First-principles study of the electronic structures and absorption spectra for the PbMoO$_4$ crystal with lead vacancy

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The electronic structures and absorption spectra for the perfect PbMoO$_4$ crystal and the crystal containing lead vacancy V$_{Pb}^{2-}$ with lattice structure optimized are calculated using density functional theory code CASTEP. The calculated absorption spectra of the PbMoO$_4$ crystal containing V$_{Pb}^{2-}$ exhibit three absorption bands peaking at 2.0 eV (620 nm), 3.0 eV (413 nm) and 3.3 eV (375 nm), which are in good agreement with experimental values. The theory predicts that the 390 nm, 430 nm and 580 nm absorption bands are related to the existence of V$_{Pb}^{2-}$ in the PbMoO$_4$ crystal.

1 Introduction

Lead molybdate, PbMoO$_4$ (PMO), has attracted attention due to its applications in acousto-optical modulators, acousto-optical deflectors and ion conductors and its great potential to be used as an effective low-temperature scintillator in nuclear instruments [1–4]. The colour of as-grown PMO crystals is yellow and can be changed easily by UV irradiation [5]. The yellowish colour of PMO crystals as grown in air and the photochromic effect restrict its applications in optical instruments. Suppression of these phenomena requires an understanding of the nature of the intrinsic defects in PMO so as to be able to refine the crystal growth techniques [1, 6–8].

The yellowish colour of as-grown PMO crystals has been found to be associated with an absorption band peaking at 430 nm [9]. This coloration has been ascribed to deviations from stoichiometry [10] or the presence of impurities [11, 12]. It has also been attributed to oxygen vacancies trapping electrons [13, 14] or Mn$^{3+}$ impurities located at Pb$^{2+}$ sites [15]. The 430 nm absorption band was later attributed to Pb$^{3+}$ created by oxidation of the crystals [16].

The photochromic effect in PMO crystals is due to the charge exchange $\text{Mo}^{6+} + \text{Pb}^{2+} \leftrightarrow \text{Mo}^{5+} + \text{Pb}^{3+}$ [5], which accounts for the appearance of all three absorption bands after UV irradiation, peaking at 435 nm, 390 nm and 580 nm. The 435 nm absorption band is due to the Pb$^{3+}$ ion and those peaking at 390 nm and 580 nm are assigned to Mo$^{5+}$. However, all the models mentioned above were deduced indirectly owning to the shortage of direct experimental evidence and hence are not widely accepted.

There are lead vacancies V$_{Pb}^{2-}$ and oxygen vacancies V$_{O}^{2-}$ in PbWO$_4$ crystals, the amount of V$_{Pb}^{2-}$ being larger than that of V$_{O}^{2-}$ [17, 18]. We suppose that V$_{Pb}^{2-}$ may also exist in PMO since PMO and PbWO$_4$ are both scheelite-type structures. There are a large number of successful simulations of the optical properties of crystals using the powerful CASTEP code [19, 20]. In this paper, the electronic structures and absorption spectra of both the perfect PMO crystal and the PMO crystal containing V$_{Pb}^{2-}$ with lattice structure optimized are calculated using the CASTEP code.

2 Cluster models and calculation methods

2.1 Cluster models

The structure of PMO is similar to CaWO$_4$ with space group $\text{C}_{4h}^1$ (I$\text{4}_1$/a) and the highest point group $\text{S}_2$. Each Mo$^{6+}$ is surrounded by four O$^{2-}$ and each Pb$^{2+}$ is surrounded by eight O$^{2-}$. The PMO super-cell used here consists of 16 Pb, 16 Mo and 64 O centred at Pb$^{2+}$. The PMO super-cell containing V$_{Pb}^{2-}$ substitutes the central Pb$^{2+}$ by V$_{Pb}^{2-}$.
2.2 Calculation methods The lattice optimization for PMO containing \( V_{\text{in}}^+ \) is performed using the CASTEP code. We use ultrasoft pseudo-potentials for the Pb, Mo and O atoms and a plane-wave cut-off of 340 eV. Optimal atomic positions are determined until satisfying the following conditions: (1) the maximal force on them is smaller than 0.5 eV/Å; (2) the maximal change of energy per atom is smaller than 0.00001 eV; (3) the maximal displacement is smaller than 0.0001 nm. All other calculations are performed on the basis of the lattice structure optimized.

