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## 1. Introduction

The structure and properties of actinide-based oxides have been extensively studied using many theoretical<sup>1–5</sup> and experimental approaches<sup>6–17</sup> due to their technological importance in the nuclear material cycle. However, protactinium pentoxide ( $Pa_2O_5$ ) is an underexplored area of the protactinium–oxygen phase diagram, and its practical applications have received little attention owing to its instability relative to the fluorite and layered protactinium oxides.<sup>18,19</sup> One of its intriguing features is that it represents the composition of a transition point between the fluorite and layered protactinium oxides, with reports of it forming in both types of structures. Since reports about the structure and properties of  $Pa_2O_5$  are extremely limited in the literature, most likely owing to its scarcity, high radioactivity and toxicity, theoretical prediction provides a way to predict and study the structure and properties of this material.

In the actinide elements, uranium (U) exhibits rich oxide phases, such as  $UO_2$ ,  $U_2O_3$ ,  $U_2O_5$ , and  $U_3O_8$ ,<sup>20-27</sup> and its two

# Theoretical prediction of some layered Pa<sub>2</sub>O<sub>5</sub> phases: structure and properties†

Tao Liu, 🔟 ab Shichang Li, 🔟 a Tao Gao\*a and Bingyun Ao 🔟 \*c

Density functional theory (DFT) was used to predict and study protactinium pentoxide ( $Pa_2O_5$ ), which presents a fluorite and layered protactinium oxide-type structure. Although the layered structure has been observed with the isostructural transition Nb and Ta metal pentoxides experimentally, the detailed structure and properties of the layered  $Pa_2O_5$  are not clear and understandable. Our theoretical prediction explored some possible stable structures of the  $Pa_2O_5$  stoichiometry according to the existing  $M_2O_5$  structures (where M is an actinide Np or transition Nb, Ta, and V metal) and replacing the M ions with protactinium ions. The structural, mechanical, thermodynamic and electronic properties including lattice parameters, bulk moduli, elastic constants, entropy and band gaps were predicted for all the simulated structures.  $Pa_2O_5$  in the  $\beta$ - $V_2O_5$  structure was found to be a competitive structure in terms of stability, whereas  $Pa_2O_5$  in the  $\zeta$ - $Nb_2O_5$  structure was found to be the most stable overall. This is consistent with Sellers's experimental observations. In particular,  $Pa_2O_5$  in the  $\zeta$ - $Nb_2O_5$  structure is predicted to be charge-transfer insulators. Furthermore, we predict that  $\zeta$ - $Nb_2O_5$ -structured  $Pa_2O_5$  is the most thermodynamically stable under ambient conditions and pressure.

> prominent oxidation states are U<sup>4+</sup> and U<sup>6+</sup>. Plutonium (Pu) has stable Pu<sup>4+</sup>, Pu<sup>5+</sup>, and Pu<sup>6+</sup> oxidation states in aqueous solutions. Neptunium (Np) has two stable oxides, NpO2 and Np2O5, corresponding to stoichiometric Np4+ and Np5+, respectively. Protactinium (Pa), like actinide Np and the transition niobium (Nb), tantalum (Ta), and vanadium (V) metals, has the predominant oxidation state of Pa<sup>5+</sup>. In particular, protactinium pentoxide is isostructural with the transition metals Nb and Ta, sharing a closed shell pentavalent oxidation state.<sup>28</sup> In addition, a study on Pa is considered to be a unique opportunity for studying the potential periodic properties of the actinide elements and their compounds with respect to their physics and chemistry, including structure and bonding. Wilson recently reported about protactinium as a potential intersection between the d-transition metals (Nb and Ta) and the 5f actinide elements U, Np and Pu owing to the participation of 5f and 6d orbitals cross in energy.28 Although U, Np and Pu oxide systems are known, a detailed structural study of the layered protactinium pentoxide  $(Pa_2O_5)$  has not been systematically reported to date.

> To develop new nuclear materials and understand their basic physical and chemical properties, a systematic study about the structure and properties of protactinium oxides is critical from a theoretical perspective.  $Pa_2O_5$  is used for the preparation of metal Pa and other oxides (PaO and PaO<sub>2</sub>), high temperature dielectrics for ceramic capacitors, in nuclear industry, *etc.*<sup>19,29</sup> Sellers *et al.*<sup>19</sup> experimentally showed that protactinium pentoxide has a fluorite structure and an orthorhombic structure. The fluorite  $Pa_2O_5$  was prepared by heating the hydrated oxide in air (500 °C). Also, density data for fluorite

<sup>&</sup>quot;Institute of Atomic and Molecular Physics, Sichuan University, Chengdu, 610065, China. E-mail: gaotao@scu.edu.cn

<sup>&</sup>lt;sup>b</sup>School of Electronic and Communication Engineering, Guiyang University, Guiyang, 550005, China

Science and Technology on Surface Physics and Chemistry Laboratory, P. O. Box 9072-35, Jiangyou, 621908, China. E-mail: aobingyun@caep.cn

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Pa<sub>2</sub>O<sub>5</sub> is not available, which suggests that it is more likely to be a defective fluorite PaO<sub>2</sub>.<sup>19</sup> The orthorhombic Pa<sub>2</sub>O<sub>5</sub>, which is isostructural with Nb<sub>2</sub>O<sub>5</sub> and Ta<sub>2</sub>O<sub>5</sub>, was obtained in the course of an attempt to prepare a fluoride by action of CuF<sub>5</sub> on the oxide (500 °C). Sellers' diffraction experiment suggested that Pa<sub>2</sub>O<sub>5</sub> is a layered phase. Our theoretical work explores some possible structures of Pa<sub>2</sub>O<sub>5</sub> by replacing the metal ions with protactinium ions from existing metal pentoxide structures. To study the potential structure and properties of layered Pa2O5, we report the structural, elastic, thermodynamic and electronic properties of some possible layered Pa2O5 phases using the Perdew-Burke-Ernzerhof generalized gradient approximation+U implemented in density functional theory (DFT). Our aim is to develop reliable structural models to aid the identification of possible phases and give a quantitative description of their relative stability.

