

## Density Functional Theory Analysis on the Structural Properties of Cubic and Monoclinic Tungsten Trioxide

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### ABSTRACT

Tungsten trioxide ( $\text{WO}_3$ ) is a transitional product in the recovery of tungsten from its minerals. Recently, it has shown a growing attention both within the theoretical and experimental research due to its special structural properties and its high potential in electronic applications. The crystal lattice of tungsten trioxide is highly dependent on temperature. In this work we investigated the equilibrium structure of tungsten trioxide in two crystal systems, i.e. monoclinic and cubic systems. We carried out our first principle calculations using a pseudo potential method based on the density functional theory (DFT) with generalized gradient approximation (GGA) as exchange correlation energy as implemented in Quantum ESPRESSO code. In each case, we calculated total energy, Fermi energy, density of states and then we made comparisons. The results show that  $\text{WO}_3$  is a semiconductor in all two crystal structures with zero total magnetization. Moreover, tungsten trioxide has a direct band gap with a gap value of about 1.02eV for cubic and indirect band gap with value of about 0.98eV for monoclinic which are all in the range of visible wavelength that improves its optical applications potentially.

**KEYWORDS:** Density functional theory (DFT), linear density approximation (LDA), Quantum ESPRESSO, and Tungsten trioxide ( $\text{WO}_3$ )

### 1.0 INTRODUCTION

Tungsten (vi) oxide, also known as tungsten trioxide or tungsten analysis,  $\text{WO}_3$  is a chemical compound containing oxygen and transition metal tungsten it is obtained as an intermediate in the recovery of tungsten from its minerals (Labbe,1992). Tungsten is treated with alkali to produce  $\text{WO}_3$  further reaction with carbon or hydrogen gas reduces tungsten trioxide to the pure metal. Tungsten trioxide has a rich history dating back to its discovery during the 18<sup>th</sup> century (Agte, & Vacek, 1963). Peter wolff was the first to recognize a new element in the naturally occurring mineral wolframite (Wolfe, 2012). Tungsten was originally known as wolfram, explaining the choice of “W” for its elemental symbol. Sweetish chemist Carl Wilhelm Scheele contributed to its discovery with his studies on the mineral scheelite (Limbaugh, 2010).

In 1841, a chemist named Robert Oxland gave the first procedures for preparing tungsten trioxide and sodium tungstate. He was granted patent for his work soon after and is considered to be the founder of systematic tungsten chemistry (Rao, 2013).

Tungsten trioxide is used in daily life for many purposes. It's often the case, used in industry to produce tungstate for x-ray screen Phosphors for fireproofing fabrics and gas sensors as a pigment in ceramics and paints is also used due to its rich yellow color (Turkez, Cakmak, & Celik, 2013). Tungsten trioxide has been used in the manufacture of electro-chrome windows or smart windows in recent years.

In 2013, highly photo catalyst active titanic tungsten (vi) oxide/noble metal composites toward oxalic acid were obtained by the means of selective noble metal photo deposition on the desired oxides surface either on ( $\text{TiO}_2$  or  $\text{WO}_3$ )

the composite showed a modest hydrogen production performance (Karácsonyi, et al. 2013).

Although the stable phase of pure  $\text{WO}_3$  at 17 330 °C is monoclinic with the  $P_{21/n}$  space group, any change in temperature may induce structural distortions and thereby causing a phase transfer. Indeed, tungsten trioxide has an orthorhombic lattice at 330 to 740 °C and a tetragonal structure above 740 °C. There are at least five different  $\text{WO}_3$  crystalline phases, including  $\varepsilon$ -monoclinic (low temperature, LT), triclinic,  $\gamma$ -monoclinic (room temperature, RT), orthorhombic, and tetragonal phase. In terms of geometric feature, some previous reports mainly focus on individual  $\text{WO}_3$  polymorphs or the phase transformation. For example, Corà et al. (1996) calculated the geometric configurations of the simple cubic and tetragonal  $\text{WO}_3$ , and found that the energy of  $\text{WO}_3$  formula unit for cubic phase is 0.8 eV higher than that for the tetragonal one, owing to the elongating of W–O covalent bond. Experimentally, Vogt et al, (1999). Investigated the high-temperature phases (orthorhombic  $\beta$ - $\text{WO}_3$  and tetragonal  $\alpha$ - $\text{WO}_3$ ) of  $\text{WO}_3$  with the help of high-resolution neutron powder diffraction. Their results further confirmed that the temperature-induced phase transitions in  $\text{WO}_3$  can be rationalized according to the changes in the tilt direction of  $\text{WO}_6$  octahedron and/or off-center displacements of the tungsten cations. Recently, Hamdi and co-workers (Hamdi, et al. 2016) have inspected about five  $\text{WO}_3$  crystal structures via a first-principles study.

