



# First-principles study on electronic structures and color centers in BaWO<sub>4</sub> crystal with barium vacancy<sup>☆</sup>

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## ARTICLE INFO

### Article history:

Received 25 September 2008

Received in revised form

3 January 2009

Accepted 12 January 2009

### PACS:

71.20.Ps

78.20.Ci

61.72.Ji

61.72.Bb

### Keywords:

BaWO<sub>4</sub> crystal

CASTEP

Electronic structures

Color center

Barium vacancy

## ABSTRACT

The electronic structures and absorption spectra for the perfect BaWO<sub>4</sub> (BWO) crystal and the BWO crystal containing barium vacancy ( $V_{Ba}^{2-}$ ) have been studied by using density functional theory code CASTEP with the lattice structure optimized. For the BWO crystal containing  $V_{Ba}^{2-}$ , there exhibit four absorption bands peaking at 0.71 eV (1751 nm), 1.85 eV (672 nm), 3.43 eV (362 nm) and 3.85 eV (322 nm), respectively. The origins of the absorption bands have been discussed and corresponding color centers also have been established.

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## 1. Introduction

In the last few years, tungstate materials (CaWO<sub>4</sub>, SrWO<sub>4</sub>, BaWO<sub>4</sub>, PbWO<sub>4</sub>, and EuWO<sub>4</sub>) have attracted a great deal of interest due to their applications as laser host materials, scintillators in high-energy physics detectors and oxide ion conductors. It is important to understand their luminescent behavior of structural properties and electro-optical properties for their applications. Among the tungstate materials, BWO is a potential material to be a universal Raman-active crystal for its high gain in both the steady state and the transient state [1,2]. It is also a suitable candidate as an efficient stimulated Raman scattering (SRS) for its emission of blue luminescence [3].

Nowadays, most people focus on the investigation of BWO thin films, SRS, the growth of BWO crystals and synthesization of nanoscale BaWO<sub>4</sub> spheres, cylinders and rods [3–6]. However, few papers deal with the absorption bands and defects study of BWO crystal. The colorless BWO crystal turns yellowish on annealing in

air or oxygen and turns darker under vacuum. The annealing in air/oxygen introduces an absorption band around 370 nm and an emission in green region [7]. BWO and PbWO<sub>4</sub> crystals having the same lattice structure belong to the scheelite structure and they are both typical non-stoichiometric crystals. They should be of some similar properties. Liu et al [8,9] have studied point defects  $V_{Pb}^{2-}$ ,  $V_0^{2+}$ , the clusters defects  $V_{Pb}^{2-} - V_0^{2+}$  and  $V_0^{2+} - V_{Pb}^{2-} - V_0^{2+}$  of PbWO<sub>4</sub> crystal. From the facts mentioned above,  $V_{Ba}^{2-}$  may also exist in BWO and should exhibit some similar physical properties. In this paper, the electronic structures, the absorption bands and corresponding color centers in the BWO crystal with  $V_{Ba}^{2-}$  have been studied by using the CASTEP code. The CASTEP code is powerful tools to study on the electronic structures and optical properties of the crystal. In fact, there are a large number of successful simulations on the optical properties of crystals using the CASTEP code [10,11].

## 2. Computational model and method

### 2.1. Computational model

BWO crystal with scheelite structure crystallized in tetragonal space group  $C_{4h}^6$  ( $I4_1/a$ ) has two molecular units in the primitive

<sup>☆</sup> Supported by the Doctor Foundation of USST (X696). Project supported by the Scientific Development Foundation of Shanghai Municipal Education Committee, China (Grant no. 06EZ032).

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cell. Lattice parameters of BWO are  $a = b = 5.61 \text{ \AA}$  and  $c = 12.71 \text{ \AA}$  [12]. The  $\text{Ba}^{2+}$  and  $\text{W}^{6+}$  sites have  $S_4$  point symmetry. The  $\text{Ba}^{2+}$  is eightfold coordinated by  $\text{O}^{2-}$  in the form of octahedron made up of elongated and compressed tetrahedral. The  $\text{WO}_4^{2-}$  groups have the shape of nearly regular tetrahedral, slightly compressed along the  $S_4$  axis. The oxygen sites have only trivial point symmetry and the crystal has an inversion center. The BWO super-cell used here consists of 16 Ba, 16 W and 64 O centered at  $\text{Ba}^{2+}$ . The BWO super-cell containing  $\text{V}_{\text{Ba}}^{2-}$  has the centered Ba ion substituted by  $\text{V}_{\text{Ba}}^{2-}$ .