## 2. Methodology

Theoretical calculations were performed using the projector augmented wave (PAW) method, as implemented in the Vienna *Ab Initio* Simulation Package (VASP).<sup>30,31</sup> The generalized gradient approximation (GGA) functional in the Perdew–Burke–Ernzerhof (PBE)<sup>32</sup> parametrization was adopted for structural optimization. The crystal structures of all systems concerned were relaxed using a  $\Gamma$ -centered *k*-mesh determined by requiring the product of the number of *k* points and the length of the lattice vectors to be ~30 Å and a large kinetic energy cutoff of 550 eV for plane waves. The energy convergence criterion was  $10^{-6}$  eV, and the force convergence criterion was  $10^{-4}$  eV Å<sup>-1</sup>. After relaxation, the electronic structures were calculated with a kinetic energy cutoff of 500 eV.

The Dudarev approach<sup>33</sup> to the Perdew-Burke-Ernzerhof generalized gradient approximation GGA (PBE)+U implementation<sup>34-38</sup> was employed to enforce localization of the Pa 5f electrons. The effective  $U_{eff}$  (U–J) parameter of 4.0 eV (ref. 39) was used. This value was tested for PaO<sub>2</sub> and all simulated Pa<sub>2</sub>O<sub>5</sub> structures, where the actinide (U, Np, and Pu) oxides in the literature<sup>6,16,17,27,40-43</sup> predicted good calculated structural properties. Spin-orbit coupling was not included in any of the calculations described herein since it has been previously demonstrated on actinide dioxides<sup>10,44</sup> that its effects on the structural properties and relative stabilities are inconsequential. The cutoff energy of 550 eV was reached for the convergence of the energy and the  $\Gamma$ -centered Monkhorst–Pack k-meshes of  $\zeta$ -Nb<sub>2</sub>O<sub>5</sub> 4 × 6 × 6; Nb<sub>2</sub>O<sub>5</sub> 4 × 6 × 4; R-Nb<sub>2</sub>O<sub>5</sub> 6 × 6 × 4; B- $Ta_2O_5 \ 4 \times 6 \times 6; \ Z\text{-}Ta_2O_5 \ 6 \times 6 \times 6; \ \beta\text{-}Ta_2O_5 \ 6 \times 6 \times 6; \ \beta\text{-}V_2O_5 \ 3$  $\times$  6  $\times$  4;  $\alpha$ -V<sub>2</sub>O<sub>5</sub> 2  $\times$  6  $\times$  2; and Np<sub>2</sub>O<sub>5</sub> 4  $\times$  6  $\times$  4 were automatically generated. The enthalpies of formation as a function of pressure and thermodynamic properties are presented in Fig. S1-S5.†

## 3. Results and discussion

#### 3.1 Structural properties

The different structures of the layered  $Pa_2O_5$  composition were simulated.  $Nb_2O_5$ ,<sup>45-47</sup>  $Ta_2O_5$ ,<sup>48,49</sup>  $V_2O_5$ ,<sup>50,51</sup>  $Np_2O_5$  (ref. 52)

structured M<sub>2</sub>O<sub>5</sub> (where M is an actinide or transition metal) structures were investigated by replacing the metal ion with protactinium. All the relaxed simulated structures retained the coordination environments of the original M2O5 structures. We report the experimental structures of ζ-Nb<sub>2</sub>O<sub>5</sub> and Np<sub>2</sub>O<sub>5</sub> in comparison to our calculated structure of  $Pa_2O_5$  in the  $\zeta$ -Nb<sub>2</sub>O<sub>5</sub> and Np<sub>2</sub>O<sub>5</sub> structures. For Pa<sub>2</sub>O<sub>5</sub> in the Np<sub>2</sub>O<sub>5</sub> structure, the calculated lattice parameters (Table 1) are in good agreement with the experimental results of Np2O5, most likely because of the similarity between the protactinium and neptunium atomic radii (0.78 and 0.75 Å, respectively). Although the large protactinium cation (0.78 Å) substitutes the transition metal ions V (0.54 Å), Nb (0.69 Å) and Ta (0.69 Å), PBE+U demonstrates that the cell volume for  $Pa_2O_5$  in the  $\zeta$ -Nb<sub>2</sub>O<sub>5</sub> structure is excellent compared to the experimental value of the original  $\zeta$ -Nb<sub>2</sub>O<sub>5</sub>. An important reason for this is the change from transition metal ions to protactinium ions in the coordinate environment of the substitute position. The original  $\zeta$ -Nb<sub>2</sub>O<sub>5</sub> structure has an alternating MO6-rich perovskite structure, and the replaced  $Pa_2O_5$  in  $\zeta$ -Nb<sub>2</sub>O<sub>5</sub> phase was transformed into alternating MO<sub>9</sub> distorted hexahedron and quadrangular pyramid layers. The structural and mechanical properties of all the simulated systems are shown in Tables 1 and 2 and their relaxed structures are presented in Fig. 1-5.

