

Ab initio study of electronic structures of BaMoO₄ crystals containing an interstitial oxygen atom

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Abstract:

The electronic structures of the perfect BaMoO₄ and BaMoO₄ crystals containing an interstitial oxygen atom situated at an appropriate position with the total energy being the lowest are studied within the framework of the density functional theory with the lattice structure optimized. The calculated results reveal that the interstitial oxygen atom situated at two different interstitial sites would combine with formal lattice oxygen ions forming molecular ions in two different ways respectively. And the interstitial oxygen atom would cause visible range absorption band peaked at about 320 nm.

Keywords: BaMoO₄ crystals; Interstitial oxygen; ABINIT

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1. Introduction

Scheelite-type tetragonal structures with formula (ABO₄) such as barium molybdate (BaMoO₄), where molybdenum atoms are arranged in tetrahedral coordination have attracted great attention due to the approved usage as scintillating materials and in electro-optical applications including solid-state lasers and optical fibers [1-6]. Numerous investigations focused on the luminescence properties of BaMoO₄, studying e.g, the intrinsic blue and green luminescence at 400-500 nm [7-9]. BaMoO₄ amorphous thin film exhibits a wide range room temperature emission band from 1.6 eV to 2.6 eV

peaking at 576 nm [10-11]. And it emits sharp emission bands peaking at 371 nm、405 nm、421 nm、440 nm、460 nm、470 nm、490 nm、542 nm and 559 nm at the room temperature with the excitations of 220 nm、230 nm、240 nm、250 nm、260 nm、270 nm、280 nm、290 nm、320 nm and 330 nm respectively [12].

It can be reduced from the reflectance spectra of BaMoO₄ amorphous thin film heat-treated at 600 °C for 2 hours that the crystal exhibits two absorption bands peaked at 240 nm and 320 nm [10]. The optical absorption bands are caused by the color centers produced by the thermal treatment. The absorption bands overlap with the excitation wavelength of the luminescence center, thus lowering the emission effect. Understanding of the color centers will be beneficial either to the revelation of the micro-mechanism of the color centers produced by the thermal treatment or to the enhancement of optical properties of the crystals.

It is known that the ABO₄ type of crystals would certainly contain a lot of intrinsic point defects, i.e. anion vacancy and cation vacancy respectively [10, 13-15]. The existence of those intrinsic vacancies makes the oxygen atom becoming movable. Once the movable oxygen atom situates at an appropriate interstitial position, it forms an interstitial oxygen atom O_i center. So the O_i center certainly exists in the crystals after thermal treatment.

In this paper the O_i center is studied by computational simulation in detail. In order to study the O_i center, it is necessary to determine the interstitial position that the oxygen atom may occupy. There are a few possible interstitial positions, but the most possible position should be the one with the lowest total energy of the crystals when one O_i is put into the position. And the most possible interstitial position of the O_i is determined by ABINIT software. Based on the location of the most possible interstitial position, the electronic structures of BaMoO₄ crystals containing O_i are calculated using the cluster [Ba₈Mo₇O₂₈O_i]²⁺ with DV-X α software.

2. Crystals structure and Computational method

2.1. Crystals structure

The BaMoO₄ crystal [16] is scheelite structured and the unit cell lattice parameters being $a = b = 5.479(9) \text{ \AA}$ and $c = 12.743(2) \text{ \AA}$, as shown in Fig.1. Its space group is $I4_1/\alpha$ (n° 88) and symmetry point group is reduced to S_4 [17]. Each molybdenum ion Mo^{6+} is surrounded by four oxygen ions O^{2-} and each barium ion Ba^{2+} is surrounded by eight oxygen ions O^{2-} , the polyhedral of four molybdenum ion Mo^{6+} surrounding O^{2-} are slightly distorted tetrahedras with the angles of O-Mo-O being 108.3° and 111.8° respectively [18].