The aim of this work is to carry out a comprehensive theoretical comparative study on cubic and monoclinic lattice of  $\text{WO}_3$  using DFT as implemented in Quantum ESPRESSO.

## 2.0 METHODOLOGY

The Kohn–Sham self-consistent equations have been solved computationally using Quantum-ESPRESSO package, within the density functional theory (DFT) with pseudopotential method (Kohn, Becke, & Parr, 1996; Giannozzi, et al. 2009). In this work, the Generalized gradient approximation (GGA) parametrized by Perdew–Burke–Ernzerhof (PBE) functional as exchange–correlation energy (Perdew, Burke, &

Ernzerhof, 1996; Ernzerhof, & Scuseria, 1999) have been used. In both crystal structures, the kinetic energy cut-off of 40 Ry was used to obtain the accuracy of about 0.001 Ry. Furthermore, a suitable Monkhorst–Pack grid (Monkhorst, & Pack, 1976) has been used for the Brillouin zone integration. Also, to reflect the possibility of a metallic phase, a gaussian broadening with a width of 0.01 eV for smearing was selected. In this calculation, two polymorphs of cubic and monoclinic systems of tungsten trioxides were studied broadly. these structures were fully relaxed and the optimized geometry using BGFS as implemented in QE such that the minimum total energy and interatomic forces was obtained. To explore the electronic properties of the polymorphs, density of states (DOS), and projected density of states (PDOS) were calculated and investigated in each case.

## 3.0 RESULTS AND DISCUSSION

### 3.1 Structural Stability

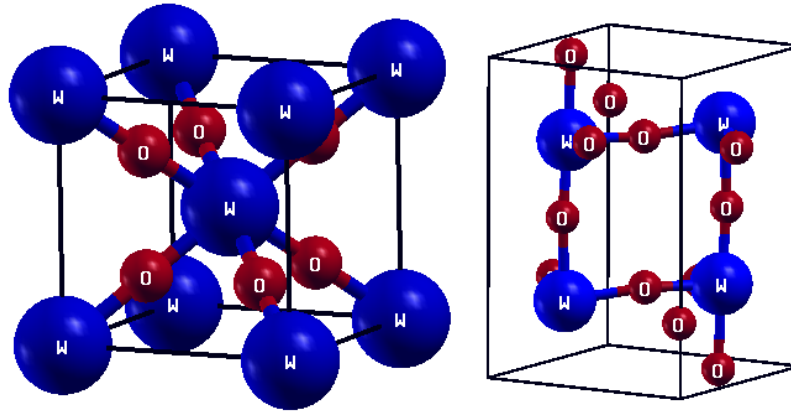
We studied  $\text{WO}_3$  in two crystal symmetries of monoclinic with  $P_{21/n}$  space group and cubic with  $\text{Pm}\bar{3}\text{m}$  space group. Regarding that a tungsten atom has six oxygen atoms as its nearest neighbors, in case of cubic structure, a cell with eight atoms containing 2 oxygen atoms and 6 tungsten atoms was used, while for the monoclinic lattice, we used a cell with 32 atoms in it (8 tungsten and 24 oxygen).

After the relaxation calculation and obtaining the optimized parameters, to investigate the effect of lattice on electronic properties of  $\text{WO}_3$  the projected density of state (PDOS) were obtained and analyzed extensively.

Table 1 shows the optimized crystal parameters obtained from our calculations and Figure 1 shows the structures in each case. The Lattice parameters,  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$ , and energy gap are also indicated in the Table 1.  $E_{\text{HOMO}}$  is the highest occupied orbital energy and  $E_{\text{LUMO}}$  is the lowest unoccupied orbital energy, this result is in good agreement with (Mansouri, & Mahmoodi, 2017). According to the DFT calculation, the absolute value of  $E_{\text{HOMO}}$  is equal to the minimum of the ionization energy (Verma, & Bartlett, 2014). Therefore, we have generated our structures with minimum of the ionization energy using XCysden software as shown in Figure 1.