**Pa**<sub>2</sub>**O**<sub>5</sub> **in Nb**<sub>2</sub>**O**<sub>5</sub> **structure.** The ζ-,<sup>45</sup> R-<sup>46</sup> and Nb<sub>2</sub>**O**<sub>5</sub> (ref. 47) polymorphs were simulated. The ζ-Nb<sub>2</sub>**O**<sub>5</sub> and Pa<sub>2</sub>**O**<sub>5</sub> in the ζ-Nb<sub>2</sub>**O**<sub>5</sub> structure are shown in Fig. 1a and b, respectively. Although the ζ-Nb<sub>2</sub>**O**<sub>5</sub> structure is a skutterudite-like structure, the optimized Pa<sub>2</sub>**O**<sub>5</sub> in the ζ-Nb<sub>2</sub>**O**<sub>5</sub> phase can be considered a diamond-like (for 4 protactinium ions) structure, which has alternating MO<sub>9</sub> distorted hexahedron and quadrangular pyramid layers. As shown in Fig. 2a and b, the Nb<sub>2</sub>**O**<sub>5</sub> and R-Nb<sub>2</sub>**O**<sub>5</sub> phases are anatase-like structures and have layers of edge-sharing MO<sub>6</sub> octahedra, respectively. For the R-Nb<sub>2</sub>**O**<sub>5</sub> structure, the layers are continuous in the *c* direction, while they are separated by 2 layers of a skutterudite-like structure for the Nb<sub>2</sub>**O**<sub>5</sub> structure. All the protactinium ions for the R- and Nb<sub>2</sub>**O**<sub>5</sub> phases are Pa<sup>5+</sup> in the distorted octahedral coordination (Table 2).

**Pa<sub>2</sub>O<sub>5</sub> in Ta<sub>2</sub>O<sub>5</sub> structure.** We simulated the Z-<sup>48</sup> and β-Ta<sub>2</sub>O<sub>5</sub> (ref. 49) polymorphs (Fig. 3a and b, respectively). Although many polymorphs exist for this oxide, they are generally very similar to Nb<sub>2</sub>O<sub>5</sub>. In particular, the structure of B-Ta<sub>2</sub>O<sub>5</sub> is very similar to ζ-Nb<sub>2</sub>O<sub>5</sub>. β-Ta<sub>2</sub>O<sub>5</sub> is a typical two-layer orthogonal structure. Z-Ta<sub>2</sub>O<sub>5</sub> does not resemble the anatase structure and is more comparable to a distorted brookite structure (Fig. 2b). For the β-Ta<sub>2</sub>O<sub>5</sub> and ζ-Nb<sub>2</sub>O<sub>5</sub> structures, all the protactinium ions are Pa<sup>5+</sup> in the distorted octahedral coordination (Table 2). In contrast, all the protactinium ions for the β-Ta<sub>2</sub>O<sub>5</sub> structure are in the octahedral coordination.

**Pa<sub>2</sub>O<sub>5</sub> in V<sub>2</sub>O<sub>5</sub> structure.** Two polymorphs,  $\alpha$ -<sup>50</sup> and  $\beta$ -V<sub>2</sub>O<sub>5</sub>,<sup>51</sup> are presented in Fig. 4. The  $\beta$ -V<sub>2</sub>O<sub>5</sub> structure is built of infinite chains made of quadruple units of edge-sharing PaO<sub>6</sub> octahedra along the *b* axis. The chains are linked by sharing corners of two octahedra along the *c* axis. The  $\alpha$ -V<sub>2</sub>O<sub>5</sub> structure has a layered structure with orthorhombic symmetry consisting of PaO<sub>5</sub> square pyramids sharing edges and corners.

#### Table 1 Predicted properties of some layered Pa<sub>2</sub>O<sub>5</sub> phases<sup>a</sup>

Phase	Method	Lattice parameters (Å)			Lattice parameters (deg)							
		а	b	с	α	β	γ	Vol. (Å <sup>3</sup> )	Space group	$E_{\mathrm{gap}}$ (eV)	B (GPa)	$E_{\rm form}$ (eV)
Pa <sub>2</sub> O <sub>5</sub>	Expt <sup>19</sup>	13.84	4.02	4.18	90.0	90.0	90.0					
ζ-Nb <sub>2</sub> O <sub>5</sub>	Expt <sup>47</sup>	12.740	4.883	5.561	90.0	105.02	90.0	334.12	C2/c (15)			
. 2 0	PBE+U	12.620	5.387	5.387	90.0	114.68	90.0	332.72	C2/c (15)	2.67	198.33	-27.92
$Nb_2O_5$	PBE+U	14.446	4.282	15.035	90.0	163.64	90.0	262.02	P1 (1)	3.05	170.67	-26.41
R-Nb <sub>2</sub> O <sub>5</sub>	PBE+U	4.235	4.283	14.445	90.0	90.29	90.0	262.00	C2/m (12)	3.49	170.61	-26.40
Z-Ta <sub>2</sub> O <sub>5</sub>	PBE+U	6.302	4.077	6.517	90.0	107.37	90.0	159.82	C2/m(12)	2.21	282.70	-26.16
$\beta$ -Ta <sub>2</sub> O <sub>5</sub>	PBE+U	6.991	4.048	8.474	90.0	90.0	90.0	239.84	Pccm (49)	1.93	178.87	-24.13
$\beta - V_2 O_5$	PBE+U	6.645	3.937	7.412	90.0	78.57	90.0	190.05	$P2_1/m(11)$	3.28	198.91	-27.89
$\alpha - V_2 O_5$	PBE+U	11.576	4.220	10.664	90.0	90.0	90.0	520.93	<i>Cmcm</i> (63)	3.05	120.63	-25.01
$Np_2O_5$	Expt <sup>52</sup>	8.17	6.58	9.31	90.0	116.01	90.0	449.81	P2/c (13)			
-	PBE+U	8.150	6.887	9.404	90.0	115.69	90.0	470.35	P2/c (13)	3.29	166.76	-26.95

<sup>*a*</sup> The enthalpy of formation ( $E_{\text{form}} = E(\text{Pa}_2\text{O}_5) - 2E(\text{Pa}) - 5E(\text{O})$ ) was calculated with respect to the energy of the Pa metal (8.72 eV per Pa) and the O<sub>2</sub> molecule (-4.90 eV per O). The energy of an O atom was predicted to be -4.90 eV, as calculated from an O<sub>2</sub> molecule in a 25 Å box using the  $\Gamma$  point.

