Predictions of electronic structures and optical performance of potential near infrared absorber Sn$_{0.33}$WO$_3$

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Predictions of electronic structures and optical performance of potential near infrared absorber \( \text{Sn}_{0.33}\text{WO}_3 \)

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ABSTRACT
For better synthesis and development of novel \( \text{WO}_3 \)-based near infrared absorbing materials for smart-window applications, the structural, electronic, and optical properties of hexagonal \( \text{Sn}_{0.33}\text{WO}_3 \) were investigated through the first-principles calculation. The optimized crystal structure parameters agree well with experimental values. The electronic structure shows that when Sn ions are doped in the host hexagonal \( \text{WO}_3 \), \( \text{Sn}_{0.33}\text{WO}_3 \) displays a typical \( n \)-type electronic conductivity, which leads to an upshift of the Fermi energy to the conduction band. It was found that \( \text{Sn}_{0.33}\text{WO}_3 \) exhibits low reflectivity and weak absorption in the visible region, while exhibiting strong reflectivity and absorption in the near infrared light region. Therefore, it significantly reduces the optical transmittance of infrared wavelengths (down to 3.9% for the compacted film and 25.3% for the coated film), while maintaining fair optical transparency for visible wavelengths. This research indicates that \( \text{Sn}_{0.33}\text{WO}_3 \) is a prospective near infrared absorber and it can be used as near infrared shielding filters for smart windows with high transparency for visible light.

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I. INTRODUCTION
For almost two decades, the alkali-metal-doped hexagonal tungsten bronzes \( \text{M}_x\text{WO}_3 \) (\( \text{M} = \text{Na}, \text{K}, \text{Rb}, \text{Cs} \)) have received attention for their remarkable near infrared (NIR) absorption, which can be applied as a solar filter for smart-windows. However, the alkali-metal-intercalated hexagonal \( \text{WO}_3 \) (h-WO\(_3\)) typically exhibits chromatic instabilities under high temperature and high humidity, which limits its application range.

Therefore, there is a surge of interest to develop novel \( \text{WO}_3 \)-based near infrared absorbing materials for solar filter applications to meet the high standards of energy saving and emission reduction in modern buildings and automobiles.

Doping is a very effective way to tune the properties of materials. Recently, it has been found that \( \text{Sn}_x\text{WO}_3 \) tungsten bronze is a novel image-guided cancer therapy, which has better chemical stability and lower elemental toxicity than \( \text{Cs}_x\text{WO}_3 \) and \( \text{Rb}_x\text{WO}_3 \), and can well absorb excellent near-infrared light. Up to now, although \( \text{Sn}_x\text{WO}_3 \) tungsten bronze could be hydrothermally synthesized, there are few reports on the physical properties and application prospects of \( \text{Sn}_x\text{WO}_3 \). Therefore, the electronic structures and optical properties of \( \text{Sn}_x\text{WO}_3 \) are still of great interest. For a better understanding of \( \text{Sn}_x\text{WO}_3 \) tungsten bronze, it is essential to study the electronic and optical properties.

Actually, the first-principles calculations based on Density Functional Theory (DFT) have become an important and powerful complementary tool for obtaining and quantifying fundamental properties of solid functional materials. Recently, the first-principles calculations of Solid Oxide Fuel Cell (SOFC) cathode materials have been performed by using the DFT method in conjunction with the supercell model. The on-site Coulombic interaction (DFT+U)
A. Geometry structure

The optimized geometry structure of the $2 \times 2 \times 1$ supercell of tin-doped h-WO$_3$ (Sn$_{0.33}$WO$_3$) is shown in Fig. 1. Fully optimized lattice parameters of hexagonal Sn$_{0.33}$WO$_3$ in comparison with the experimental results are summarized in Table I. The calculated results in this work agree well with the previous experimental data.

B. Electronic structures

The calculated band structures of undoped h-WO$_3$ and Sn$_{0.33}$WO$_3$ are shown in Fig. 2. The dotted lines at zero indicate the Fermi energy level. It can be found that the bandgap for undoped h-WO$_3$ is 0.62 eV from Fig. 2(a), which is close to the reported value of 0.66 eV, as the DFT simulation generally underestimates this value. From Fig. 2(b), it is interesting to observe that the Fermi level moves up to the conduction band for the insertion of Sn ions, rendering Sn$_{0.33}$WO$_3$ to have metal-like properties.

C. Optical properties

Figure 4 shows the dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ of hexagonal Sn$_{0.33}$WO$_3$. $\varepsilon(\omega)$ is related to the interaction of electrons with photons, which comes from the contributions of intraband and interband transitions. From Fig. 4, the critical peaks of imaginary part $\varepsilon_2(\omega)$ associated with the electron excitation are as follows. Peak A at 0.05 eV and peak B at 4.07 eV are attributed to the transition from W states of the valence band to Sn 5p states of the conduction band.