For the ground-state electronic structure, calculations based on the density functional theory (DFT) within generalized gradient approximations (GGA) were performed using the CASTEP code. The DFT is a ground-state theory which is not able to describe excited states. In setting up the CASTEP run, basic parameters were chosen as follows: kinetic energy cut-off = 340 eV; fast Fourier transform (FFT) grid dimensions = \( 60 \times 60 \times 64 \); space representation = reciprocal; SCF tolerance = \( 1.0 \times 10^{-6} \) eV/atom. The optical absorption spectrum arises from two factors: the interband transitions and the Drude terms. Here we focus on the interband transitions because the structural transformation occurs in the interband channel. 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 that it can be computed based on the knowledge of single-particle orbits and energies approximated by the solution of the Kohn–Sham equations. However, it is well known that DFT calculations within GGA underestimate the band gap. To take this into account, a ‘scissors operator’ is used, allowing a shift of the bands situated above the valence band and core electrons of the ions in the PMO crystal. Similarly, the partial density of states (PDOS) of O 2p is shown in Fig. 2.

3 Results and discussion

3.1 Structure optimization The results of the optimized lattice structure are listed in Table 1. Compared with the perfect PMO structure, the optimized lattice structures containing \( V_{\text{in}}^+ \) exhibit the following characteristics: (1) the Pb\(^{2+}\) cations nearest to \( V_{\text{in}}^+ \) shift slightly towards \( V_{\text{in}}^+ \); (2) the O\(^{2-}\) and Mo\(^{6+}\) nearest to \( V_{\text{in}}^+ \) shift slightly away from \( V_{\text{in}}^+ \). The displacement of Mo\(^{6+}\) is much smaller than that of O\(^{2-}\). The distortion will significantly affect the electronic structure of the PMO crystal containing \( V_{\text{in}}^+ \).

Once a \( V_{\text{in}}^+ \) is created in PMO, there can be two types of potentials caused by it: one is the electrical potential caused by \( V_{\text{in}}^+ \); the other is the mechanical potential originating from the structure deficiency of the Pb ion. The latter attracts all the other ions towards the \( V_{\text{in}}^+ \), while the former only attracts the Pb\(^{2+}\) and Mo\(^{6+}\) cations but simultaneously repulses the O\(^{2-}\) anions nearest to the \( V_{\text{in}}^+ \). Since the electrical forces are larger than the mechanical ones, the Pb\(^{2+}\) cations shift towards the \( V_{\text{in}}^+ \) and O\(^{2-}\) anions shift away from the \( V_{\text{in}}^+ \). The Mo\(^{6+}\) nearest to the \( V_{\text{in}}^+ \) shifts slightly away from it because Mo–O is bonded tightly.

3.2 Electronic structure The electronic structures are calculated in the region from −20 eV to 10 eV. The total density of states (TDOS) of the PMO crystal containing \( V_{\text{in}}^+ \) is shown in Fig. 1, comparing with that of the perfect PMO crystal. Similarly, the partial density of states (PDOS) of O 2p is shown in Fig. 2.

Compared with a perfect PbWO\(_4\) crystal, the TDOS of PMO containing \( V_{\text{in}}^+ \) is quite similar to that of perfect PMO, and it can be seen from Fig. 2 that the top of the valence band is mainly contributed by the O 2p states. This means that the existence of \( V_{\text{in}}^+ \) has little effect on valence band and core electrons of the ions in the PMO crystal. The difference between the TDOS of the PMO containing \( V_{\text{in}}^+ \) and that of the perfect PMO is that a small-intensity peak of the O 2p state occurs within the forbidden band at ~2.5 200 eV.