 $Pa_2O_5$  in  $Np_2O_5$  structure. The simulated  $Np_2O_5$  structure consists of 8 protactinium environments,<sup>52</sup> 4 with pentagonal bipyramidal coordination and 4 with octahedral coordination (Fig. 5 and Table 2). All the protactinium ions are predicted to be  $Pa^{5+}$ .

#### 3.2 Stability

To confirm the thermodynamic stabilities of the predicted structures, the enthalpy of formation ( $E_{\text{form}}$ ) for the simulated  $Pa_2O_5$  structures are listed in Table 1. The relative enthalpy of formation  $E_{\text{form}}$  was calculated for each stoichiometry with respect to all the simulated  $Pa_2O_5$  structures and gas  $O_2$ , as follows:

$$E_{\rm form} = E({\rm Pa}_2{\rm O}_5) - 2E({\rm Pa}) - 5E({\rm O})$$
 (1)

For clarity, the energies against the volume per  $Pa_2O_5$  unit are plotted in Fig. 6. There is a clear dependence of the formation energy on the volume, with a decrease in stability for volumes smaller or larger than the most stable phases ( $\zeta$ -Nb<sub>2</sub>O<sub>5</sub>).

The distribution of protactinium charges and protactinium coordination influence the stability. The  $\zeta$ -Nb<sub>2</sub>O<sub>5</sub>-structured Pa<sub>2</sub>O<sub>5</sub> is the most stable overall, although this structure

contains all the Pa in a distorted hexahedron and quadrangular pyramid coordination.  $\beta$ -V<sub>2</sub>O<sub>5</sub> was found to be just slightly less stable than  $\zeta$ -Nb<sub>2</sub>O<sub>5</sub> (0.03 eV) in terms of formation energy. The stability of the other phases follows the order of Np<sub>2</sub>O<sub>5</sub> > Nb<sub>2</sub>O<sub>5</sub> > R-Nb<sub>2</sub>O<sub>5</sub> > Z-Ta<sub>2</sub>O<sub>5</sub> >  $\alpha$ -V<sub>2</sub>O<sub>5</sub> >  $\beta$ -Ta<sub>2</sub>O<sub>5</sub>. Since Pa<sup>5+</sup> prefers higher coordination numbers compared to the 6-fold distorted octahedral coordination, all the structures featuring protactinium ions entirely in the 6-fold coordination are consequently less stable. The V<sub>2</sub>O<sub>5</sub>-structured oxides are the least stable with the  $\beta$ -polymorph less stable than the  $\alpha$ -V<sub>2</sub>O<sub>5</sub> structure due to the presence of Pa in mixed oxidation states (Pa<sup>4+</sup> and Pa<sup>5+</sup>) compared to  $\alpha$ -V<sub>2</sub>O<sub>5</sub>, which is comprised of only Pa<sup>5+</sup> ions.

The DFT work from Molinari *et al.*<sup>25</sup> predicted that the Np<sub>2</sub>O<sub>5</sub>-structured U<sub>2</sub>O<sub>5</sub> is the most stable among those considered under ambient conditions. However, the observed  $\delta$ -U<sub>2</sub>O<sub>5</sub> structure is found to be the second most stable. In particular, Pa<sub>2</sub>O<sub>5</sub> in the  $\beta$ -V<sub>2</sub>O<sub>5</sub> structure, given that it contains only octahedrally coordinated Pa, is closely followed by  $\beta$ -V<sub>2</sub>O<sub>5</sub>. The higher coordination numbers are also very similar to U<sub>2</sub>O<sub>5</sub> since U is closely followed by R-Nb<sub>2</sub>O<sub>5</sub>.

These energetics show that  $Pa_2O_5$  can crystallize in the  $\zeta$ -Nb<sub>2</sub>O<sub>5</sub> structure, but due to the relative instability of the  $Pa_2O_5$  stoichiometry compared to the other protactinium oxides, it has not been synthesized or reported experimentally. The difficulty

	No. of Pa environments per simulated unit cell									
Pa environment	$\zeta$ -Nb <sub>2</sub> O <sub>5</sub>	$Nb_2O_5$	R-Nb <sub>2</sub> O <sub>5</sub>	Z-Ta <sub>2</sub> O <sub>5</sub>	$\beta$ -Ta <sub>2</sub> O <sub>5</sub>	$\beta$ -V <sub>2</sub> O <sub>5</sub>	$\alpha$ -V <sub>2</sub> O <sub>5</sub>	Np <sub>2</sub> O <sub>5</sub>		
Pa <sup>5+</sup> distorted octahedron		4	4				8			
Pa <sup>5+</sup> octahedron					2			4		
Pa <sup>5+</sup> pentagonal bipyramid					2			4		
Pa <sup>5+</sup> distorted hexahedron and quadrangular pyramid	8			4						
Pa <sup>5+</sup> 7-fold						2				
Pa <sup>4+</sup> 7-fold						2				



Fig. 1 (a) Original  $\zeta\text{-Nb}_2O_5$  structure and (b)  $Pa_2O_5$  in the  $\zeta\text{-Nb}_2O_5$  structures.

