Theoretical studies on the structural, electronic, and optical properties of $Ag_2HgSnSe_4$*

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We investigate the electronic structure of $Ag_2HgSnSe_4$ in a wurtzite–stannite structure with the first principles method. This crystal is a direct band-gap compound. In addition the dielectric function, absorption coefficient, reflectivity, and energy-loss function are studied using the density functional theory in the generalized gradient approximation. We discuss the optical transitions between the valence bands and the conduction bands in the spectrum of the imaginary part of the dielectric function at length. We also find a very high absorption coefficient and a wide absorption band for this material. The prominent structures in the spectra of reflectivity and the energy-loss function are discussed in detail.

Keywords: wurtzite–stannite, density functional theory, generalized gradient approximation

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1. Introduction

In recent years, many quaternary compounds I_2–II–IV–VI_4 (I=Cu, Ag; II=Zn, Cd, Hg; IV=Si, Ge, Sn; VI=S, Se) have generated wide interest due to their potential applications in solar cell materials, owing to their p-type conductivity and high optical absorption ($> 1 \times 10^4$ cm^{-1}).[1–10] These compounds are synthesized by replacing half of the III atoms in chalcopyrite I–III–VI_2 (I=Cu, Ag; III=Al, Ga, In; VI=S, Se) with II atoms and the other half with IV atoms. Most of them crystallize into the tetragonal stannite structure or the orthorhombic wurtzite–stannite structure.

The $Ag_2HgSnSe_4$ crystal exists in the quasi-ternary Ag_2Se–$HgSe$–$SnSe_2$ system. For the first time it was synthesized by Haeuseler and Himmrich[11] using the interaction between the components at 970 K. It was also observed that the sample of $Ag_2HgSnSe_4$ crystallizes into a wurtzite–stannite structure [space group $Pmn2_1$] with the lattice parameters $a = 8.494$, $b = 7.314$, and $c = 6.972$ Å (1 Å=0.1 nm). Additionally, its FIR-absorption spectrum was studied by Himmrich and Haeuseler,[12] and the crystal structures were measured with X-ray powder diffraction.[11,13,14] To our knowledge, there is no systematical report on the theoretical electronic and optical properties of $Ag_2HgSnSe_4$. Therefore, we studied the structural, electronic, and optical properties for $Ag_2HgSnSe_4$ in orthorhombic phase with the first principles method.

2. Method of calculation

To our best knowledge, the first principles method is a very effective tool for studying material properties.[15–19] Our calculations are performed based on the density functional theory (DFT) using the ultrasoft pseudopotential and plane-wave pseudopotential method in the CASTEP (Cambridge Serial Total Energy) package.[20,21] The exchange–correlation energy of the electrons is described in the generalized gradient approximation (GGA) in the scheme of Perdew *et al.*[22] In the whole calculation, we consider only the valence electrons, and the electronic configurations of constituent elements are Ag ($4d^{10}5s^1$), Hg ($5d^{10}6s^2$), Sn($5s^25p^2$), and Se ($4s^24p^4$), separately.

The quaternary compound $Ag_2HgSnSe_4$ is optimized with a specific $4 \times 4 \times 4$ k-point grid according to the Monkhorst–Pack scheme.[23] The tolerance in the self-consistent field (SCF) calculation is 1.0×10^{-6} eV/atom. We employ 350 eV as the plane-wave cutoff energy. For the calculations of the electronic and optical properties, $4 \times 4 \times 4$ and $8 \times 8 \times 8$

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k-point grids are used for numerical integrations over the Brillouin zone (BZ) respectively.

3. Results and discussion

3.1. Structural parameters

We use the initial crystallographic parameters[14] analysed by X-ray diffraction (XRD) as a beginning for geometry optimization. The simulated equilibrium lattice constants of $Ag_2HgSnSe_4$ are compared with the available experimental data in Table 1. Our calculated lattice parameters a, b, and c are in agreement with the previous data.[11,13,14] It can be seen that the optimized structure is reasonable. Therefore the following calculations about the electronic and the optical properties for this compound are very credible.

