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Structural, electronic and optical properties of Li intercalated on MO_3 (M: Mo, W): A first principle investigation

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ABSTRACT

The correlations between electronic and optical properties of pure MO_3 (M=Mo, W) and the effect of Li intercalated in the matrix are investigated within density functional theory using both the revised gradient-corrected Perdew–Burke–Ernzerhof (GGA-PBE), GGA+U and HSE06 functional frameworks along with ab initio pseudopotentials method. Calculation performed with HSE06 functional proves that all these compounds are wide band gap semiconductors. The energy gap value is found to decrease with lithium incorporation, affecting the visible absorption coefficients.

1. Introduction

Transition metal oxides (TMOs) represent a very interesting class of semiconducting materials, widely known, for their important technological applications, especially, in the field of display devices, optical smart windows, electrochromic devices (ECD) and gas-sensors [1–4]. Among various transition metal oxides such as MoO_3, WO_3, V_2O_5, NiO, IrO_2, etc., it is well known that the electrochromic response of MoO_3 is superior [5]; because the former shows stronger and more uniform absorption of light in its colored state. Transition metal oxides of MoO_3 [6–8] and WO_3 [9] exhibit various important properties, including the electrochromic effect [10].

Electrochromic materials change their optical properties, due to the action of an electric field, which can be changed back to the original state by a field reversal. There are two major categories of those materials: transition metal oxides including intercalated compounds, and organic compounds including polymers. The electrochromic effect occurs in inorganic compounds by the absorption of the electrons (e^-) and ions (A) generated simultaneously and injected into the network. This is expressed by the equation: (Transparent) $MO_3 + xA^+ + xe^- \leftrightarrow A_xMO_3$ (Colored). Usually, the MO_3 (M=Mo, W) doped with alkali metals (H^+, Li^+, Na^+, K^+, Rb^+ or Cs^+) are also known to possess excellent electrochromic effect [3]. Injection made a Mo^{+6} reduced to Mo^{+5}. MoO_3 film has good electrochromic performance with respect to other materials, such as WO_3, TiO_2, etc., so that performance of nanomaterials molybdenum trioxide is currently the focus of huge researches.

First-principles density functional theory calculations have been widely used to shed light on the structural, electronic and optical properties of transition metal oxide compounds. Linear muffin-tin orbital (LMTO-FP) approach was used by two groups to study this kind of compounds. Corà et al. [11] studied the MO_3 (M=W and Re) and the effect of Na intercalated in WO_3 matrix, de Wijs et al. [12] studied anomalous behaviors of the semiconducting gap in WO_3. Other three groups have used the projected augmented wave (PAW) incorporated in the Vienna ab initio simulation package (VASP), Sha et al. [13] studied the hydrogen absorption and diffusion in bulk α-MoO_3, Huang et al. [14] studied the band gap narrowing of TiO_2, Ricardo Grau-Crespo et al. [15] studied the description of band gap of VO_2 compound by hybrid functional (HSE). Their results showed that density functional theory (DFT) calculations can give satisfactory results that would often not be easy to obtain directly from experiments. In this paper, we report our computational results for lithium inserted in MO_3 (M=Mo, W) transition metal oxides in order to understand the origin of correlations between the optical and electronic properties reported in experimental works, using *ab initio* calculations.

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2. Computational methods

All calculations presented in this work were performed using the revised gradient-corrected Perdew–Burke–Ernzerhof (GGA-PBE) [16,17] and the projector augmented wave (PAW) pseudo-potential methods based on density functional theory (DFT) [18,19], implemented in the Vienna Ab-initio Simulation Package (VASP) [20,21]. In this paper, the exchange-correlation functional was treated by different approximations. Generally, DFT+U [22] give much better band gaps results and better positions of gap states than simple DFT and the Heyd–Scuseria–Ernzerhof (HSE06) [23–25] density functional which are popular for their ability to improve the accuracy of standard semi local functional such as GGA-PBE and give a good estimation of band gap. Nevertheless, the usual LDA and GGA approximations cannot describe correctly the strongly correlated systems with partially filled *d* or *f* shells. The strong electronic correlations between *d* electrons on the transition metal atoms suggest using GGA+U approximation [26,27] with correlation energy correction; "*U*" parameters are optimized previously for the same systems by Sha et al. and González-Borrero et al. which are equal to 7 and 5 for "d" electrons of Mo and W respectively [13,28]. The exchange parameter "*J*" fixed to 0.95 eV, is applied to the *d* states of all transition metals cations. As well as, the hybrid functional approach (HSE), use the standard choice for the fraction of Hartree–Fock exchange ($\alpha = 0.25$). Sampling of the Brillouin zone was done via $9 \times 9 \times 9$ and $11 \times 11 \times 11$ *k*-points grid generated according to the Monkhorst–Pack scheme [29] for conventional cells of MoO_3 and WO_3 respectively, using GGA-PBE and GGA+U approximations, and the *k*-point sampling was 6x6x6 for the HSE06 approach. The cut-off energy restricting the number of plane waves in the basis set was set to 500 eV for MoO_3 and WO_3 compounds.

