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Optical polarized properties related to the oxygen vacancy defect in the $PbWO_4$ crystal*

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The electronic structures, dielectric functions, complex refractive index and absorption spectra for the $PbWO_4$ (PWO) crystal with and without oxygen vacancy V_O^{2+} have been calculated using the full-potential (linearized) augmented planewave (FP-LAPW)+local orbitals (LO) method with the lattice structure optimized. The calculated results indicate that the optical properties of the PWO crystal show anisotropy and its optical symmetry coincides with the lattice structure geometry of the PWO crystal. The calculated absorption spectra indicate that the stoichiometric PWO crystal does not display absorption band in the visible and near-ultraviolet range. However, in this range, the absorption spectra of the PWO crystal containing V_O^{2+} exhibit two peaks at 3.35eV (370nm) and 2.95eV (420nm), respectively. It is revealed that the 350nm and 420nm absorption bands are related to the existence of V_O^{2+} in the PWO crystal.

Keywords: $PbWO_4$ crystal, electronic structure, optical properties, oxygen vacancy
PACC: 4225J, 3345, 7820, 7850

1. Introduction

In recent years, $PbWO_4$ (PWO) crystal has attracted special interest, since it was chosen as a scintillator for detectors at the large collider in CERN.[1−3] The PWO is a typical non-stoichiometric crystal. There are lead vacancies V_{Pb}^{2-} and oxygen vacancies V_O^{2+} in the PWO crystal and the amount of lead vacancy is larger than that of oxygen vacancy.[1,4−8] Up to now, many defect models [9−13] related to V_{Pb}^{2-} and V_O^{2+} have been proposed but are still in open question. The PWO crystal has 4 absorption bands peaking at 350, 420, 550 and 680nm.[12,13] Many papers discussed the origins of the four bands but few conclusions are generally accepted. Unfortunately, almost all the models proposed were deduced indirectly, in lack of either direct experimental evidence or theoretical calculations. There are many successful simulations on the optical properties of crystals using the code of WIEN97 and WIEN2K.[14−16] The simulation on the PWO crystal containing V_{Pb}^{2-} has been performed and its results predicated that all the 350, 420, 550 and 680nm absorption bands are related to the existence of the V_{Pb}^{2-} in PWO.[17] The absorption spectra of polarized light are sensitive to the structure symmetry. In order to further study the physical properties of oxygen-related defects, in this paper the electronic structures, dielectric functions, complex refractive index and absorption spectra of polarized light for the PWO crystal either stoichiometric or containing oxygen vacancy V_O^{2+} will be calculated using the full potential (linearized) augmented planewave + local orbital (FP-LAPW+LO) method with the lattice structure optimized. Because the existence of V_O^{2+} would cause lattice distortion, the lattice structure optimization is necessary before we study the optical properties of the crystal.

2. The cluster models and calculation methods

2.1. The cluster models

The structure of PWO is similar to $CaWO_4$, having the space group C_{4h}^6 ($I4_1/a$) and the highest point group S_4. Each W^{6+} is surrounded by four O^{2-} and each Pb^{2+} is surrounded by eight O^{2-}. The PWO cluster used here consists of 16 Pb, 16 W and 64

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O centred at Pb^{2+} having the chemical formula of $[Pb_{16}W_{16}O_{64}]$.[5] Its symmetry group is S_4. The PWO cluster containing V_O^{2+} has the oxygen ions O^{2-} lying to the nearest centred Pb ion to be substituted by V_O^{2+}.

2.2. The calculation methods

The lattice structure optimization for the PWO containing V_O^{2+} is performed by using FP-LAPW, with generalized gradient correction in the form of Perdew-Wang-91. We use the planewave cut-off of 550eV. Optimal atomic positions are determined until satisfying the conditions: (1) the maximal force on them is smaller than 0.5eV/nm, (2) the maximal change of energy per atom is smaller than 0.00001eV, and (3) the maximal displacement was smaller than 0.0001nm. All the other calculations are performed on the basis of the optimized lattice structure.

The FP-LAPW+LO method implemented in the WIEN2K code was used for electronic structure calculations. Details of the FP-LAPW+LO method have been described in Refs.[14-16]. The exchange and correlation effects were treated within the density functional theory (DFT) using the Perdew–Burke–Ernzerhof generalized gradient approximation (GGA). 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 ε_i is given by[16,18]

$$\varepsilon_{\rm i}(\omega) = \frac{e^2\pi^2}{\varepsilon_0 m^2(\omega - \Delta c/h)^2} \times \sum_{\rm V,C}\left\{\int\limits_{BZ} \frac{2{\rm d}\boldsymbol{K}}{(2\pi)^3} |\boldsymbol{a}\cdot\boldsymbol{M}_{\rm v,c}|^2\, \delta[E_{\rm c}(\boldsymbol{K}) + \Delta c/h - E_{\rm v}(\boldsymbol{K}) - \hbar\omega]\right\}, \quad (1)$$