Table I. Calculated and experimental crystal structure parameters of Sn$_{0.33}$WO$_3$.

|        | $a_0$ (Å) | $b_0$ (Å) | $c_0$ (Å) |
|--------|-----------|-----------|-----------|
| Cal.   | 7.4549    | 7.4549    | 3.8128    |
| Expt.  | 7.4304$^a$| 7.4304$^a$| 3.8014$^b$|
|        | 7.429$^a$ | 7.429$^a$ | 3.7868$^b$|

$^a$Reference 22.
$^b$Reference 23.
band near the Fermi energy. It can be found that the calculated static real part $\varepsilon_1(\omega)$ of hexagonal Sn$_{0.33}$WO$_3$ is 161.28.

Figure 5 shows the reflectivity spectra of hexagonal Sn$_{0.33}$WO$_3$. Figure 5 shows that the average reflection is over 60% in the NIR region from 1000 to 2500 nm. However, the reflection curve is V-shaped distribution for the visible light from 380 to 780 nm and the reflectivity minimum is 7.5% at about 621 nm (2.0 eV).

Figure 6 plots the absorption spectra of hexagonal Sn$_{0.33}$WO$_3$. From Fig. 6, we can see that a strong absorption coefficient appears in the ultraviolet and NIR region, and the absorption coefficient maximum for NIR light is 346 255 cm$^{-1}$ at 1211 nm (1.02 eV).
However, the absorption valleys occur in the visible region and the absorption coefficient minimum for visible light is 75,176 cm$^{-1}$ at 541 nm (2.29 eV), which is attributed to the plasma oscillation of the metalloid characteristic.

The energy-loss spectra $L(\omega)$ displayed in Fig. 7 describe the energy loss of a fast electron traversing in the materials. The sharp peak in the low energy range of the $L(\omega)$ spectra is associated with the plasma oscillation, and the peak position is corresponding to the relevant plasma frequency ($\omega_p$). In a word, the position of the plasma oscillation corresponds to the sharp decrease in the reflectance and absorption spectrum. As illustrated in Fig. 7, we can reasonably deduce that the plasma energy ($\hbar\omega_p$) of Sn$_{0.33}$WO$_3$ is 1.78 eV. Simultaneously, Sn$_{0.33}$WO$_3$ exhibits low reflectivity and weak absorption when the incident light energy is close to its plasma energy.

Finally, we calculated the transmittance of diverse Sn$_{0.33}$WO$_3$ films by employing the calculated reflectance and the absorption spectra according to the formula

$$T = \frac{(1 - R)^2 \exp(-\alpha d)}{1 - R^2 \exp(-2\alpha d)},$$

where $d$ is the thickness of the material film, and the possibility of multiple reflections between the front and back surface of the film is ignored. The systematic presentation of the theory associated with appropriate models has been reported by Xiao et al.$^{28}$

Figure 8 shows the transmittance of the compacted film and the coated film for Sn$_{0.33}$WO$_3$. It should be noted that the theoretical transmittance of the coated film for Sn$_{0.33}$WO$_3$ is only deduced from the absorption coefficient (Fig. 6), whereas the transmittance of the...
compacted film is deduced from the absorption coefficient (Fig. 4) and the calculated reflectance (Fig. 5) of hexagonal Sn$_{0.33}$WO$_3$. From Fig. 8, we can see that the curves of the transmission of diverse Sn$_{0.33}$WO$_3$ films form "hanging bell" shape distribution in the visible region. The largest transmission of the visible light for the compacted film and the coated film is 60.3% at 573 nm and 74.0% at 541 nm, respectively. However, the minimum transmittance of NIR for the compacted film and the coated film is 3.9% at 1319 nm and 25.3% at 1210 nm, respectively. The difference between the transmittance maximum and the transmittance minimum for the compacted film and the coated film are 56.4% and 48.7%, respectively. These data indicate that Sn$_{0.33}$WO$_3$ is a perfect NIR absorber with a high visible transmittance which could serve as an NIR shielding material for transparent windows.

IV. CONCLUSIONS

In closing, we systematically studied the electronic structure and optical properties of Sn$_{0.33}$WO$_3$ using the first-principles method. The solar radiation shielding performance of diverse Sn$_{0.33}$WO$_3$ films was predicted. The results of optical properties show that Sn$_{0.33}$WO$_3$ is a perfect NIR absorber. The theoretical transmittance of different hexagonal Sn$_{0.33}$WO$_3$ films indicates that Sn$_{0.33}$WO$_3$ possesses an outstanding high blocking effect for NIR radiation with high transmittance of visible light.

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