Density Functional Study on the adsorption of O_2 and H_2O on $PtSb_2$ (100) surface.

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Introduction

- $PtSb_2$ is a transition metal dipnictide with the cubic pyrite (Pa-3) structure with a relatively narrow band gap of approximately 0.073 eV [1].
- The hydration of surface determines the wettability that is hydrophobicity and hydrophilicity of the mineral and significantly influences the oxidation process that determines the final oxidation product resulting in the obvious variation in the mineral oxidation process [2].
- It has been reported on the oxidation of stockpile of pentlandite and pyrrhotite minerals that water plays an important role in the oxidation [3].
- Previously the interactions of H_2O with minerals surface have been conducted and indicated different modes, orientations and binding energies on the surfaces [2–4].
- In this study a computational simulation density functional theory (DFT) method was employed to investigate the adsorption of O_2 and H_2O on the $PtSb_2$ (100) surface to observe formation of reactant species, preferential bonding modes, and adsorption strength.

Structures and Applications

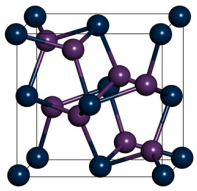


Fig. 1. Relaxed $PtSb_2$ bulk model.

The structure on the side is a face-centered cubic. It has the $T_h(m3)$ symmetry rather than $O_h(3m3)$.

a=6.531Å,. Sb-Sb=2.67Å

PGMs find applications in hard disks and anti-cancer drugs among others.

Methodology

- In our investigations tools being employed involve techniques based on DFT: CASTEP (Materials Studio) [5].
- The exchange–correlation function: we used plane-wave (PW) ultrasoft pseudopotential method with GGA-PBE [6].
- Supercells: (2×2) for (100) surfaces with 20 Å vacuum slab.
- Parameters: The convergence tolerances 1.0×10^{-6} eV/atom.
- Energy cut–off bulk and surfaces: 500 eV.
- k-points sampling: 6×6×6 Bulk structure and 4×4×1 for surfaces, scheme proposed by Monkhorst-Pack [7].
- Bulk and surfaces optimized using above set parameters.

Results and Discussions

$$E_{Surface} = \frac{[E_{Slab} - (n_{Slab})(E_{Bulk})]}{2A},$$

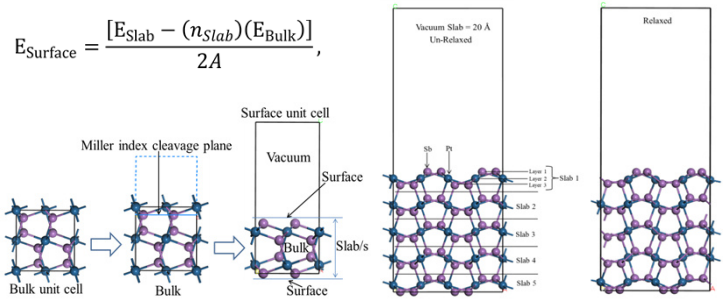
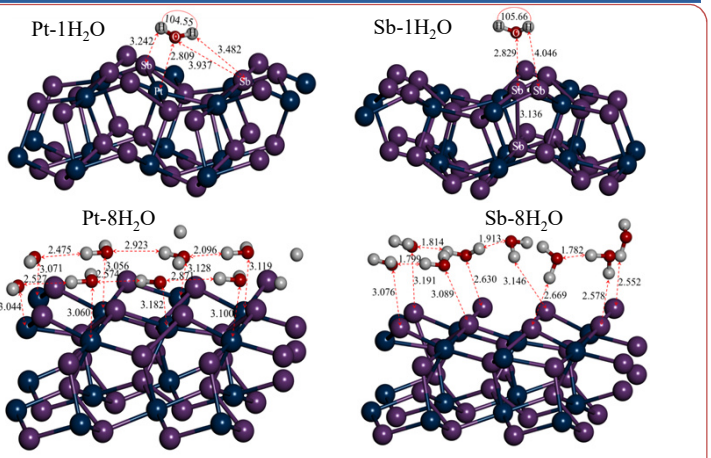


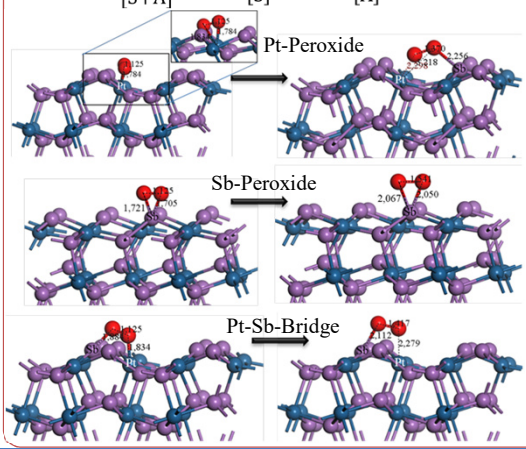
Fig. 2. Surface cleavage and $PtSb_2$ (100) surface.

Surface	Surface Pt coordination		Surface Sb coordination		Surface energies (J/m^2)
	Unrelaxed	Relaxed	Unrelaxed	Relaxed	
(100)	5	5	3	3	0.807

Table 1. Surface energies and coordination (CASTEP)



$$E_{ads.} = E_{[S+A]^0} - (E_{[S]^0} + NE_{[A]^0}),$$



O_2 Adsorptions	$E_{Ads.}$ (kJ/mol)	
	Pt	Sb
O_2 (Superoxide)	–	–17.94
O_2 (Peroxide)	–64.29	–32.56
Pt-O-O-Sb	–49.12	

Table 2. Adsorption energies ($E_{Ads.}$) of oxidation of $PtSb_2$ (100) surface

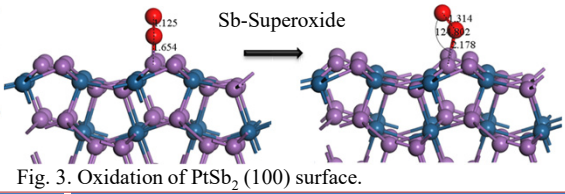


Fig. 3. Oxidation of $PtSb_2$ (100) surface.

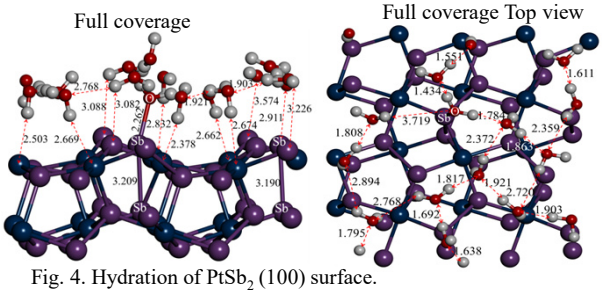


Fig. 4. Hydration of $PtSb_2$ (100) surface.

H_2O Adsorptions	$E_{Ads.}/N$ (kJ/mol)	
	Pt	Sb
$1H_2O$	–6.37	10.34
$8H_2O$	–21.64	–29.26
Full coverage	–38.19	

Table 3. Adsorption energies ($E_{Ads.}$) of water interaction with $PtSb_2$ (100) surface

Conclusion

- Oxidation: Preferred the Sb atoms forming superoxide
- Hydration: The water molecules do not form bonds on the surface, except for full surface coverage where only one H_2O remained bonded on Sb atom.
- Generally the oxidation adsorb stronger than H_2O, thus the mineral may easily oxidise.
- The water molecule lie parallel to the surface and in most case interacts with the surface through hydrogen atoms.

References

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Acknowledgments

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