in synthesizing layered  $Pa_2O_5$  is likely to stem from the fact that  $Pa^{5+}$  is more stable in the pentagonal bipyramidal coordination. One can also consider the formation of the studied  $Pa_2O_5$  phases as a function of pressure, representing a range of conditions from low pressure to high pressure. The formation enthalpies as a function of pressure are presented in Fig. S1<sup>†</sup> and are normalized with respect to the most stable  $Pa_2O_5$  (*i.e.*, the  $\zeta$ -Nb<sub>2</sub>O<sub>5</sub> structure) such that

$$\delta H_{\rm f} = \Delta H(x) - \Delta H(\zeta - Nb_2O_5) \tag{2}$$

where *x* is the phase in question and  $\Delta H(x)$  corresponds to  $E_{\text{form}}$  in Table 1. Interestingly, we predicted that at high pressure (above 100 kbar), Pa<sub>2</sub>O<sub>5</sub> will be more thermodynamically stable in the  $\zeta$ -Nb<sub>2</sub>O<sub>5</sub> structure.

Using the density functional perturbation theory (DFPT)<sup>53,54</sup> calculated for each unit cell, the Helmholtz free energy,  $F_{vib}$  (Fig. S2†), vibrational entropy,  $S_{vib}$  (Fig. S3†), vibrational energy,  $E_{vib}$  (Fig. S4†), Helmholtz free energy,  $F_{tot} = E_{form} + F_{vib}$  (Fig. S5†), and the heat capacity,  $C_v$  (Table 3), were evaluated. The Helmholtz free energy, F, entropy, S, internal energy, E, and



Fig. 2 Pa<sub>2</sub>O<sub>5</sub> in (a) Nb<sub>2</sub>O<sub>5</sub> and (b) R-Nb<sub>2</sub>O<sub>5</sub> structures.



Fig. 3  $Pa_2O_5$  in (a) Z-Ta<sub>2</sub>O<sub>5</sub> and (b)  $\beta$ -Ta<sub>2</sub>O<sub>5</sub> structures.

constant volume specific heat capacity,  $C_v$ , can be directly calculated as a function of temperature using the following equations:

$$F = rNk_{\rm B}T \int_0^\infty g(\omega) \ln\left(2\sinh\left(\frac{\hbar\omega}{2k_{\rm B}T}\right)\right) d\omega \tag{3}$$

$$S = rNk_{\rm B}T \int_0^\infty g(\omega) \left[ \frac{\hbar\omega}{2k_{\rm B}T} \left( \coth \frac{\hbar\omega}{2k_{\rm B}T} - 1 \right) \right]$$

$$-\ln\left(1 - \exp\left(-\frac{\hbar\omega}{k_{\rm B}T}\right)\right) \right] \mathrm{d}\omega \tag{4}$$

$$E = \frac{1}{2} Nr \int_0^\infty g(\omega) \hbar \omega \coth \frac{\hbar \omega}{2k_{\rm B}T} d\omega$$
(5)

$$C_{\rm v} = rNk_{\rm B} \int_0^\infty g(\omega) \left(\frac{\hbar\omega}{2k_{\rm B}T}\right)^2 \frac{\exp\left(\frac{\hbar\omega}{k_{\rm B}T}\right)}{\left(\exp\left(\frac{\hbar\omega}{k_{\rm B}T}\right) - 1\right)^2} \tag{6}$$

where the indices  $\omega$  is the phonon frequency,  $g(\omega)$  is the normalized phonon density of states  $(\int_0^{\infty} g(\omega)d\omega = 1)$ , *r* is the number of degrees of freedom in the primitive unit cell, and *N* is the number of primitive unit cells.  $\hbar$  is Planck's constant,  $k_{\rm B}$  is the Boltzmann constant, and *T* is the temperature in kelvin [K]. All these properties are expressed per Pa<sub>2</sub>O<sub>5</sub> unit, and a sample of their values at 300 K is presented in Table 3. A full calculation of the phase stability for the Pa<sub>2</sub>O<sub>5</sub> phases is beyond the scope of this work; however, our calculations show that the energy-minimized  $\zeta$ -Nb<sub>2</sub>O<sub>5</sub> phase has a lower enthalpy of formation ( $E_{\rm form}$ ) and vibrational entropy ( $S_{\rm vib}$ )



Fig. 4 Pa<sub>2</sub>O<sub>5</sub> in (a)  $\alpha$ -V<sub>2</sub>O<sub>5</sub> and (b)  $\beta$ -V<sub>2</sub>O<sub>5</sub> structures.



Fig. 5  $Pa_2O_5$  in the Np<sub>2</sub>O<sub>5</sub> structure.



Fig. 6 Stability plot of the formation energy per  $Pa_2O_5$  in electronvolt vs. volume per  $Pa_2O_5$  unit. Phases are named with the original  $M_2O_5$  structures for clarity.

than the other phases. Hence, using our calculated values,  $\zeta$ -Nb<sub>2</sub>O<sub>5</sub> is predicted to be the preferred structure at around 300 K and 0 bar (Fig. S5†).

