First-principles study on electronic structures of BaMoO₄ crystals containing F and F⁺ color centers

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A B S T R A C T
The electronic structures of perfect crystals of barium molybdate (BaMoO₄) and of crystals containing F and F⁺ color centers are studied within the framework of the fully relativistic self-consistent Dirac-Slater theory by using the numerically discrete variational (DV-Xα) method. The calculated results suggest that the donor energy level of the F center as well as F⁺ center is located within the band gap. The respective optical transition energies are 1.86 eV and 2.105 eV corresponding to the wavelength of the absorption band of 668 nm and 590 nm. It is therefore suggested that these bands are originate from the F and F⁺ centers in the crystal.

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 [1–4]. Numerous investigations focused on the luminescence properties of BaMoO₄, studying e.g. the intrinsic blue and green luminescence at 400–500 nm. At room temperature a decay time of a few nanoseconds was reported due to the radiating transition of the MoO₂⁴⁻ group [5]. Ryu et al. [6] gave evidence that at room temperature the photoluminescence (PL) emission spectra of BaMoO₄ colloidal nanoparticles using an excitation wavelength of 260 nm exhibits a triplet bands structure and can be decomposed by five bands peaked at 340, 440, 465, 500 and 600 nm, respectively, by Gaussian analysis. It is different to the single structured PL spectra of BMO powder and thin film excited by 488 nm reported by Marques et al. [7,8]. After analyzing the shape of the emission bands considering Jahn-Teller splitting of the excited MoO₂⁴⁻ anion, it is believed [6] that the weak red emission band is probably caused by Frenkel defects due to an oxygen atom shifting to a suitable inter-site position and simultaneous creating an oxygen vacancy. It is well known that the oxygen vacancy existed in the crystal would electrons to maintain the local electrical neutrality. An oxygen vacancy traps two electrons or one electron would form the F or F⁺ center, respectively, [9,10]. These vacancies are responsible for the luminescence with green-red emission, while the blue emission is due the slightly distortion on the tetrahedrons in the lattice [11]. The creation of color centers would certainly influence the optical properties of the crystal. Understanding of the color centers can not only reveal the micro-mechanism of the color centers but also enhance the optical properties of the crystal.

In this paper, the electronic structures of perfect BaMoO₄ crystal and BaMoO₄ containing F or F⁺ center are studied based on the density functional theory (DFT) by computational simulation. The calculated results indicated that the existence of F or F⁺ center would introduce an electrical state corresponding to 1s of either F or F⁺ center within the band gap. The transition energy from this 1s state to the bottom of the conduction band of F center and F⁺ center is 1.86 eV and 2.105 eV corresponding to 668 nm and 590 nm absorption band respectively. Hence the 668 nm and 590 nm absorption band of the crystal is attributed to F and F⁺ center, respectively.

2. Computational model and method

2.1. Crystal structure

The BaMoO₄ crystal [12] is scheelitelike structured and the unit cell lattice parameters being \( a = b = 0.5479(9) \) nm and \( c = 1.2743(2) \) nm, as shown in Fig. 1. Its space group is \( I4_1/\alpha \) (n° 88).
and symmetry point group is reduced to $S_4$ [13]. 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 dis-
torted tetrahedras with the angles of O–Mo–O being 108.3°
and 111.8°, respectively [14].

2.2. Computational method

ABINIT code based on density functional theory using the pseudo-
potential method [15–17] is employed to calculate the lattice
parameters and interatomic distances. The pseudo-potential was
generated following the norm-conserving scheme of Troullier
and Martins [18,19]. The cell parameters are selected from the
experimental reported [12]. 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 density of k-point unit
cell and also for the energy cutoff have shown that the $4\times4\times4$
points in BZ and a plane-wave basis set with an energy cutoff of
40 Hartree correspond to a quite stable state of the system energy
and therefore this choice of parameters is adequate for the
calculations.

The calculated results are listed in Table 1. It can be seen from
Table 1 that the calculated results fitted well with the experimental
values, therefore the parameters used in the calculation are
believable for further calculations.

