API should be the optimal phase transition temperature.

The decomposition energy (ΔE_{dec}) of API was predicted to be 5.9 and 0.8 kJ/mol for tetragonal and monoclinic phases, which is much less than -77.5 kJ/mol for APC. The enthalpy of decomposition (ΔH_{dec}) was calculated for temperatures in the range of 100–1000 K. At room temperature, API_T has ΔH_{dec} of -12 kJ/mol and API_M has -17 kJ/mol while APC has -104 kJ/mol. The more exothermic decomposition of APC agrees with previously reported calculated heat of combustion.

Finally, the modeling results demonstrate a possible polymorphism of ammonium periodate that strongly influences mechanical sensitivity, especially friction. As a sample of API_T is subject to shear, localized phase changes to API_M intensify the shear strain and yield plastic deformation, a temperature increase, and ignition. The model shows that a change in crystalline lattice structure is responsible for molecular-level instabilities that lead to ignition sensitivity. Results shown here will have an impact on synthetic chemists who are developing new solid oxidizers by providing insight into lattice structure properties that promote ignition sensitivity.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.3c07439.

Structures obtained at $1 \times 2 \times 2$ supercell compression of API_T at CR = 25% and API_M at CR = 11.5%; equations of electronic properties; definition of the compression ratio (CR); theoretical XRD of API_T and API_M; and relevant elastic constants (C_{ij}) of API_T and API_M (PDF)

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Notes

The authors declare no competing financial interest.

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