Table 3  $\,$  Predicted thermodynamic properties of some layered  $\text{Pa}_2\text{O}_5$  phases at 300 K  $\,$ 

Phase	$F_{\rm vib}$ (meV)	$S_{\rm vib} ({\rm meV} {\rm K}^{-1})$	$C_{\rm V}$ (meV)	$E_{\rm vib}$ (meV)	$F_{\rm tot} ({\rm eV})$
K 11 0				54 <b>2</b> 0	
$\zeta$ -Nb <sub>2</sub> O <sub>5</sub>	214.2	1.43	135.5	612.0	-2/./1
$Nb_2O_5$	18.9	2.03	145.3	628.7	-26.40
$R-Nb_2O_5$	45.3	1.95	145.4	629.3	-26.35
Z-Ta <sub>2</sub> O <sub>5</sub>	218.3	1.49	123.5	606.7	-25.94
$\beta$ -Ta <sub>2</sub> O <sub>5</sub>	56.6	1.46	105.3	494.2	-24.07
$\beta - V_2 O_5$	212.5	1.46	137.2	650.9	-27.68
$\alpha - V_2O_5$	47.0	1.46	85.1	395.2	-24.96
$Np_2O_5$	107.6	1.72	140.7	622.8	-26.84



Fig. 7 Total and projected density of states of  $Pa_2O_5$  in the  $\zeta$ -Nb<sub>2</sub>O<sub>5</sub> (a) and  $\beta$ -V<sub>2</sub>O<sub>5</sub> (b) structures computed for the ground states in PBE+U. The Fermi energy stands at 0 eV.

#### 3.3 Elastic properties

To evaluate the mechanical stability of all the simulated structures at ambient pressure, the calculated elastic constants are shown in Table S1,<sup>†</sup> which were calculated using the strain– stress relationship. The key criterion for the mechanical stability of a crystal is that the strain energy must be positive, which implies that the elastic constants should satisfy the generalized elastic stability criteria. In all the simulated structures, the *Pccm* phase ( $\beta$ -Ta<sub>2</sub>O<sub>5</sub>) is the only orthorhombic structure, and the others are monoclinic structures. For the orthorhombic structure, the nine independent elastic constants are *C*<sub>11</sub>, *C*<sub>22</sub>, *C*<sub>33</sub>, *C*<sub>44</sub>, *C*<sub>55</sub>, *C*<sub>66</sub>, *C*<sub>12</sub>, *C*<sub>13</sub> and *C*<sub>23</sub>, and the corresponding mechanical stability criteria are given as<sup>55</sup>

$$C_{11} > 0, C_{11}C_{12} > C_{122}, C_{44} > 0, C_{55} > 0, C_{66} > 0, C_{11}C_{22}C_{33} + 2C_{12}C_{13}C_{23} - C_{11}C_{23}^{2} - C_{22}C_{13}^{2} - C_{33}C_{12}^{2} > 0.$$

Meanwhile, the monoclinic structure has thirteen independent elastic constants ( $C_{11}$ ,  $C_{22}$ ,  $C_{33}$ ,  $C_{44}$ ,  $C_{55}$ ,  $C_{66}$ ,  $C_{12}$ ,  $C_{13}$ ,  $C_{23}$ ,  $C_{15}$ ,  $C_{25}$ ,  $C_{35}$ ,  $C_{46}$ ) and the corresponding mechanical stability criteria are given as<sup>55</sup>

$$\begin{split} &C_{11} > 0, \ C_{22} > 0, \ C_{33} > 0, \ C_{44} > 0, \ C_{55} > 0, \ C_{66} > 0, \ [C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})] > 0, \ (C_{33}C_{55} - C_{35}^2) > 0, \ (C_{44}C_{66} - C_{46}^2) > 0, \ (C_{22} + C_{33} - 2C_{23}) > 0, \ [C_{22}(C_{33}C_{55} - C_{35}^2) + 2C_{23}C_{25}C_{35} - C_{23}^2C_{35} - C_{25}^2C_{33}] > 0, \ [2[C_{15}C_{25}(C_{33}C_{12} - C_{13}C_{23}) + C_{15}C_{35}(C_{22}C_{13} - C_{22}C_{23}) + C_{25}C_{35}(C_{11}C_{23} - C_{12}C_{13})] \\ &- \ [C_{15}^2(C_{22}C_{33} - C_{23}^2) + C_{25}^2(C_{11}C_{33} - C_{13}^2) + C_{35}^2(C_{11}C_{22} - C_{12}^2)] + C_{55}(C_{11}C_{22}C_{33} - C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2 + 2C_{12}C_{13}C_{23})\} > 0. \end{split}$$

From the elastic constants listed in Table S1,<sup>†</sup> we find that the monoclinic phase of  $Pa_2O_5$  in the  $\zeta$ -Nb<sub>2</sub>O<sub>5</sub> structures satisfies their respective mechanical stability criteria at ambient pressure, thus confirming their mechanical stability. However, the *Pccm* phase of  $Pa_2O_5$  in the  $\beta$ -Ta<sub>2</sub>O<sub>5</sub> structure is not the ground-state structure because this orthorhombic phase does not satisfy its mechanical stability criteria. Combining the thermodynamic and mechanical stability results, we conclude that the monoclinic phase is the ground-state structure for  $\zeta$ -Nb<sub>2</sub>O<sub>5</sub>-structured  $Pa_2O_5$  at ambient pressure. In addition, there is no evident correlation between the bulk moduli *B* and the volume (Vol.) or formation energy ( $E_{form}$ ) of the layered  $Pa_2O_5$ structured  $Pa_2O_5$ , but the bulk modulus, *B*, for the  $\zeta$ -Nb<sub>2</sub>O<sub>5</sub>structure  $Pa_2O_5$ , but the bulk modulus of the Z-Ta<sub>2</sub>O<sub>5</sub> structure is the largest.