where $\boldsymbol{a}$ is the unit vector potential $\boldsymbol{A}$, $\boldsymbol{M}_{\rm v,c}$ is the matrix of dipole transition. C is the conductor band. V is valence band. BZ is 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 free electron mass. ω is the frequency of the incident wave. h is Planck's constant. $\boldsymbol{K}$ is wave vector. The Kramers–Krönig transformation[18] links the real and the imaginary parts of the dielectric function. The Kramers–Krönig transformation and the Lorentz broadening of 0.12eV is used to obtain the real part $\varepsilon_{\rm r}(\omega)$ of the dielectric function. According to the fact that the calculated band gap is 3.3eV and the experimental value is 4.8eV, the shifting value of the scissors operator ΔC is chosen to be 1.5eV. The refractive index n and the extinctive coefficient κ follow from the equations $n^2 - K^2 = \varepsilon_{\rm r}$ and $2nK = \varepsilon_{\rm i}$, where $\varepsilon_{\rm r}$ and $\varepsilon_{\rm i}$ denote the real and the imaginary parts of the dielectric function, respectively. The complex refractive index and extinctive coefficient are obtained by solving the above two equations.

3. Results and discussion

3.1. Electronic structure

The electronic structures have been calculated in the region from -20eV to 10eV. The total density of states (TDOS) of the stoichiometric PWO crystal is given in Fig.1, compared with that of the PWO crystal containing V_O^{2+}. In this paper all the curves related to the stoichiometric PWO are plotted in dotted lines and those related to the PWO containing V_O^{2+} are plotted in solid lines. The TDOS of the stoichiometric PWO have been discussed in detail in Ref.[17]. Compared with the stoichiometric PWO crystal, the TDOS of PWO containing V_O^{2+} in the regions below Fermi level E_F is quite similar to that of stoichiometric PWO, and the top of the valence band is mainly contributed by the O 2p states. This means that the existence of V_O^{2+} has few effects on the valance band and core electrons of the ions in the crystal. While the PWO containing V_O^{2+} differs from the stoichiometric PWO in the fact that the band gap in the former decreases by about 0.5eV, and a small peak of the DOS occurs within the forbidden band peaking at about 1.3eV. The differences between the stoichiometric PWO crystal and the PWO crystal containing

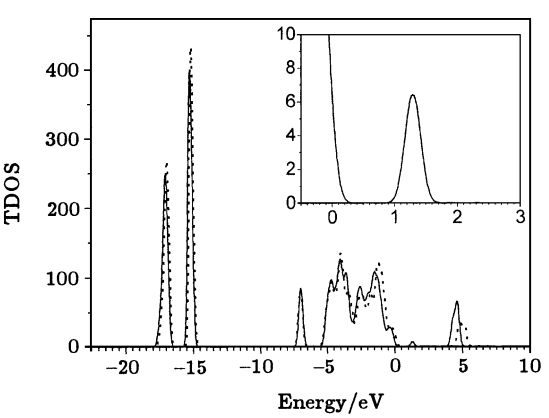


Fig.1. The TDOS of the stoichiometric PWO crystal (dotted lines) and the PWO crystal containing V_O^{2+} (solid lines). The inset shows the TDOS in the forbidden band for the PWO containing a V_O^{2+} on an expanded scale.

V_O^{2+} will significantly affect the optical properties of the crystal. The oxygen vacancy V_O^{2+} catching an electron will form an F^+ colour centre and that catching two electrons will form an F colour centre. The energy level of F and F^+ colour centres could be located in the forbidden band. Our calculated results are in good agreement with those published in Refs.[19–21].

3.2. The imaginary part of the dielectric function

The frequency-dependent dielectric functions ε_i and ε_r have been calculated. Figure 2 shows our calculated imaginary part for the polarized light as the electrical amplitude vector $\boldsymbol{E}$ parallel to axis $\boldsymbol{a}$, $\boldsymbol{b}$ or $\boldsymbol{c}$ (marked as $\boldsymbol{E}//\boldsymbol{a}$, $\boldsymbol{E}//\boldsymbol{b}$ and $\boldsymbol{E}//\boldsymbol{c}$).