Table 1. Equilibrium lattice constants (a, b, and c) of $Ag_2HgSnSe_4$ in wurtzite–stannite structure.

		a/Å	b/Å	c/Å
$Ag_2HgSnSe_4$	This work	8.48324	7.42642	7.05182
	Expt.	8.494[11]	7.314[11]	6.972[11]
		8.480(3)[13]	7.323(3)[13]	6.996(4)[12]
		8.461(1)[14]	7.340(1)[14]	6.9901(6)[14]

3.2. Electronic structure

The energy band structure of $Ag_2HgSnSe_4$ is calculated, and the results are presented in Fig. 1(a). It can be obviously seen that this compound is a direct gap semiconductor. The calculated band gap is 0.23 eV. We also calculated the band structure of the Ag_2HgSnS_4 crystal in the same structure, and the results are shown in Fig. 1(b) for reference. A similar direct band gap of 0.17 eV is also obtained. It is well known that the band gaps predicted by DFT are smaller than experimental data, which means that our results underestimate the real band gaps of these two materials. According to the previous report,[19] Ag_2HgSnS_4 is a direct band-gap semiconductor with an energy gap of 1.38 eV at room temperature.[24] Obviously, our calculated band gap of Ag_2HgSnS_4 is much smaller than that of the experimental value and the difference between them is 1.21 eV. So we modify the electronic structures with a rigid shift of the conduction bands (CBs) upwards by 1.21 eV for the above two materials in our calculation. The results of the corrected band structures are also shown in Figs. 1(a) and 1(b) with dashed lines. It can be seen that the valence bands (VBs) do not change but the CBs shift toward higher energy. Thus the modified band gaps are enlarged and the values are 1.44 eV and 1.38 eV for $Ag_2HgSnSe_4$ and Ag_2HgSnS_4, respectively. The former could serve as a reference for the future experimental study.

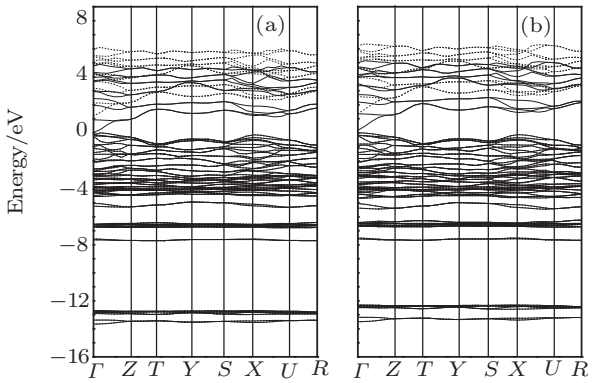


Fig. 1. Uncorrected (solid curve) and corrected (dashed curve) band structures of (a) $Ag_2HgSnSe_4$ and (b) Ag_2HgSnS_4.

Figures 2 and 3 show the total density of the states (TDOS) and partial density of states (PDOS) for $Ag_2HgSnSe_4$ respectively. The Se 4s and 4p states are clearly located at around −14 eV to −12 eV and −8 eV to 0 eV in the valence bands, respectively. The VBs at about −7 eV are mainly influenced by Hg 5d states, which presents a sharp peak because of its strong localization characteristic. An obvious hybridization between Se 4p and Ag 4d states is observed in an energy range from −6 eV to the Fermi level. The Sn 5s and Hg 6s states dominate two narrow bands located from −8 eV to −6 eV and −6 eV to −4 eV, respectively. While the conduction bands are dominated mainly by the hybridization of Hg 6s, Ag 5s, Se 4s, 4p, Sn 5s and 5p states. Apparently, this crystal has a strong covalent feature.

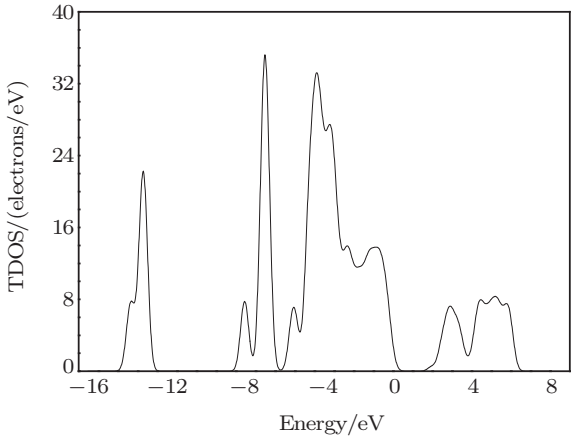


Fig. 2. Total density of states for $Ag_2HgSnSe_4$.