## 2.2. Computational method

The lattice optimization for the BWO containing  $\text{V}_{\text{Ba}}^{2-}$  is performed by using CASTEP code. We use ultrasoft pseudopotentials for the barium, tungsten and oxygen atoms and a plane-wave cutoff of 340 eV. Optimal atomic positions are determined until satisfying the conditions: (1) the maximal force on them was smaller than 0.5 eV/nm; (2) the maximal change of energy per atom was smaller than 0.00001 eV; (3) the maximal displacement was smaller than 0.0001 nm. All other calculations are performed on the basis of the lattice structure optimized.

The ground-state electronic structures are calculated using the CASTEP code with the DFT method. Generalized gradient approximations (GGA) are chosen for the theoretical basis of density function. GGA density functional we used in the paper is Perdew and Wang (PW91). The PW91 is widely used in DFT. And several density functions, such as PBE, RPBE and LDA, have been tested in the calculations of electronic structures and optical properties for the  $\text{PbWO}_4$  and  $\text{CaMoO}_4$  crystal. The calculated results using the PW91 are more close to the experimental results. The structure of  $\text{BaWO}_4$  is similar to  $\text{PbWO}_4$  and  $\text{CaMoO}_4$  crystal. So they must be the similar properties and the PW91 is selected in the paper. In addition there are many successful calculations using PW91 [13–16]. In the process of setting up the CASTEP run, basic parameters were chosen as follows: kinetic energy cutoff = 340 eV, fast Fourier transform (FFT) grid dimensions =  $60 \times 60 \times 64$ , and space representation = reciprocal, SCF tolerance =  $1.0 \times 10^{-6}$  eV/atom. The dielectric function of an anisotropic material is a complex symmetric second-order tensor describing the linear response of an electronic system to an applied external electric field. The imaginary part of the dielectric tensor is directly related to the band structure of a solid, so it can be computed from the knowledge of single-particle orbitals and energies approximated by the solutions of the Kohn–Sham equations. However, it is a well known fact that DFT calculations underestimate the band gap. To take this into account, a “scissors operator” was used, allowing a shift of the bands situated above the valence band and a rescaling of the matrix elements. This was shown computationally (comparing GW and LDA band structures) that most of the difference between Kohn–Sham eigenvalues and the true excitation energies can be accounted for by a rigid shift of the conduction band upwards with respect to the valence band [17]. Assuming the one-electron rigid-band approximation and neglecting the electron polarization effects (Koopmans’ approximation), in the limit of linear optics and of the visible–ultraviolet range, the imaginary part of dielectric function  $\epsilon_i$  is given by Refs. [18,19]

$$\epsilon_i(\omega) = \frac{e^2 \pi^2}{\epsilon_0 m^2 (\omega - \Delta c / \hbar)^2} \times \sum_{V,C} \left\{ \int_{\text{BZ}} \frac{2d\mathbf{k}}{(2\pi)^3} |\mathbf{a} \cdot \bar{M}_{V,C}|^2 \times \delta[E_C(\bar{\mathbf{k}}) + \Delta c - E_V(\bar{\mathbf{k}}) - \hbar\omega] \right\} \quad (1)$$

where  $\mathbf{a}$  is the unit vector potential  $\bar{A}$ .  $\bar{M}_{V,C}$  is the matrix of dipole transition.  $C$  is unoccupied electronic states (mainly implies the

conduction band).  $V$  is occupied electronic states (mainly implies the valence band). BZ is Brillouin zone.  $\Delta c$  is the shifting value of the scissors operator.  $e$  is the electron charge.  $\epsilon_0$  is the dielectric constant in vacuum.  $m$  is the free electron mass.  $\omega$  is the frequency of the incident wave.  $\mathbf{k}$  is wave vector. The Kramers–Kronig transformation links the real and the imaginary parts of the dielectric function. The Kramers–Kronig transformation and the smearing factor of 0.12 eV are used to obtain the real part  $\epsilon_r(\omega)$  of the dielectric function. According to the fact that the calculated band gap of the perfect BWO crystal is 4.2 eV and the experimental value is 5.2 eV [20], the shifting value of the scissors operator  $\Delta c$  is chosen as 1.0 eV. For dielectric tensor calculation, the Brillouin zone (BZ) integration was made with 64 independent  $k$ -points for BWO crystal.