Fig.1 The structure of BaMoO₄ crystal

2.2. Computational method

ABINIT code based on density functional theory and by using the pseudo-potential method [19-21] is employed to calculate the lattice parameters, interatomic distances and to locate the most possible position of the interstitial oxygen atom in the crystals. The pseudo-potential was generated following the norm-conserving scheme of Troullier and Martins [22]. The cell parameters are selected from the reported experimental values [16]. The wave functions at each k-point in the first Brillouin zone (BZ) are represented by the numerical coefficients of a finite set of plane waves, determined by a kinetic energy cutoff. The performed tests for the convergence of defects energies vs. the supercell size, the density of k-point unit cell and also for the energy cutoff have shown that for a $2 \times 2 \times 1$ super-cell, the $4 \times 4 \times 4$ points in BZ and a plane-wave basis set with an energy cutoff of 40 Hartree correspond to a quite stable state of the calculated system energy with $1.0 \times 10^{-4} \text{ eV/\AA}$ for the force tolerance and 1.0×10^{-10} hartree for the energy tolerance, therefore, this choice of parameters is adequate for the calculations.

After the most possible position of interstitial oxygen atoms in BaMoO₄ crystals were obtained, the molecular-cluster model within the framework of the fully relativistic self-consistent Dirac-Slater

theory, using a numerically discrete variational (DV- $X\alpha$) method, was adopted to study the electronic structures in the BaMoO₄ crystal. The method can save large computational time and keep high precision [23]. A set of the atomic orbital functions 4p, 4d and 5s of Mo, 5p, 5d and 6s of Ba, 2s, 2p and 3s of O reported by Nassif et al. [16] were chosen for the calculation. The simulation parameters are listed in Tab.1. This method turns out to be effective and easier to calculate the electronic structures in solids [24].

Tab. 1. Initial basis sets and the funnel potential well parameters

3. Results and discussion

The calculated results of lattice parameters and inter-atomic distances are listed in Tab.2. The calculated lattice parameters differ by an average of 0.16% from the experimental values [16]. Such a good agreement between the simulated results and the experimental results indicates that the chosen potential parameters are valid. So the inter-atomic potential model for BaMoO₄ crystals provides a good basis for the interstitial oxygen center calculation.

Tab.2. Calculated lattice parameters of perfect BaMoO₄ crystal

The most possible position interstitial oxygen atom might occupy corresponds to the lowest total energy of the crystals. Therefore, in the process of the lattice relaxation, the conjugate gradient energy minimization method (within ABINIT program code) is used to optimize lattice, in order to keep the total energy of the crystals being the lowest. Some possible interstitial positions that the interstitial oxygen atom might occupy are shown in Fig.2 and the total energy of the crystals containing an interstitial oxygen atom, which occupies one of these possible positions, are calculated and shown in Tab.3.

Fig.2. (a) Structure of the normal MoO_4^{2-} (b) the structure of MoO_4^{2-} containing the interstitial oxygen atoms. A-F, and X are the possible positions where the interstitial oxygen atoms exist in $BaMoO_4$ crystal.

Tab.3. Total energies of the crystal containing the interstitial oxygen atoms at the different sites

The figures of the calculated total density of states and partial densities of states for the perfect $BaMoO_4$ crystal are shown in Fig. 3. It can be easily seen that the upper valence band is composed dominantly by the O 2p states and slightly by the Mo 4d states, and the bottom of conduction band is mainly attributed to O 2p states and Mo 4d states. It demonstrates that the covalent property of the crystals, mainly contributed by the Mo-O bond, coincides with the viewpoint reported [16]. The calculated band gap is about 4.6 eV similar to the reported experimental value [25, 26] and the band gap of $PbWO_4$ (3.7 - 4.7 eV) [27, 28]. It is well known that the nature of the electropositive ions (Ba^{2+} , Pb^{2+}) seems to have small impact on the band gap values [25]. Meanwhile the electro-negativity as inferred from the band gap changes in the sequence of $Mo^{6+} > W^{6+} > Nb^{6+}$. Therefore for two isostructural solids, the W-containing one should have higher band gap value than the Mo-containing counterpart.

Fig.3 Total density of states and partial densities of states for the perfect $BaMoO_4$ crystal.

