First-principles study of cadmium vacancy in CdWO$_4$ crystal

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ABSTRACT

The structural relaxation, electronic structures and optical properties of CdWO$_4$ crystal containing cadmium vacancy (CWO:V_{Cd}) are studied by the CASTEP code. The cadmium vacancy (V_{Cd}) would trap two holes to maintain the local electrical neutrality. The calculated structural relaxation and electronic density of states reveals that the existent form of the hole in CWO:V_{Cd} should be oxygen molecular ion (O_2^{3-}). Therefore an associated color center [O_2^{3-}–V_{Cd}–O_2^{3-}] named as V_F center would form in the crystal. The calculated optical absorption spectrum for CWO:V_{Cd} indicates that this V_F center would cause an absorption band peaking at about 650 nm with a shoulder at around 400 nm, which is in agreement with the experimental optical absorptions of the blue–grey colored CWO crystal.

1. Introduction

CdWO$_4$ (CWO) crystal has gained increasing attentions in recent years for its industrial and medical importance as a detector for X-rays and gamma-rays. CWO is a good intrinsic scintillator with excellent properties, such as high light yield, short radiation length, high density, and strong high-energy-radiation absorption [1–4]. Thus CWO has wide applications for medical X-ray computer tomography (CT) [1], security checking [5] and high-energy spectroscopy [4].

However, the existence of various defects would strongly affect the optical properties of the crystal. They may degrade the transparency of a crystal and decrease its light yield. It is therefore necessary to understand the behavior of the defects in CWO and their effect on the physical properties of the crystal. The predominant intrinsic defects existing in CWO are oxygen vacancy V_O and cadmium vacancy V_{Cd} due to the fact that CdO sublimates more easily than WO$_3$ during the crystal growth of CWO [6]. Our previous work [7] has theoretically studied the electronic structures and optical properties of CWO containing V_O. It was concluded that the existence of V_O would cause 350 nm and 400 nm optical absorption bands. Chirila et al. [8] reported the infrared absorption of V_{Cd} adjacent to OH$^-$ in CWO. However, the detailed physical properties of V_{Cd} in CWO are still unknown; further studies are necessary to understand its effects on the optical properties of CWO.

In this work, the structural relaxation, electronic density of states (DOS) and optical absorption spectrum for CWO containing V_{Cd} (CWO:V_{Cd}) are calculated using the Cambridge Serial Total Energy Package (CASTEP) code [9]. Based on the calculated results, the possible color center associated with V_{Cd} and its effects on the optical properties of CWO are discussed.

2. Computational models and methods

2.1. Computational models

The lattice structure of the CWO is shown in Fig. 1. It has wolframite-type structure [10], which is in the monoclinic class and has the space group of P2/c (No. 13). In this structure, each W site and Zn site is surrounded by six oxygen ions. The WO$_6$ octahedra form a chain by edge sharing, so that there are two distinct oxygen ions around the W site. Type A (O$_A$) forms bond to one W ion with

Fig. 1. Lattice structure of CWO.

Table 1
Crystal parameters and atomic positions (x; y; z) used in the present calculations.

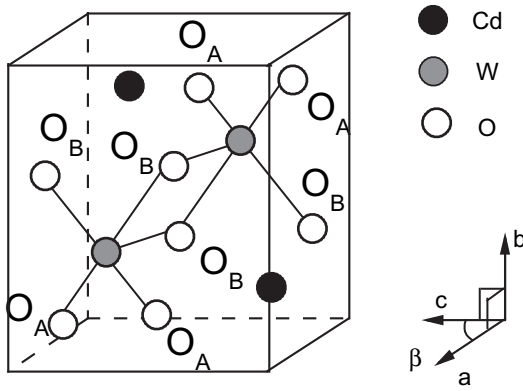| Crystal parameters	Atomic positions			
	Atom	x	y	z
$a = 5.026$Å	Cd	0.5	0.75	0.302
$b = 5.867$Å	W	0	0.25	0.1784
$c = 5.078$Å	O1	0.189	0.454	0.901
$\beta = 91.47°$	O2	0.250	0.393	0.360

a very short bond length (1.787 Å) and to two Cd ions with distances of 2.467 Å and 2.205 Å respectively. Type B (O_B) connects to two different W ions with longer bond lengths (2.139 Å and 1.858 Å) and to one Cd ion with a distance of 2.24 Å. The unit cell contains two formula units of $CdWO_4$. The crystal parameters and atom positions (x, y, z) used in the present calculations are listed in Table 1. In this work, we use the parameters obtained by Daturi et al. [11].

As for the calculating model for CWO:V_{Cd}, a super-cell ($2 \times 2 \times 2$ unit cell) including 96 atoms is used. A Cd atom is removed from the super-cell to simulate V_{Cd}. As a result, we obtain a 95-atom super-cell to study V_{Cd} in CWO.