The supercell approach was employed in order to simulate the effects of Lithium (Li) atoms in MO_3 (M: Mo and W) structure. We adopted $6 \times 6 \times 6$ (GGA+U and GGA-PBE) and $2 \times 2 \times 2$ (HSE) for orhorhombic-MoO_3 and cubic-WO_3 supercell containing 32 and 64 atoms.

3. Results and discussions

3.1. Structural properties

Metal oxides belong to the class showing topologically open-packed structures. They have the general composition MO_3, with M atoms representing transition metals.

The structural relaxation and optimization have been performed for MoO_3 and WO_3 compounds. The energies of these oxides were minimized to determine the internal atomic coordinates. The obtained optimal atomic coordinates from energy minimization were Mo 4*c* (0.087, 0.102, 0.250),O1 4*c*(0.499, 0.435, 0.250), O2 4*c*(0.521, 0.088, 0.250) and O3 4*c*(0.037, 0.221, 0.250) sites for MoO_3 orthorhombic structure, W (0, 0, 0), O1 (0.5, 0, 0), O2 (0, 0.5, 0) and O3 (0, 0, 0.5) sites for WO_3 cubic structure shown in Fig. 1.

At ambient conditions, the α-MoO_3 is the most thermodynamically stable phase of the molybdenum trioxide and is described in an orthorhombic unit cell with *Pbnm* space group. Whereas, the cubic structure is the stable phase of WO_3 compound with *Pm-3m* crystallographic space group.

All polymorphs of WO_3 can be described as distortions from the cubic ReO_3 structure, which consists of a three-dimensional network of corner-sharing WO_6 octahedra. The bulk crystals of MoO_3 have a structure consisting of corner-sharing chains of MoO_6 octahedra [30]. This structure consists of an α-phase is similar to a WO_3 perovskite type.

The lattice parameters of pure Li shown in Table 1, is over-estimated, whereas many previous calculations on transition metals clearly indicated that cell constants were usually under-estimated with standard DFT method, even GGA is applied, and it is the same for the bulk modulus. In other words the calculation of cell parameters and bulk modulus of pure Mo and W are in good agreement with the experimental values (Table 1).

Supercells with a total of 32 and 64 atoms were constructed based on the optimized structure parameters of the unit cell. A single Li atom was inserted (Fig. 2). This corresponds to the configurations: LiM_8O_{24} and $LiM_{16}O_{48}$, respectively.

3.2. Enthalpy of formation

The stability of pure compound and different configurations of doped one, with the dopant atom occupying interstitial sites can be discussed following the enthalpy of formation (ΔE_{form}) defined

Table 1
Bulk properties of Mo, W and Li elements.

Parameters/metals	Mo	W	Li
Valence electrons	$4d^5\ 5s^1$	$5d^4\ 6s^2$	$2s^1$
Space group	Im-3m	Im-3m	Im-3m
Lattice parameter (Å)			
a	3.150	3.170	3.514
	3.150[a]	3.160[a]	3.491[a]
Bulk modulus	267.43	311.16	13.17
B (GPa)	272.50[a]	323.20[a]	11.60[a]

[a] Ref. [31].

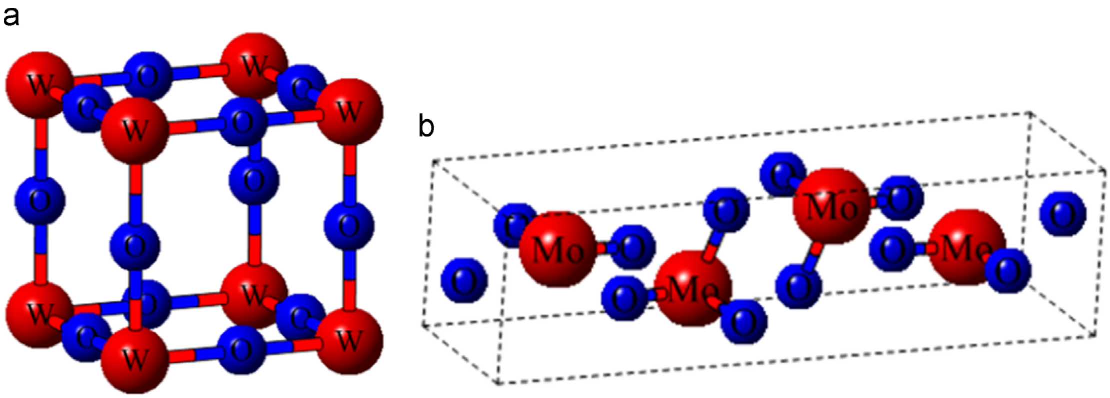

Fig. 1. Cubic WO_3 structure (a), orthorhombic MoO_3 structure (b).