It can be seen from Fig.2 that, for the stoichiometric PWO crystal, the imaginary part of the dielectric function for $\boldsymbol{E}//\boldsymbol{a}$ is the same as that for $\boldsymbol{E}//\boldsymbol{b}$; while for PWO crystal containing V_O^{2+}, there is a small difference, and the main difference occurs in the region below 4eV. This can be interpreted on the basis of the lattice structure. The lattice structure of the stoichiometric PWO crystal along axis $\boldsymbol{a}$ is the same as along axis $\boldsymbol{b}$, while in the PWO crystal containing V_O^{2+}, this is more or less destroyed by the existence of the V_O^{2+}. The destruction might be small, leading to a small change in the absorption spectra of the PWO crystal containing V_O^{2+}. The imaginary part of the dielectric function under $\boldsymbol{E}//\boldsymbol{a}$ and under $\boldsymbol{E}//\boldsymbol{b}$ is obvious different from that under $\boldsymbol{E}//\boldsymbol{c}$ for either stoichiometric PWO crystal or that containing V_O^{2+}.The symmetry of the imaginary part of the dielectric function reflects the symmetry of the lattice structure.

Compared with the stoichiometric PWO crystal, the imaginary part spectra of the dielectric function under $\boldsymbol{E}//\boldsymbol{a}$ and $\boldsymbol{E}//\boldsymbol{b}$ for the PWO crystal containing V_O^{2+} are shifted to the region of lower energies and have two new additional structures peaking at about 2.95 and 3.35eV.

Compared with the imaginary part of the dielectric function under $\boldsymbol{E}//\boldsymbol{a}$ and $\boldsymbol{E}//\boldsymbol{b}$ for the PWO crystal containing V_O^{2+}, the imaginary part of dielectric function under $\boldsymbol{E}//\boldsymbol{c}$ for the PWO crystal containing V_O^{2+} exhibits the disappearance of the peak located at 4.4eV. It predicts that the transition at 4.4eV (transition from the top of the valance band to the bottom of the conduction band) is a forbidden transition under $\boldsymbol{E}//\boldsymbol{c}$. In other words, the probability of the correspondent transition is very low. The other peaks of the imaginary part of the dielectric function under $\boldsymbol{E}//\boldsymbol{a}$, $\boldsymbol{E}//\boldsymbol{b}$ and $\boldsymbol{E}//\boldsymbol{c}$ are similar to each other.

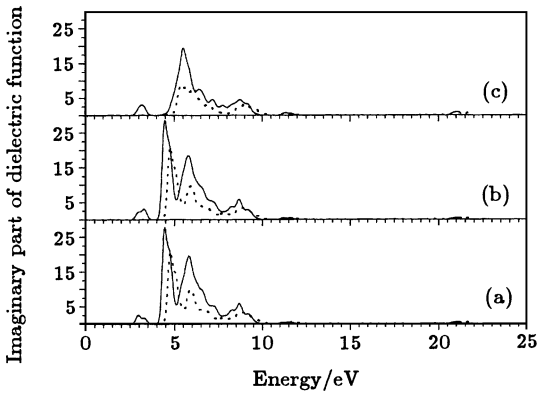


Fig.2. The imaginary part of the dielectric function for the stoichiometric PWO crystal (dotted lines) and the PWO crystal containing V_O^{2+} (solid lines) under irradiation of a polarized light under (a) $\boldsymbol{E}//a$, (b) $\boldsymbol{E}//b$, (c) $\boldsymbol{E}//c$.

3.3. Absorption spectra

The absorption coefficient follows the relationship $\alpha = \omega\varepsilon_i/(nC)$. The absorption spectra for $\boldsymbol{E}//\boldsymbol{a}$, $\boldsymbol{E}//\boldsymbol{b}$ and $\boldsymbol{E}//\boldsymbol{c}$ calculated from the stoichiometric PWO crystal and that containing V_O^{2+} are shown in Fig.3.

The absorption spectra for the stoichiometric PWO crystal also have been described in detail.[17] Compared with the absorption spectra under $\boldsymbol{E}//\boldsymbol{a}$ and $\boldsymbol{E}//\boldsymbol{b}$ for the stoichiometric PWO crystal shown in Fig.3, the absorption spectra under $\boldsymbol{E}//\boldsymbol{a}$ and $\boldsymbol{E}//\boldsymbol{b}$ for the PWO containing V_O^{2+} exhibit characteristics as follows. (1) The absorption spectrum shifts toward the low energy side. (2) There emerge two new bands peaking at 3.35eV (370nm) and 2.95eV (420nm), caused by the occurrence of the small TDOS peak in the forbidden band. These two peaks are very close to those observed in experiment, located at 350 and 420nm.[12,13] So it can be concluded that the absorption bands at 350 and 420nm are related to the existence of V_O^{2+} in PWO crystal. This conclusion is in good agreement with the results published in Ref.[10]. It also may give an important clue to the explanation of the most recent experimental results.[22] These theoretical and experimental values further confirm that the 350 and 420nm absorption bands are related to the existence of V_O^{2+} in PWO crystal.