2.2. Computational methods

The used approach is density functional theory (DFT) using the generalized gradient approximation in the form of Perdew–Wang-91 (GGA-PW91) combined with nonlocal, ultrasoft pseudopotentials and plane-wave expansions in the CASTEP program [12,13]. Geometrical optimization is made and convergence is assumed when: the forces on the lattice ions are less than 0.5 eV/nm; the changes of energy per atom are less than 0.00001 eV; and the atomic displacements are less than 0.0001 nm.

For the ground-state electronic structure calculations, the valence electronic configurations are $4d^{10}5s^2$ for Cd, $5d^46s^2$ for W and $2s^22p^4$ for O. The GGA calculations use Brillouin-zone sampling with $2 \times 2 \times 2$ grid of Monkhorst–Pack k-points and plane-wave cutoff energy of 340 eV; fast Fourier transform (FFT) grid dimensions are $60 \times 60 \times 64$ and space representation is reciprocal; self-consistent field (SCF) tolerance is 1.0×10^{-6} eV/atom.

The imaginary part of the dielectric function (ε_i) is calculated to obtain the optical absorption coefficient. Assuming the one-electron rigid-band approximation and neglecting the electron polarization effects, in the limit of linear optics and of the visible–ultraviolet range, the imaginary part of dielectric function ε_i can be calculated by the following formula [10,14]:

$$\varepsilon_i(\omega) = \frac{e^2\pi^2}{\varepsilon_0 m^2(\omega - \Delta c/\hbar)^2} \sum_{V,C} \left\{ \int_{BZ} \frac{2d\boldsymbol{K}}{(2\pi)^3} |\boldsymbol{a} \cdot \boldsymbol{M}_{v,c}|^2 \delta[E_c(\boldsymbol{K}) + \Delta c \right.$$
$$\left. - E_V(\boldsymbol{K}) - \hbar\omega] \right\} \tag{1}$$

where $\boldsymbol{a}$ is the unit vector of potential $\boldsymbol{A}$; $\boldsymbol{M}_{v,c}$ is the matrix of dipole transition; C is the conduction band; V is the valence band. BZ denotes the Brillouin-zone; Δc is the shifting value of the scissors-

operator; e is the electron charge; ε_0 is the dielectric constant in vacuum; m is the mass of free electron; ω is the frequency of the incident photons; h is Planck's constant; $\boldsymbol{K}$ is the wave vector.

It is well known that band gap is underestimated in DFT calculations. This limitation of DFT for excitations from the ground-state is usually solved by employing the GW formalism [15]. However, if the k-dependence of the error in the excitation energies is negligible, the scissors-operator approximation [16–18] can be used to correct the error of the DFT calculations of the dielectric function. This approach has been widely and successfully used for the calculations of the optical properties for many bulk crystals and semiconductors [19,20]. In our previous work, the calculated band gap of perfect CWO is 2.3 eV; therefore the scissor operator of 1.5 eV is chosen to fit the calculated absorption edge to the experimental value of 3.8 eV [21–26]. Then the absorption coefficient can be obtained from the following equation [14]:

$$\alpha = \omega\varepsilon_i(\omega)/n(\omega)c. \tag{2}$$

where α is the absorption coefficient, n is the refractive index, c is the speed of light in vacuum.

3. Calculated results

3.1. Structural relaxation

Table 2 lists the distances between V_{Cd} and its ten neighboring ions before and after lattice relaxation, including six O ions, two W ions and two Cd ions. In $CdWO_4$, each Cd ion is surrounded by six oxygen ions, pairwise, equidistantly. As listed in Table 2, O_1 and O_2 have the short Cd–O distance of 2.205 Å; O_3 and O_4 have the medium Cd–O distance of 2.240 Å; O_5 and O_6 have the long Cd–O distance of 2.467 Å. The inter-distances of the three pairs of O ions are also listed in Table 2.

Table 2
Distances between V_{Cd} and ten vacancy-neighboring ions and the inter-distances between each two equidistant O ions before (R_0) and after (R) lattice relaxation. ΔR ($=R - R_0$) are the displacements of these ten ions.

Distance to V_{Cd}	R_0(Å)	R(Å)	ΔR(Å)
O1–V_{Cd}	2.205	2.263	0.057
O2–V_{Cd}	2.205	2.296	0.091
O3–V_{Cd}	2.240	2.168	−0.072
O4–V_{Cd}	2.240	2.177	−0.063
O5–V_{Cd}	2.467	2.387	−0.080
O6–V_{Cd}	2.467	2.358	−0.109
Cd1–V_{Cd}	3.442	3.289	−0.153
Cd2–V_{Cd}	3.442	3.281	−0.160
W1–V_{Cd}	3.600	3.558	−0.042
W2–V_{Cd}	3.600	3.578	−0.022
O–O inter-distance			
O1–O2	4.358	4.449	
O3–O4	3.794	3.581	
O5–O6	2.935	2.981	