### Table 1 The distance between \( V_{\text{in}}^+ \) and its nearest ions for pre-optimized and optimized structures.

<table>
<thead>
<tr>
<th>system</th>
<th>Mo–( V_{\text{in}}^+ ) (Å)</th>
<th>O–( V_{\text{in}}^+ ) (Å)</th>
<th>Pb–( V_{\text{in}}^+ ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pre-optimized</td>
<td>3.840</td>
<td>2.606/2.636</td>
<td>4.066</td>
</tr>
<tr>
<td>optimized</td>
<td>3.850</td>
<td>2.751</td>
<td>3.924</td>
</tr>
<tr>
<td></td>
<td>3.851</td>
<td>2.752</td>
<td>3.924</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.776</td>
<td></td>
</tr>
</tbody>
</table>
about 1.7 eV. The difference between the perfect PMO and the PMO crystal containing $V_{\text{Pb}}^{2-}$ will significantly affect the optical properties of the crystal. The $V_{\text{Pb}}^{2-}$ is negative divalent and requires positive charges to compensate its electronegativity. Compared with Pb$^{2+}$ and Mo$^{6+}$, we find that O$^{2-}$ turns out to be able to trap holes in both the cases when O$^{2-}$ is the nearest neighbour of $V_{\text{Pb}}^{2-}$ and O$^{2-}$ itself is negative divalent. However, there are eight nearest O$^{2-}$ surrounding $V_{\text{Pb}}^{2-}$, which are divided into two groups each having four equal O$^{2-}$ symmetrically distributed around $V_{\text{Pb}}^{2-}$. None can be more able than the others to trap a hole. Comparing with the formation of hole centres in alkali halides, once a negative alkali vacancy is formed, the compensator is a hole shared by two halide ions nearest to the alkali ion vacancy forming a halide diatomic molecular structure rather than being trapped by one halide ion nearest to the alkali vacancy forming a halide atom [25]. It can be reasonably believed that a similar result will occur in an oxide compound crystal. Therefore once a hole is created in the crystal, the hole is shared by the two nearest oxygen ions (3.027 Å) forming an oxygen diatomic molecular ion, O$_2^-$, rather than being trapped by one O$^{2-}$ forming O$^-$. The reaction formula can be written as $2\text{O}^{2-} + \hbar = \text{O}_2^-$, a possible model being illustrated in Fig. 3.

### 3.3 Absorption spectra

The absorption coefficient follows the relationship $\sigma = \alpha \varepsilon / nc$. The absorption spectra under $E \parallel a$, $E \parallel b$ and $E \parallel c$ for the perfect PMO crystal and for PMO containing $V_{\text{Pb}}^{2-}$ are shown in Fig. 4.

Compared with the absorption spectra for perfect PMO crystals, the absorption spectra under $E \parallel a$, $E \parallel b$ and $E \parallel c$ for PMO crystals containing $V_{\text{Pb}}^{2-}$ exhibit three additional absorption bands peaking at about 2.0 eV (620 nm), 3.0 eV (413 nm) and 3.3 eV (375 nm). The peaks of these absorption bands obtained in our calculation are in good agreement with those from measurements [5]. The absorption spectra in the region from 1 eV to 5.0 eV for the PMO crystal containing $V_{\text{Pb}}^{2-}$ with $E \parallel c$ and $E \perp c$ are shown in Fig. 5. Compared with the absorption
spectra under $E \perp c$ for the PMO containing V_{ps}^{2}−, the absorption spectra under $E \parallel c$ exhibit two characteristics: (1) the peak located at 5.0 eV becomes very small, which means the probability of the transition at 5.0 eV under $E \parallel c$ is very low, as shown in Fig. 4; (2) the intensities of the bands peaking at about 2.0 eV to 3.0 eV under $E \perp c$ are much larger than those under $E \parallel c$, while the intensities of the bands peaking at 3.3 eV and 3.8 eV under $E \perp c$ are a little less than those under $E \parallel c$. The intrinsic reasons are as follows. The absorption of polarized light in the direction of $E \parallel c$ and $E \perp c$ depends on the angle between the crystal $c$-axis and the symmetric axis of O$_{2}^{2−}$.[26]. If the angle between the crystal $c$-axis and the symmetric axis of O$_{2}^{2−}$ is $\alpha$, the projection of $E$ with $E \parallel c$ on the symmetric axis of O$_{2}^{2−}$ would be $E \cos \alpha$ and the projection of $E \perp c$ on the symmetric axis of O$_{2}^{2−}$ would be $E \sin \alpha$. At present the angle between the crystal $c$-axis and the symmetric axis of O$_{2}^{2−}$ is about 68.6°, so the projection $E \sin \alpha$ is larger than $E \cos \alpha$. However, there might be other types of O$_{2}^{2−}$ which are not nearest to the V_{ps}^{2}− and the angles between the crystal $c$-axis and the symmetric axes of these O$_{2}^{2−}$ are multiform. This is the reason why the absorption bands peaking at 3.3 eV and 3.8 eV under $E \perp c$ are a little smaller than those under $E \parallel c$. From the calculated results and the analysis above, we believe that the absorption spectra of PMO crystal containing V_{ps}^{2}− exhibit some anisotropy.

4 Conclusions The electronic structures and absorption spectra under $E|a$, $E|b$ and $E|c$ for a perfect PMO crystals and a PMO crystal containing V_{ps}^{2}− with lattice structure optimized have been calculated using the density function theory code CASTEP. The calculated results show that the absorption spectra under polarized light are consistent with the experimental results. The theory reasonably predicts that all the absorption bands peaking at 390 nm, 435 nm and 580 nm are related to the existence of V_{ps}^{2}− in PMO crystals. The V_{ps}^{2}− may be one kind of common intrinsic defect in sheelite-structured materials.

References