## 3. Results and discussion

### 3.1. Electronic structures

The electronic structures are calculated in the region from  $-30 \text{ eV}$  to  $10 \text{ eV}$ . Comparing with that of the BWO crystal containing  $\text{V}_{\text{Ba}}^{2-}$ , the total density of states (TDOS) of the perfect BWO crystal is given in Fig. 1 too. In this paper, all the curves related to the perfect BWO crystal are plotted in dot lines and those related to the BWO crystal containing  $\text{V}_{\text{Ba}}^{2-}$  are plotted in solid lines.

Compared with the perfect BWO crystal, the TDOS of BWO crystal containing  $\text{V}_{\text{Ba}}^{2-}$  has obvious features as follows: (1) the band gap increases about 0.5 eV; (2) the figure shifts to the higher energy region; (3) there is a new peak in the forbidden band. It is that the existence of  $\text{V}_{\text{Ba}}^{2-}$  cause increase of the band gap of about 0.5 eV and a small peak of the TDOS occurs at about 0.75 eV within the forbidden band, as shown an inset in Fig. 1. It can be seen from Fig. 2 that the small state peak occurred in the forbidden band is the state of O 2p.

The optimized results of the detail structure of the crystal caused by the introduction of  $\text{V}_{\text{Ba}}^{2-}$  are listed in Table 1. The existence of  $\text{V}_{\text{Ba}}^{2-}$  changed the distances between the  $\text{V}_{\text{Ba}}^{2-}$  and its neighboring ions. Compared to the perfect BWO crystal it can be obviously seen from Table 1 that (1) the anions ( $\text{O}^{2-}$ ) nearest to  $\text{V}_{\text{Ba}}^{2-}$  are slightly displaced outwards  $\text{V}_{\text{Ba}}^{2-}$ , (2) the cations ( $\text{W}^{6+}$  and  $\text{Ba}^{2+}$ ) next nearest to  $\text{V}_{\text{Ba}}^{2-}$  are slightly shifted towards  $\text{V}_{\text{Ba}}^{2-}$ , (3) the W–O bond length between  $\text{W}^{6+}$  and  $\text{O}^{2-}$  ions nearest to  $\text{V}_{\text{Ba}}^{2-}$  are slightly decreased.

The increase of the band gap will make the absorption spectra shift to the higher energy region. And the occurrence of the peak of the TDOS in the forbidden band might result in additional absorption spectra locating in the visible and the near-ultraviolet region. Therefore the differences between the perfect BWO crystal and the BWO crystal containing  $\text{V}_{\text{Ba}}^{2-}$  will significantly affect the optical properties of the crystal.

### 3.2. Absorption spectra

The absorption coefficients also have been calculated. Fig. 3 shows the calculated absorption spectra for the polarized light with the electrical amplitude vector  $\mathbf{E}$  parallel to axes  $\mathbf{a}$ ,  $\mathbf{b}$  and  $\mathbf{c}$  (marked as  $\mathbf{E} \parallel \mathbf{a}$ ,  $\mathbf{E} \parallel \mathbf{b}$  and  $\mathbf{E} \parallel \mathbf{c}$ ), respectively.

It can be seen from the curve of the perfect BWO crystal in Fig. 3 that the perfect BWO crystal exhibits no absorption in the visible region and thus the perfect BWO crystal should be transparent crystal. While for the BWO crystal with  $\text{V}_{\text{Ba}}^{2-}$  there are four additional absorption spectra peaking at 0.71, 1.85, 3.43 and 3.85 eV, which correspond to the 1751, 672, 362 and 322 nm

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