The electronic structures of the crystal were calculated by using
the cluster-embedding calculation method. The as-grown BaMoO$_4$
crystal in laboratory has the scheelite lattice structure. The cluster
chosen in the calculation has the chemical formula of [Ba$_8$Mo$_7$O$_{28}$]$^{2+}$
and consists of 8 Ba 7 Mo and 28 O centered at Mo$^{6+}$. The boundary
conditions for the clusters are described by the embedding cluster
scheme [20]. The potentials of the crystal ions around the cluster
are simulated by Madelung potentials. Pseudo-potentials are used
for the cluster ions to avoid false charge transfer from the clusters
to the external “host” [21,22].

The molecular–cluster model with the framework of the fully
relativistic self-consistent Dirac-Slater theory, using a numerically
discrete variational (DV-X02) method is adopted to study the elec-
tronic structures of BaMoO$_4$ crystal. This method has been shown
to be effective and easier to calculate the electronic structures in
solids of saving large computational time and keeping high precision
[23]. A set of atomic orbits W 5p, W 5d, W 6s, Ba 5s, Ba 5d,
Ba 6s, O 2s, O 2p and O 3s reported by Nassif et al. [12] are calcu-
lated as basic functions in BaMoO$_4$ crystal. The simulation param-
eters are listed in Table 2.

Considering the relaxation effect produced by the electronic
transitions in the crystal, the transition state method is used to
calculate the excitation energy. Ionization energy $E_{\text{ion}}$ is the minimum
energy required to remove an electron from the ground state of the
isolated neutral atom

$$E_{\text{ion}} = E(n_i - 1) - E(n_i) \approx \frac{\partial E}{\partial n_i} = -e_i T.$$  

(1)

Similarly, excitation energy is the minimum energy required to
bring a system to a specified higher energy level, thus the excita-
tion energy can be expressed as the energy difference between i or-
bit and j orbit

$$E_{i-j} = E(n_i - 1, n_j + 1) - E(n_i, n_j) = \varepsilon_i T - \varepsilon_j T.$$  

(2)

3. Results and discussion

The total densities of states (TDOS) and partial densities of states
(PDOS) for the perfect BaMoO$_4$ crystal are calculated, as shown in
Fig. 2. Comparing TDOS with PDOS, it can be easily observed that
the top part of valence band is mainly composed by the O 2p states
and the bottom of conduction band is mainly attributed to O 2p
states accompanied by some Mo 4d states, while the bottom of the
conduction band is mainly composed of Mo 4d states and some
O 2p states. However the Ba 6s states distribute mainly on the con-
duction band and do not overlap with the O 2p states on the top of
the valence band. It means that the Mo-O bond presents stronger
covalence properties than the Ba 6s bond. The calculated results
are in good agreement with the results reported by Nassif et al.
[12]. The calculated band gap is about 4.6 eV which is similar to
the result reported by Afanasyev [24] and slightly smaller than the
band gap of PbWO$_4$ (4.7 eV) [22]. It is well known that [24] the nat-
ure of the electropositive ions (Ba$^{2+}$, Pb$^{2+}$) seemed to have small im-
 pact on the band gap values. Meanwhile the electro-negativity as
inferred from the band gap changes in the sequence Mo$^{6+}$ > W$^{6+}$ >
Nb$^{6+}$. Therefore for two isostructural solids, the W-containing one

Table 1

<table>
<thead>
<tr>
<th>Ions</th>
<th>Frozen core</th>
<th>Orbits for basis functions</th>
<th>Funnel potential well $V_0$ (eV)</th>
<th>$R_1$ (nm)</th>
<th>$R_2$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo$^{6+}$</td>
<td>1s–4d</td>
<td>4p, 4d, 5s</td>
<td>−2.5</td>
<td>0.16</td>
<td>0.26</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>1s–4s</td>
<td>5s, 6d, 6s</td>
<td>−2.6</td>
<td>0.25</td>
<td>0.30</td>
</tr>
<tr>
<td>O$^{2-}$</td>
<td>1s</td>
<td>2s, 2p, 3s</td>
<td>−3.0</td>
<td>0.25</td>
<td>0.30</td>
</tr>
<tr>
<td>F$^-$</td>
<td>1s, 2s</td>
<td></td>
<td>−3.0</td>
<td>0.30</td>
<td>0.82</td>
</tr>
<tr>
<td>F$^+$</td>
<td>1s, 2s</td>
<td></td>
<td>−3.5</td>
<td>0.32</td>
<td>0.56</td>
</tr>
</tbody>
</table>

The initial basis sets and the funnel potential well.