#### 3.4 Electronic properties

The experimental band gaps of the layered  $Pa_2O_5$  phase are not currently available. In accordance with the higher layered oxide  $M_2O_5$ , all the structures are predicted to be ligand-to-metal charge-transfer (LMCT) insulators (O-2p to Pa-5f), with a conductance band composed of Pa 5f states and valence band comprised of O 2p states, with higher energy Pa 5f states at the core. To clearly describe the electronic properties of the most stable structure, the densities of states (DOS), projected density of states (PDOS) and band structure of  $Pa_2O_5$  in the  $\zeta$ -Nb<sub>2</sub>O<sub>5</sub> and β-V<sub>2</sub>O<sub>5</sub> structures are provided in Fig. 7 and S6.† These characteristics of Pa are attributed to its partially occupied 5f orbitals, which favors itinerancy for the early actinides. The appearance of significant Pa-5f/O-2p mixing arises from the increasing stabilization of the Pa 5f band due to incomplete shielding of the nuclear charge as one proceeds across the actinide series. There is a great variation in the predicted band gaps, with  $Pa_2O_5$  in the  $\zeta$ -Nb<sub>2</sub>O<sub>5</sub> structure predicted to be 2.67 eV, which is more than the PaO<sub>2</sub> band gap of 1.40 eV.<sup>56</sup> As a comparison, the DOS and PDOS of  $Pa_2O_5$  in the  $\beta$ -V<sub>2</sub>O<sub>5</sub> structure are shown in Fig. 7b. Our PBE+U calculation predicts  $Pa_2O_5$  in the  $\beta$ -V<sub>2</sub>O<sub>5</sub> structure as a charge-transfer insulator with a band gap of 3.28 eV, which is bigger than the  $Pa_2O_5$  in the  $\zeta$ -Nb<sub>2</sub>O<sub>5</sub> structure with a predicted gap of 0.61 eV. The presence of Pa 5f states in the valence band suggests a degree of covalent mixing with O 2p (fully ionic bonding would feature no overlapping states).

### 4. Conclusions

In this work, we presented some possible structures of the Pa<sub>2</sub>O<sub>5</sub> stoichiometry starting from existing actinide and transition metal pentoxides based on density functional theory. Our calculations showed that the Pa<sub>2</sub>O<sub>5</sub> structures prefer the Pa ions in homogeneous Pa<sup>5+</sup> oxidation states and that all are in distorted hexahedron and quadrangular pyramid coordination. Our simulations predict that the  $\zeta$ -Nb<sub>2</sub>O<sub>5</sub>-structured Pa<sub>2</sub>O<sub>5</sub> is the most stable under zero temperature and ambient conditions. The observed  $\beta$ -V<sub>2</sub>O<sub>5</sub> structure was found to be the second most stable structure. Thus, it is expected that protactinium can crystallize with the  $\zeta$ -Nb<sub>2</sub>O<sub>5</sub> structure; however, this has not been observed experimentally. ζ-Nb2O5-structured Pa2O5 is a charge-transfer insulator and its calculated band gap is 2.67 eV. Thus, this stoichiometry is clearly worthy of synthetic investigation since the ζ-Nb<sub>2</sub>O<sub>5</sub> structure is found to be a stable phase. To better understand the fluorite to layered transformation, we will focus on using a more pragmatic approach to model fluorite-based Pa2O5 phases in future simulation work.

## Conflicts of interest

There are no conflicts to declare.

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## References

T. Mark McCleskey, E. Bauer, Q. Jia, A. K. Burrell, B. L. Scott,
 S. D. Conradson, A. Mueller, L. Roy, X. Wen and
 G. E. Scuseria, *J. Appl. Phys.*, 2013, 113, 013515.

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- 2 T. Yaashita, N. Nitani, T. Tsuji and H. Inagaki, *J. Nucl. Mater.*, 1997, **245**, 72–78.
- 3 S. Kern, R. Robinson, H. Nakotte, G. Lander, B. Cort, P. Watson and F. Vigil, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **59**, 104.
- 4 L. Asprey, F. Ellinger, S. Fried and W. Zachariasen, J. Am. Chem. Soc., 1955, 77, 1707–1708.
- 5 P. Santini, S. Carretta, G. Amoretti, R. Caciuffo, N. Magnani and G. H. Lander, *Rev. Mod. Phys.*, 2009, **81**, 807.
- 6 B. T. Wang, H. Shi, W. Li and P. Zhang, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2010, **81**, 045119.
- 7 Q. Yin and S. Y. Savrasov, Phys. Rev. Lett., 2008, 100, 225504.
- 8 P. Zhang, B. T. Wang and X. G. Zhao, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2010, 82, 144110.
- 9 I. D. Prodan, G. E. Scuseria, J. A. Sordo, K. N. Kudin and R. L. Martin, *J. Chem. Phys.*, 2005, **123**, 014703.
- 10 X. D. Wen, R. L. Martin, T. M. Henderson and G. E. Scuseria, *Chem. Rev.*, 2012, **113**, 1063–1096.
- 11 X. D. Wen, R. L. Martin, L. E. Roy, G. E. Scuseria, S. P. Rudin, E. R. Batista, T. M. McCleskey, B. L. Scott, E. Bauer and J. J. Joyce, *J. Chem. Phys.*, 2012, 137, 154707.
- 12 A. Bouasria, A. Zaoui, S. Ait Abderrahmane, S. Kacimi, A. Boukortt, M. Bejar and E. Dhahri, *Int. J. Comput. Mater. Sci. Eng.*, 2017, **6**, 1750006.
- 13 K. N. Kudin, G. E. Scuseria and R. L. Martin, *Phys. Rev. Lett.*, 2002, **89**, 266402.
- 14 I. D. Prodan, G. E. Scuseria and R. L. Martin, *Phys. Rev. B:* Condens. Matter Mater. Phys., 2007, **76**, 033101.
- 15 D. Andersson, J. Lezama, B. Uberuaga, C. Deo and S. Conradson, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2009, **79**, 024110.
- 16 G. Jomard, B. Amadon, F. Bottin and M. Torrent, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, 78, 075125.
- 17 B. Sun, P. Zhang and X. G. Zhao, *J. Chem. Phys.*, 2008, **128**, 084705.
- 18 K. T. Moore and G. van der Laan, *Rev. Mod. Phys.*, 2009, **81**, 235.
- 19 P. A. Sellers, S. Fried, R. E. Elson and W. Zachariasen, J. Am. Chem. Soc., 1954, 76, 5935–5938.
- 20 H. R. Hoekstra, S. Siegel and F. X. Gallagher, *J. Inorg. Nucl. Chem.*, 1970, **32**, 3237–3248.
- 21 N. A. Brincat, S. C. Parker, M. Molinari, G. C. Allen and M. T. Storr, *Dalton Trans.*, 2015, 44, 2613–2622.
- 22 D. Andersson, G. Baldinozzi, L. Desgranges, D. Conradson and S. Conradson, *Inorg. Chem.*, 2013, **52**, 2769–2778.
- 23 C. Guéneau, M. Baichi, D. A. A. Labroche, C. Chatillon and B. Sundman, *J. Nucl. Mater.*, 2002, **304**, 161–175.
- 24 R. J. McEachern and P. Taylor, J. Nucl. Mater., 1998, 254, 87– 121.
- 25 M. Molinari, N. A. Brincat, G. C. Allen and S. C. Parker, *Inorg. Chem.*, 2017, **56**, 4468–4473.
- 26 N. A. Brincat, S. C. Parker, M. Molinari, G. C. Allen and M. T. Storr, *Inorg. Chem.*, 2014, 53(23), 12253–12264.
- 27 N. A. Brincat, M. Molinari, S. C. Parker, G. C. Allen and M. T. Storr, *J. Nucl. Mater.*, 2015, **456**, 329–333.
- 28 R. E. Wilson, S. Sio and V. Vallet, Nat. Commun., 2018, 9, 622.