As to the $BaMoO_4$ crystal containing interstitial oxygen, two cases were taken into account: the interstitial oxygen atom exists at position A and position C, as shown in Fig. 2. When the interstitial oxygen atom exists at position A, the total density of states and partial densities of states are shown in Fig.4. Comparing the total densities of states of the perfect crystal with that of the crystal containing an interstitial oxygen atom, it is evident that a new weak peak appears in the forbidden band and located near the valence band when there is an interstitial oxygen existing in the crystal, as is shown in

Fig.3. The partial densities of states in Fig.4 reveals that this new weak peak is simultaneously contributed by the 2p states of the interstitial oxygen atom situated at A and the two nearest neighbor lattice oxygen ions O1 and O2. Comparing the distances between the interstitial oxygen A to O1 and O2 for the non-optimized structure with that for the optimized structure, it is found that, after structure optimization, the distance between the interstitial oxygen A and the oxygen ions O1, O2 both change from $1.4576 \overset{\circ}{\text{Å}}$ to $1.4967 \overset{\circ}{\text{Å}}$, which tends to the chemical bond length of O-O in O_2 ($1.49 \overset{\circ}{\text{Å}}$) [29]. In alkali halides, an interstitial halogens atom can fill an alkali ion vacancy and combine with two nearest neighbor lattice halogens ions forming halogens molecule ion X_3^{2-} [30]. In our calculation, although the interstitial oxygen is not the barium vacancy, by analyzing the chemical combination properties of oxygen and the distances between the two oxygen atoms after structure optimization, we can reasonably conclude that the interstitial oxygen should combine two nearest neighbor lattice oxygen ions O1 and O2 forming the molecular ion O_3^{4-} , when it exists at position A in the BaMoO_4 crystal.

The molecular formula can be expressed by the chemical equation as:

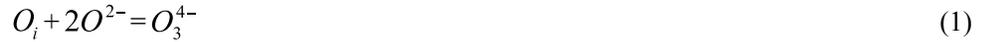


Fig.4. Total density of states and partial densities of states of BaMoO_4 crystal containing an interstitial oxygen atom; the interstitial oxygen atom is in position A of Fig. 2. O_N indicates normal lattice oxygen ions

When the interstitial oxygen exists at position C, the total density of states and partial densities of states being shown in Fig.5, a similar situation occurs to the interstitial oxygen atom existing at position A, namely a new weak peak also appears in the forbidden band. The main difference from the former case is that this new peak is mainly attributed to the 2p states of the interstitial oxygen atom situated at position C and the formal lattice oxygen ion O3, together with the 2p states of the formal lattice oxygen ions O1 and O2 contributing a little. Comparing the distances between the interstitial oxygen C and O3 for the non-optimized structure with that for the optimized structure, it is found that, after structure optimization, the distance between the interstitial oxygen C and the oxygen ions O3

becomes $1.5192 \overset{\circ}{\text{Å}}$, which tends to the chemical bond length of O-O in O_2 ($1.49 \overset{\circ}{\text{Å}}$) [29]. For the formation of color centers in alkali halides, we know an interstitial haloids atom can easily combine with three formal lattice haloids ions forming haloids molecule ion X_4^{3-} [30]. It can be reasonably believed that a similar result will occur in BaMoO_4 crystal. Therefore once an interstitial oxygen atom exists at position C in the crystal, it will combine with three formal lattice oxygen ions forming the molecular ion O_4^{6-} . The molecular formula can be expressed by the chemical equation as:



Fig.5. Total density of states and partial density of states of BaMoO_4 crystal containing interstitial oxygen atom; the interstitial oxygen atom is in position C of Fig. 2. O_N indicates normal lattice oxygen atoms

As previously illustrated, the interstitial oxygen atoms would form a molecular ion together with the nearest neighbor lattice oxygen ions. According to the definition of color centers in alkali halides [30], the molecular ion formed by interstitial oxygen atom with its neighbor anions is defined by H center. The existing of H center would cause optical absorption, thus influencing the optical properties of the BaMoO_4 crystals. When the interstitial oxygen is located at position A, the energy related to the transition of the energy peak caused by O_3^{4-} to the bottom of the conduction band is 3.88 eV corresponding to the 320 nm absorption. When the interstitial oxygen is located at position C, the energy related to the transition of the energy peak caused by O_4^{6-} to the bottom of the conduction band is 3.86 eV corresponding to the 322 nm absorption. The two transition energies are so close that the optical absorptions caused by the transitions would overlap as one band, becoming difficult to be distinguished. Hence the absorption band peaked at 320 nm of the crystals by the thermal treatment is attributed to the interstitial oxygen atom center.