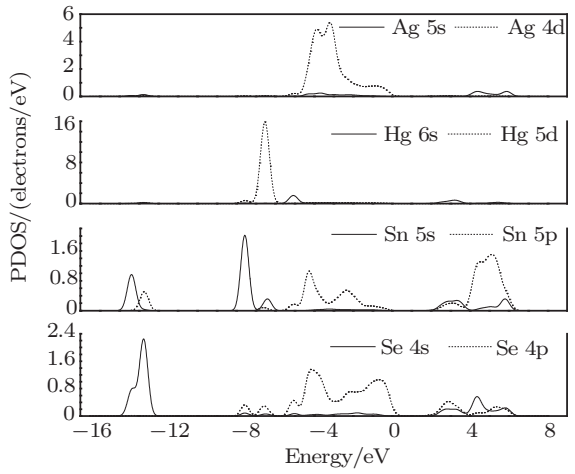


Fig. 3. Partial density of states for $Ag_2HgSnSe_4$.

3.3. Optical properties

Among many optical properties, the dielectric function $\varepsilon(\omega)$ of a material is the most important property[25,26] which is calculated based on the electronic structure. The imaginary part $\varepsilon_2(\omega)$ of the dielectric function $\varepsilon(\omega)$ can be obtained from the momentum matrix elements between the occupied and the unoccupied electronic states, which is given as follows:[27]

$$\varepsilon_2(\omega) = \frac{2e^2\pi}{\Omega\varepsilon_0}\sum_{k,v,c}\left|\left\langle\psi_k^c\right|\hat{u}\cdot r\left|\psi_k^v\right\rangle\right|^2 \times\delta(E_k^c - E_k^v - E), \quad (1)$$

where the integral runs over the first BZ, ω is the light frequency, e is the electronic charge, and ψ_k^c and ψ_k^v are the conduction- and the valence-band wave functions at k, respectively. According to the Kramers–Kronig transformation, the real part $\varepsilon_1(\omega)$ of the dielectric function $\varepsilon(\omega)$ can be obtained from the imaginary part $\varepsilon_2(\omega)$ as[28]

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi}\,\mathrm{P}\int_0^\infty \frac{\omega'\varepsilon_2(\omega')}{\omega'^2-\omega^2}\,\mathrm{d}\omega', \quad (2)$$

where P denotes the principal value of the integral.

We show the real part and the imaginary part of the dielectric function spectrum of $Ag_2HgSnSe_4$ in Fig. 4 from 0 eV to 20 eV. The beginning of the calculated $\varepsilon_2(\omega)$ spectrum corresponds to a transition at Γ point, which is equal to the energy gap. Our simulated onset energy of $Ag_2HgSnSe_4$ is 1.44 eV. There are nine peaks in $\varepsilon_2(\omega)$ spectrum for this compound. Peaks A (1.93 eV), B (2.48 eV), C (3.84 eV), and D (4.70 eV) are ascribed mainly to the transitions from Ag 4d, Sn 5p, and Se 4p states in the VBs to the band-edge of the CBs. Peak E is located at around 6.30 eV which corresponds to the transition from Hg 6s to the CBs. And peaks F (8.02 eV), G (9.14 eV), H (10.86 eV), and I (12.26 eV) correspond to the transitions from Hg 5d and Sn 5s states to the CBs. From the $\varepsilon_1(\omega)$ spectrum, we also easily obtain the static dielectric constant for $Ag_2HgSnSe_4$, corresponding to the value of 6.57.