Table 2

<table>
<thead>
<tr>
<th>Property</th>
<th>Calculated</th>
<th>Experimental [12]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice energy ($\text{Ha/formula}$)</td>
<td>$-292.8996$</td>
<td>$-292.8996$</td>
</tr>
<tr>
<td>Lattice parameters ($\text{Å}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a = b$</td>
<td>5.5364</td>
<td>5.5479</td>
</tr>
<tr>
<td>$c$</td>
<td>12.7153</td>
<td>12.7432</td>
</tr>
<tr>
<td>Volume ($\text{Å}^3$)</td>
<td>$389.746$</td>
<td>$392.225$</td>
</tr>
<tr>
<td>Interatomic distance ($\text{Å}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba–O</td>
<td>$\times 4$</td>
<td>$2.7582$</td>
</tr>
<tr>
<td>Mo–O</td>
<td>$\times 4$</td>
<td>$2.7112$</td>
</tr>
</tbody>
</table>
should have higher the band gap value than the Mo-containing counterpart.

The TDOS and PDOS of BaMoO₄ crystal containing F color center are also calculated using the cluster (Ba₈Mo₇O₂₇F⁺)³⁺. The calculated results are shown in Fig. 3. It can be seen from the figure that the top part of the valence band and the bottom of the conduction band are also mainly distributed by the O 2p states and Mo 4d states and the bottom of the conduction band are also distributed by the Mo 4d states and O 2p states. The main difference between the perfect crystal and the F center contained crystal is the energy gap of the F center contained crystal becoming narrower than that of the perfect crystal and there is a new electronic state peak appearing within the energy gap. The F center is defined by an oxygen vacancy trapping two electrons [9]. The oxygen vacancy makes its neighbor ions approach to the vacancy therefore higher the 2p states of the oxygen ions nearest to the central F center resulting in narrows the energy gap of the crystal. The new electronic state peak appeared within the energy gap is just the 1s ground state of the F center.

The TDOS and PDOS of BaMoO₄ crystal containing F⁺ color center are also calculated using the cluster (Ba₈Mo₇O₂₇F⁺)³⁺. The calculated results are shown in Fig. 4. Similarly to the results of the crystal containing F center, it can be seen from Fig. 4 that the energy gap is narrower than that of the perfect crystal and there is a new electronic state peak appearing within the energy gap. The calculation indicated that the state peak appeared within the energy gap is attributed by the 1s state of the F⁺ center.

It can be seen from Figs. 3 and 4 that the position of the 1s state of the F⁺ center lies lower in energy than the 1s state of the F center. Since the F⁺ center is an oxygen vacancy trapping one electron, however the F center is an oxygen vacancy trapping two electrons. So the electron in the F⁺ center is more tightly trapped by the oxygen vacancy than the two electrons in the F center. Therefore the ground state of the F⁺ center physical reasonable lies lower in energy than that of the F center.

The optical absorption transition of F or F⁺ center corresponding to 1s–2p electronic transition. The calculation of the crystal containing either F or F⁺ center indicated that the 2p first excited state of F or F⁺ center emerges in the conduction band. Hence the optical absorption transition of the present cases corresponding to the F or F⁺ electron transit from the ground state to the bottom of the conduction band. Hence it can be physically predicted that the optical absorption of the F center should peaks in the longer wavelength side of that of the F⁺ center. The similar results of PbWO₄ and PbMoO₄ crystals containing F and F⁺ centers were reported [22,25].

The calculated transition from the 1s state of the F center to the bottom of the conduction band is 1.86 eV corresponding to 668 nm and from the 1s state of the F⁺ center to the bottom of the conduction band is 2.105 eV corresponding to 590 nm, respectively. So it is concluded that F and F⁺ color centers in the crystal could be responsible for the absorption bands peaking at 668 nm and 590 nm respectively. It coincides with the conclusion that the oxygen vacancy exhibited in the scheelite structured crystal would cause absorptions in the range of 500–700 nm [26,27].

### 4. Conclusions

The electronic structures of the perfect BaMoO₄ and the defect BaMoO₄ crystal containing F and F⁺ color centers have been studied by using the relativistic self-consistent Discrete Variational embedded cluster method with the lattice optimized. The calculated results indicate that the 668 nm and 590 nm absorption bands is originated from the F and F⁺ color centers contained in the crystal, respectively.

### References