4. Conclusions

The positions of the interstitial oxygen atom in BaMoO_4 crystals were obtained by using the conjugate gradient energy minimization method in the process of the lattice relaxation. It is found

that the total energy of the crystal is low when interstitial oxygen atom exists around the Mo^{6+} ion. Based on the calculated results, the electronic structures of perfect BaMoO_4 and BaMoO_4 crystals containing an interstitial oxygen atom with the lattice structure optimized are studied within the framework of the density functional theory. By analyzing the calculated results it can be concluded that an interstitial oxygen atom could combine with the nearest neighbor lattice oxygen ions to form molecular ions O_3^{4-} and O_4^{6-} , which cause the experimentally observed 320 nm absorption band. For the future work, it might be worth to solve the molecular orbital (MO) diagram and the electron configurations of the O_3^{4-} and O_4^{6-} complexes, as well as the excitations inside of the molecules of O_3^{4-} and O_4^{6-} complexes to understand fundamentally of the experimental observed red shift [12] between the absorption (320nm) and emission (542 nm) in room temperature.

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Tab.1. Calculated lattice parameters of perfect BaMoO₄ crystal

property	calculated	experimental[16]	difference (%)
lattice energy (Ha/formula)	-292.8996		
lattice parameters (Å)			
a=b	5.5364	5.5479	-0.207
c	12.7153	12.7432	-0.219
volume (Å^3)	389.746	392.225	-0.632
interatomic distance (Å)			
Ba-O ×4	2.7582	2.7643	0.221
×4	2.7112	2.7183	0.261
Mo-O ×4	1.7623	1.7653	-0.170

Tab.2. Total energies of crystal containing the interstitial oxygen atoms at the difference sites

Defect	energy (Hartree)	defect	energy (Hartree)
OA	-306.4367930	OE	-308.4730431
OB	-306.3250785	OF	-308.4730429
OC	-308.4757218	OX	-305.7447807
OD	-308.4757216		

Tab.3 The initial basis sets and the funnel potential well

Ions	Frozen core	Orbits for basis functions	<i>Funnel potential well</i>		
			V_0/ eV	R_1/ nm	R_2/ nm
Mo ⁰	1s—4d	4p, 4d, 5s	-2.5	0.1.6	0.26
Ba ²⁺	1s—4s	5s, 5d, 6s	-2.6	0.25	0.30
O ²⁻	1s	2s, 2p, 3s	-3.0	0.25	0.30
O _i	1s	2s, 2p, 3s	-3.0	0.25	0.30

Fig.1 The structure of BaMoO₄ crystal

Fig.2 (a) Structure of the normal MoO_4^{2-} (b) the structure of MoO_4^{2-} containing the interstitial oxygen atoms. A-F and X are the probable positions where the interstitial oxygen atoms exist in the BaMoO₄ crystal. Black circles are Mo atoms, hollow circles are O atoms.

Fig.3 Total densities of states and partial densities of states for the perfect BaMoO₄ crystal

Fig.4 Total density of states and partial density of states of BaMoO₄ crystal containing an interstitial oxygen atom; the interstitial oxygen atom is in position A of Fig. 2. O_N indicates normal lattice oxygen atoms

Fig.5 Total density of states and partial density of states of BaMoO₄ crystal containing interstitial oxygen atom; the interstitial oxygen atom is in position C of Fig. 2. O_N indicates normal lattice oxygen atoms