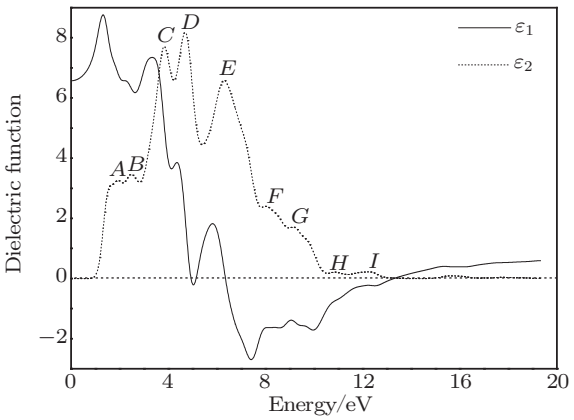


Fig. 4. Real part $\varepsilon_1(\omega)$ and imaginary part $\varepsilon_2(\omega)$ of the dielectric function for $Ag_2HgSnSe_4$.

We also calculated the absorption coefficient $I(\omega)$, reflectivity $R(\omega)$, and energy-loss function $L(\omega)$, and their results are presented in Figs. 5(a)–5(c) respectively. The optical absorption coefficient is one of the most crucial evaluation criteria in application of the photoelectric materials. It is calculated by $I(\omega) = \sqrt{2}\omega\left[\sqrt{\varepsilon_1(\omega)^2+\varepsilon_2(\omega)^2}-\varepsilon_1(\omega)\right]^{1/2}$. From Fig. 5(a), we observe a very high absorption coefficient ($> 10^4$ cm^{-1}) and a wide absorption band (0 eV–19 eV) for $Ag_2HgSnSe_4$, so it could be a good option as absorber layer in thin-film solar cells. In Fig. 5(b), several peaks are seen in the spectrum of reflectivity, the

strongest located at 10.48 eV. The energy-loss function is usually used to describe the energy loss of a fast electron traversing in the material.[29] Its main peak is always defined as the bulk plasma frequency, which occurs when $\varepsilon_2(\omega) < 1$ and $\varepsilon_1(\omega)$ reaches the zero point.[30] The sharp structure is located at 13.30 eV, corresponding to a rapid decrease of reflectance. To our knowledge, there have not been any detailed theoretical results on the electronic and optical properties of $Ag_2HgSnSe_4$ in wurtzite–stannite phase, including the dielectric function, the absorption coefficient, the reflectivity, and the energy-loss function. Therefore, we hope that our results could serve as a reference for future study.

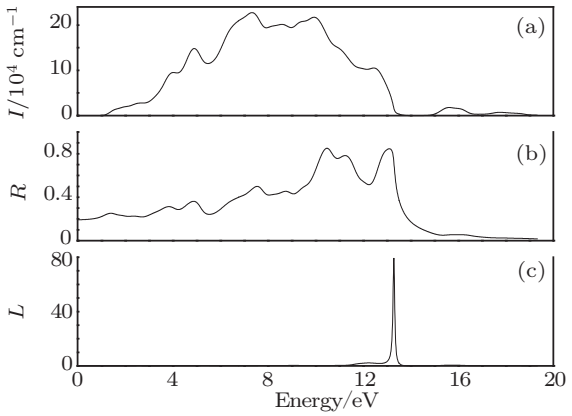


Fig. 5. Optical constants for $Ag_2HgSnSe_4$: (a) absorption coefficient $I(\omega)$, (b) reflectivity $R(\omega)$, and (c) energy-loss spectrum $L(\omega)$.

4. Conclusions

We reported on a systematic study of the structural, electronic, and optical properties of $Ag_2HgSnSe_4$ in wurtzite–stannite phase using the DFT with GGA. Our calculated lattice constants are in good agreement with the previous data. We discussed the energy band structure, the TDOS, and the PDOS for this material in detail. It is a direct gap semiconductor. In addition, we simulated optical properties including the dielectric function, the absorption coefficient, the reflectivity, and the energy-loss function. The electron transitions of nine prominent peaks in $\varepsilon_2(\omega)$ spectrum are studied at length. The high absorption coefficient of $Ag_2HgSnSe_4$ is very important for application in absorber material of thin-film solar cells. We also discussed the main peaks of $R(\omega)$ and $L(\omega)$ spectra.

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