Compared with the absorption spectra under $\boldsymbol{E}//\boldsymbol{a}$ and $\boldsymbol{E}//\boldsymbol{b}$ for the PWO crystal containing V_O^{2+}, the absorption spectra under $\boldsymbol{E}//\boldsymbol{c}$ for the PWO crystal containing V_O^{2+} disclose the following facts. (1)

The peak located at 4.6eV disappears. It means that the probability of transition at 4.6eV under $\boldsymbol{E}//\boldsymbol{c}$ is very low. Thus, the intrinsic mechanism needs to be further studied by analyzing the symmetry of PWO crystal and the transition rule. (2) All the spectra have two absorption bands peaking at about 2.95 and 3.35eV, which obviously occur anisotropically. The intensity of the bands under $\boldsymbol{E}//\boldsymbol{c}$ is a little larger than that under $\boldsymbol{E}//\boldsymbol{a}$ and $\boldsymbol{E}//\boldsymbol{b}$ in the region of 300–500nm. While the intensity of the 2.95eV absorption band under $\boldsymbol{E}//\boldsymbol{a}$ is larger than that under $\boldsymbol{E}//\boldsymbol{b}$; however, the intensity of the 3.35eV absorption band under $\boldsymbol{E}//\boldsymbol{a}$ is smaller than that under $\boldsymbol{E}//\boldsymbol{b}$.

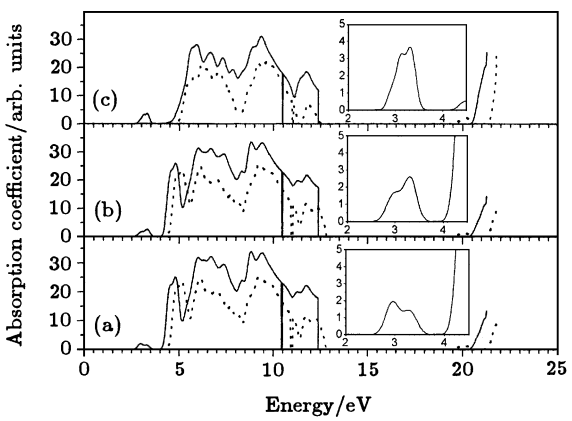


Fig.3. The absorption spectra of the stoichiometric PWO crystal (dotted lines), the PWO crystal containing V_{O}^{2+} (solid lines). The insets show the absorption band in the region from 2.0 to 4.5eV for the PWO containing a V_{O}^{2+} on an expanded scale, under the irradiation of a polarized light under (a) $\boldsymbol{E}//a$, (b) $\boldsymbol{E}//b$, (c) $\boldsymbol{E}//c$.

3.4. Complex refractive index

The refractive index and the extinction coefficient follow the relationship $n^2 - \kappa^2 = \varepsilon_{\mathrm{r}}$ and $2n\kappa = \varepsilon_{\mathrm{i}}$, and the calculated refractive index is shown in Fig.4. The polarized properties of the refractive index are also similar to that of the imaginary part of dielectric function and the absorption bands. This reflects the inner relationship among the three physical quantities. The calculated refractive index is in good agreement with the experimental values[23] in the visible and near-ultraviolet range.

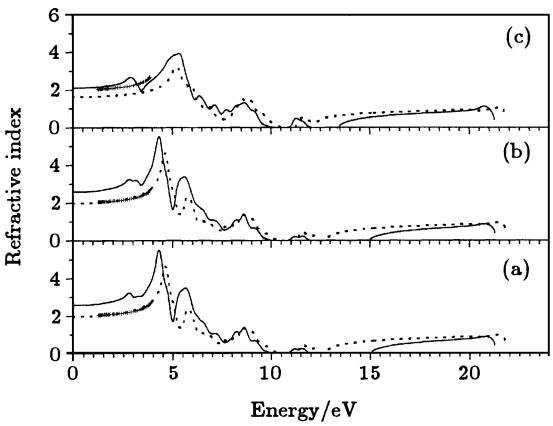


Fig.4. The refractive index of the stoichiometric PWO crystal (dotted lines) and PWO crystal containing V_{O}^{2+} (solid lines) under irradiation of a polarized light under (a) $\boldsymbol{E}//a$, (b) $\boldsymbol{E}//b$, (c) $\boldsymbol{E}//c$.

4. Conclusion

The electronic structures, dielectric functions, complex reflectivity index and absorption spectra obtained under the polarized light for the stoichiometric PWO crystal and PWO crystal containing V_{O}^{2+} have been calculated using FP-LAPW+LO method. The optical properties of PWO crystal exhibit anisotropy. They reflect the anisotropy of PWO crystal lattice structure. Our calculated results indicate that the stoichiometric PWO crystal does not show absorption band in the visible and near-ultraviolet range. However, the PWO crystal containing V_{O}^{2+} exhibits two additional absorption bands in this region, which are very close to the experimental results. This can reasonably predict that the 350 and 420nm absorption bands are related to the existence of V_{O}^{2+} in PWO crystal.

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