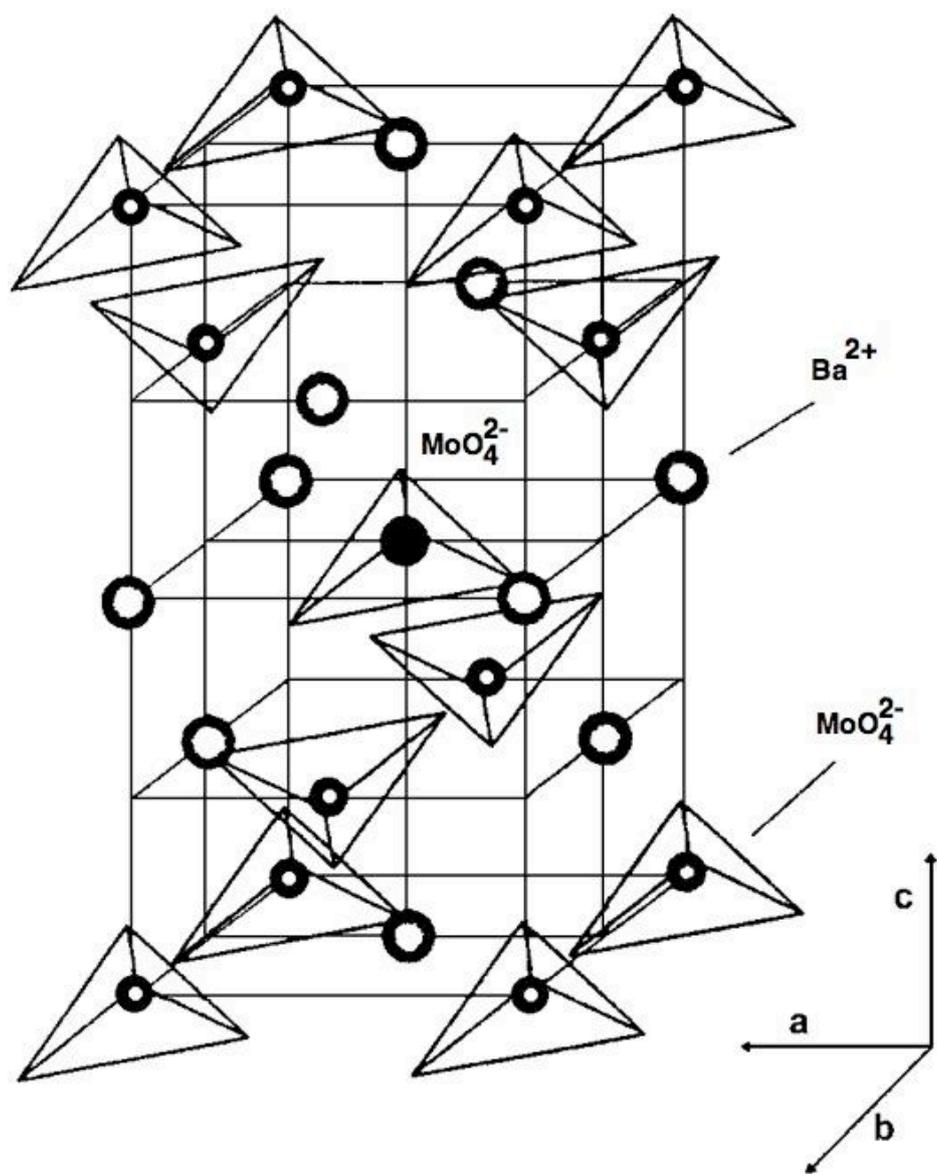
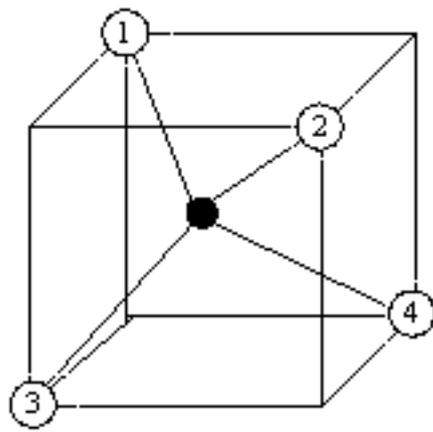
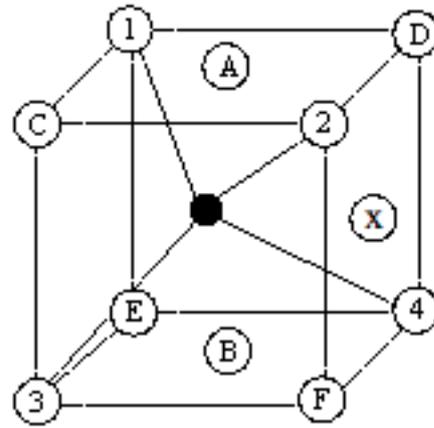