**Table 1: Lattice parameter and energetic of WO<sub>3</sub> polymorphs**

LATTICE	Lattice Parameter			E <sub>HOMO</sub>	E <sub>LUMO</sub>	E <sub>gap</sub>
	a(Å)	b(Å)	c(Å)	(eV)	(eV)	(eV)
CUBIC	3.92	3.92	3.92	5.82	5.70	0.78
MONOCLINIC	7.679	7.720	7.756	6.60	8.60	1.93



**Figure 1 Crystal Structures of Cubic and Monoclinic WO<sub>3</sub>**

### 3.2 Electronic Properties

From Figures 2, the density of states with valance band (VB) and conduction band (CB) is presented for the two structures. In monoclinic systems Figures 2(b) it shows that there is a relatively uniform concentration of states in VB, while it is more dispersive in cubic systems Figures 2(a) and leads to a VB of 6.33eV and 7.6eV widths, respectively. Number of valance electrons can be calculated through the integral of the VB, this result is in good agreements with many results such as (Ming, et al. 2011; Wang,

Valentin, & Pacchioni, 2012). There are 36 valance electrons in the cells with 8 atoms in them and 144 electrons in monoclinic with a 32-atom cell. Furthermore, as indicated in the plots in Figure 2(a) the VB is made of oxygen which we are expecting is the p-orbital and tungsten d-orbitals. Therefore, each W atom with [Xe] 4f<sup>14</sup> 5d<sup>4</sup> 6s<sup>2</sup> electronic configurations is expected to shares 4 d-electrons and each O atom with [He] 2s<sup>2</sup> 2p<sup>4</sup> electronic configuration is also expected to shares 4 p-electrons in the VB.

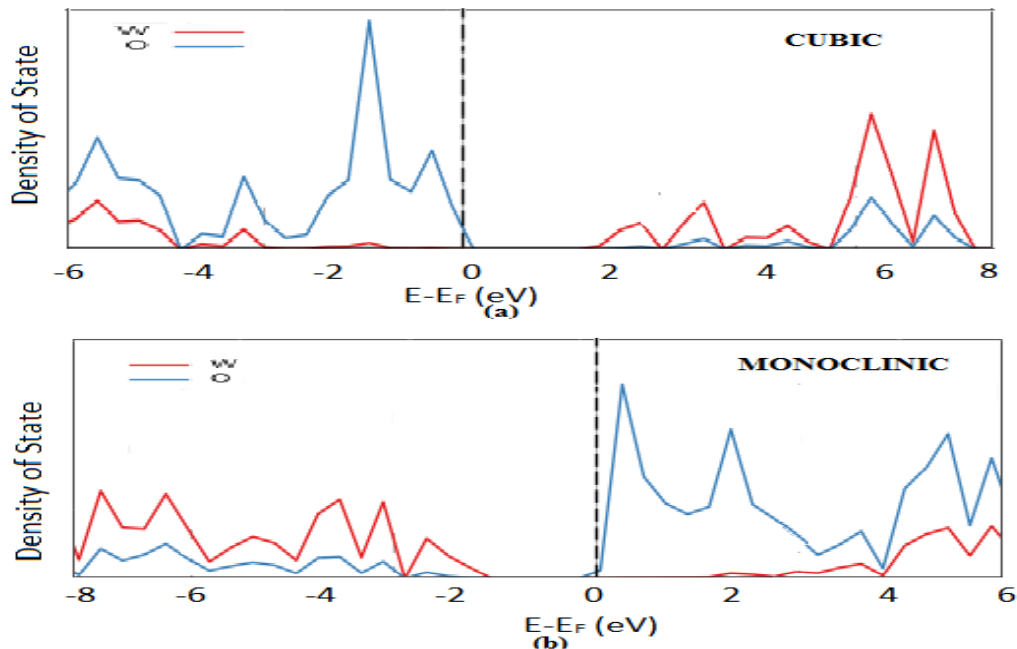


Figure 2 Calculated PDOS of Cubic and Monoclinic WO<sub>3</sub>

#### 4.0 CONCLUSION

It has been found that tungsten trioxide has a temperature dependent structure, with the two polymorphs. We have done an ab initio calculation in the DFT framework to explore the electronic properties of these polymorphs. The results show that WO<sub>3</sub> is a nonmagnetic semiconductor in all two crystal lattices of monoclinic and cubic. The electronic d-orbitals are located deep inside the VB, while p-orbitals determine the characteristic of VB edge electrons, which contribute in electronic transport. Moreover, WO<sub>3</sub> has a direct band gap with a gap value of about 1.02eV for cubic and indirect band gap with value of about 0.98eV for monoclinic, these values are in agreement with many reported results (Loaiza-Orduz, et al.2018).

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