- 29 L. R. Morss, N. M. Edelstein and J. Fuger, *The Chemistry of the Actinide and Transactinide Elements*, Springer, The Netherlands, 2010.
- 30 G. Kresse and J. Hafner, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, **49**, 14251.
- 31 G. Kresse and J. Furthmüller, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, **54**, 11169.
- 32 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, 77, 3865.
- 33 S. Dudarev, G. Botton, S. Savrasov, C. Humphreys and A. Sutton, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1998, 57, 1505.
- 34 V. I. Anisimov, J. Zaanen and O. K. Andersen, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1991, 44, 943.
- 35 J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou and K. Burke, *Phys. Rev. Lett.*, 2008, **100**, 136406.
- 36 V. I. Anisimov, F. Aryasetiawan and A. I. Lichtenstein, J. Phys.: Condens. Matter, 1997, 9, 767.
- 37 A. Liechtenstein, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1995, **52**, R5467.
- 38 M. T. Czyżyk and G. A. Sawatzky, Phys. Rev. B: Condens. Matter Mater. Phys., 1994, 49, 14211.
- 39 T. Yamazaki and A. Kotani, J. Phys. Soc. Jpn., 1991, 60, 49–52.
- 40 V. I. Anisimov, A. I. Poteryaev, M. A. Korotin, A. O. Anokhin and G. Kotliar, *J. Phys.: Condens. Matter*, 1997, **9**, 7359.
- 41 Y. Yun, J. Rusz, M. T. Suzuki and P. Oppeneer, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2011, **83**, 075109.
- 42 K. O. Obodo and N. Chetty, J. Phys.: Condens. Matter, 2013, 25, 145603.
- 43 X. D. Wen, R. L. Martin, G. E. Scuseria, S. P. Rudin, E. R. Batista and A. K. Burrell, *J. Phys.: Condens. Matter*, 2012, **25**, 025501.
- 44 J. Flitcroft, M. Molinari, N. Brincat, M. Storr and S. Parker, *Chem. Commun.*, 2015, **51**, 16209–16212.
- 45 T. S. Ercit, Mineral. Petrol., 1991, 43, 217-223.
- 46 B. O. Marinder, Acta Chem. Scand., 1990, 44, 123-134.
- 47 J. Spyridelis, P. Delavignette and S. Amelinckx, *Phys. Status Solidi B*, 1967, 19, 683–704.
- 48 I. Zibrov, V. Filonenko, M. Sundberg and P. E. Werner, Acta Crystallogr., Sect. B: Struct. Sci., 2000, 56, 659–665.
- 49 L. Aleshina and S. Loginova, *Crystallogr. Rep.*, 2002, 47, 415–419.
- 50 J. Cocciantelli, P. Gravereau, J. Doumerc, M. Pouchard and P. Hagenmuller, *J. Solid State Chem.*, 1991, **93**, 497–502.
- 51 V. Filonenko, M. Sundberg, P. E. Werner and I. Zibrov, Acta Crystallogr., Sect. B: Struct. Sci., 2004, 60, 375–381.
- 52 T. Z. Forbes, P. C. Burns, S. Skanthakumar and L. Soderholm, *J. Am. Chem. Soc.*, 2007, **129**, 2760–2761.
- 53 S. Baroni, S. De Gironcoli and A. D. Corso, *Rev. Mod. Phys.*, 2001, **73**, 515–562.
- 54 X. Gonze, Phys. Rev. A: At., Mol., Opt. Phys., 1995, 52, 1096-1114.
- 55 F. Mouhat and F. X. Coudert, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2014, **90**, 224104.
- 56 I. D. Prodan, G. E. Scuseria and R. L. Martin, *Phys. Rev. B:* Condens. Matter Mater. Phys., 2007, **76**, 033101.