Fig. 1



(a)



(b)

Fig. 2

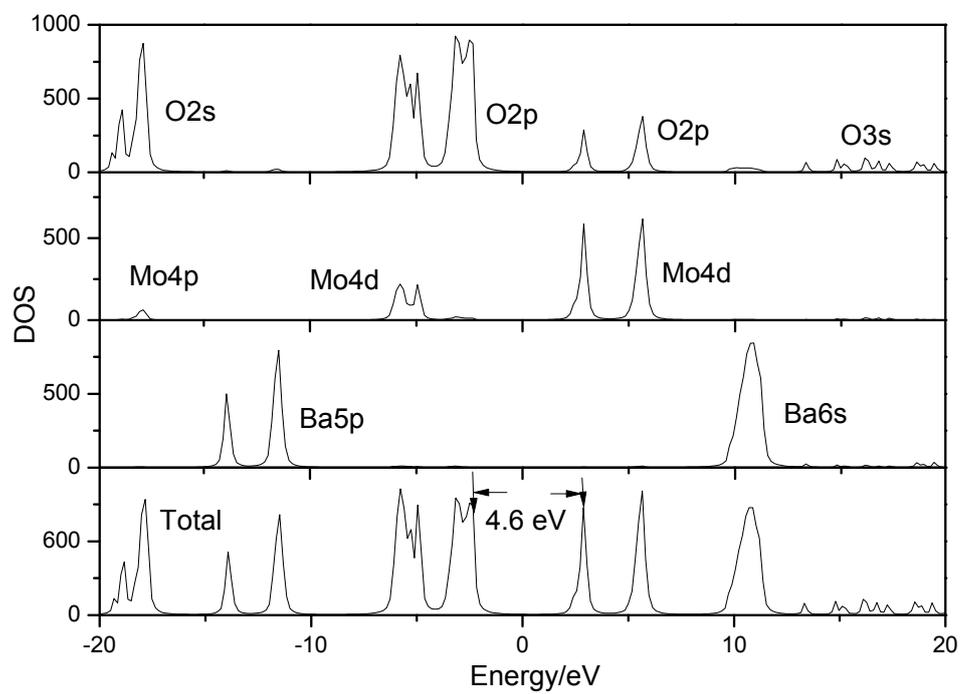


Fig.3

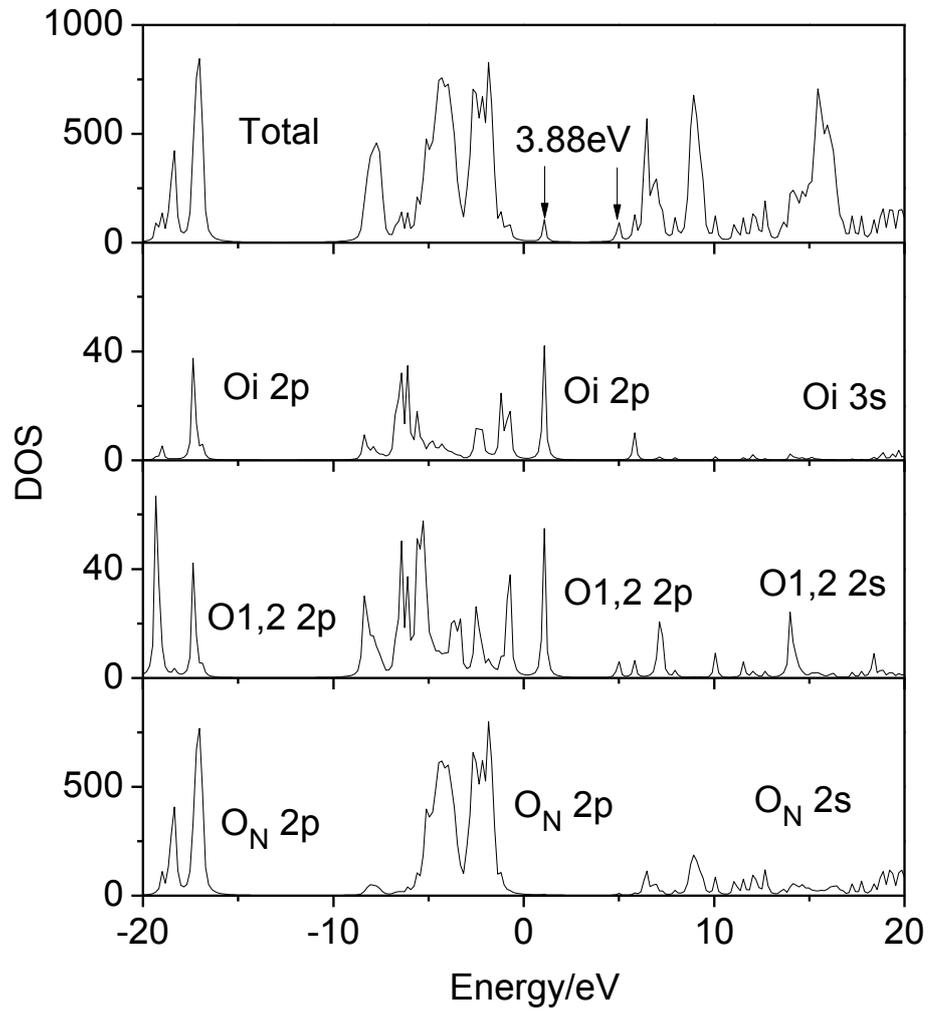


Fig. 4

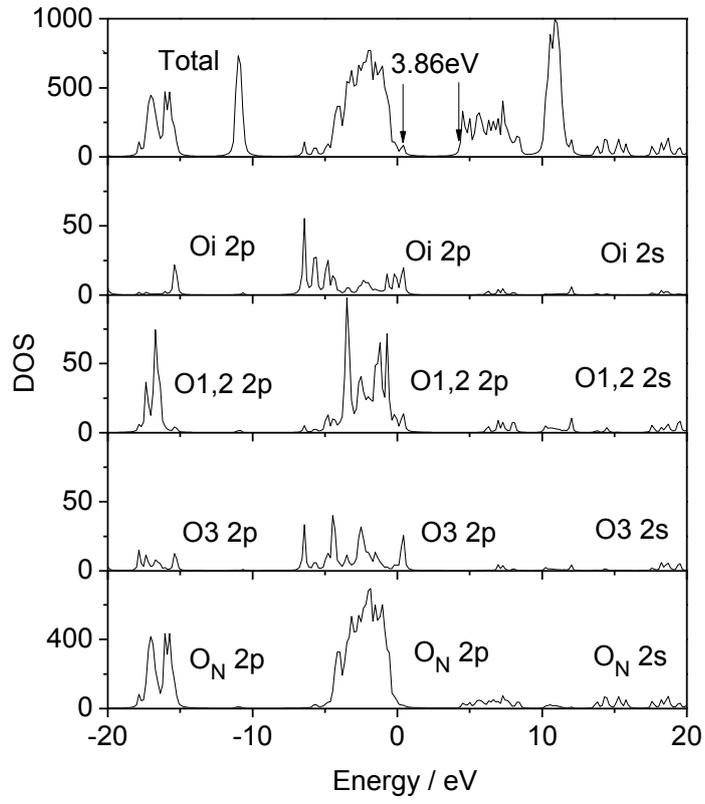


Fig.5