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Electronic structures and optical properties of $Cu_{1-x}Ag_xInTe_2$ (x = 0, 0.25, 0.5, 0.75 and 1) chalcopyrite compounds

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ABSTRACT

ABC_2 chalcopyrite compounds are receiving increasing attention recently, and there are many researches of B-site or C-site doping. The current work mainly redresses the effects of A-site doping. The electronic structures and optical properties of $Cu_{1-x}Ag_xInTe_2$ (x = 0, 0.25, 0.5, 0.75 and 1) compounds have been investigated by the first-principles approach based on density functional theory (DFT). $Cu_{1-x}Ag_xInTe_2$ compounds are direct band-gap semiconductors, and the calculated band gaps are respectively 1.128, 1.086, 1.053, 1.029 and 1.01 eV, which coincide well with the experimental results. The $Cu_{1-x}Ag_xInTe_2$ monocrystals with optical anisotropies have the potential applications in the fields of second harmonic generation and optical parametric oscillator. The polycrystalline $Cu_{1-x}Ag_xInTe_2$ compounds have high absorption and reflection coefficients. Doping Ag atoms can further increase the photoconductivities of $Cu_{1-x}Ag_xInTe_2$ compounds. Besides, $CuInTe_2$, $Cu_{0.25}Ag_{0.75}InTe_2$ and $AgInTe_2$ compounds have high absorption capacities and photoconductivities in the visible light region, promising them great potentials to be photoelectric materials.

1. Introduction

ABC_2 ternary compounds with chalcopyrite structure are now receiving increasing attention mainly because of their wide applications, such as in nonlinear optical devices, semiconductor lasers and solar cells [1–3]. Among these materials, $CdSiP_2$ with large effective nonlinear coefficient, wide transparent region and good mechanical properties [4,5] has already been investigated. Similarly, $ZnGeP_2$ exhibits good transparency at the wavelength region from 0.7 to 12 μm, and its electronic, elastic and optical properties are researched experimentally and theoretically [6].

Besides $CdBC_2$ and $ZnBC_2$ compounds, Cu-based chalcopyrite compounds have been also studied. Wagner [7] once reported $CuInSe_2$/CdS p-n heterojunction photovoltaic detector which displays uniform quantum efficiency of up to ~ 70% between 0.55 and 1.25 μm. This work has made the $CuInSe_2$ solar cell into practice and brought Cu-based chalcopyrite compounds into valuable optoelectronic materials. $CuInSe_2$ solar cells are low-cost, high efficient, well-stable and resistant to radiation. Further, after doping Ga, $CuInSe_2$ will be transformed into $CuIn(Ga)Se_2$ which has an adjustable band gap and makes solar cells to achieve 20% higher efficiency [8]. Similar to $CuInSe_2$, $CuInS_2$ is also used as a solar cell layer material due to its excellent optoelectronic properties [9]. Moreover, the electronic structures, structural phase transitions, elastic behaviors and optical properties of $CuAlC_2$(C=S, Se, Te) compounds [10,11] are investigated all sidedly in experiments. Several researchers, such as Mousa et al. [12], have measured the electrical conductivity and thermoelectric power of $CuInTe_2$ in experiment, revealing that $CuInTe_2$ is a good thermoelectric material with a high thermoelectric figure of merit.

As is well known, doping atoms in crystals can lead to the change of lattice symmetry and the diversification of chemical composition, which eventually results in a great diversity of the crystals' performances [13]. Doping Cr or Mn atoms in chalcopyrites leads to the appearance of magnetic moments, and substitution of A-site yields a stable configuration with a ferromagnetic state [14]. Furthermore, there are other studies on doped $CuInTe_2$ compounds. Recently, the thermoelectricity in Cd-doped $CuInTe_2$ compounds and the synthesis, crystal structures, optical characters and electric properties of Ce-doped $CuInTe_2$ compounds have been completed [15]. Gaafar [16] has researched the elastic moduli and acoustic impedance of Ag-doped $CuInTe_2$ compounds through measuring their longitudinal and shear ultrasonic wave velocities by using the pulse echo technique. Nevertheless, to the best of our knowledge, although there are a few studies on the doped $CuInTe_2$ compounds mentioned above, most of them focus on experimental researches of their synthesis, as well as their thermoelectric, mechanical, optical and electric properties. Up to now, theoretical research on the electronic structures and optical properties of Ag-doped $CuInTe_2$ compounds has not been reported. To fill this gap,

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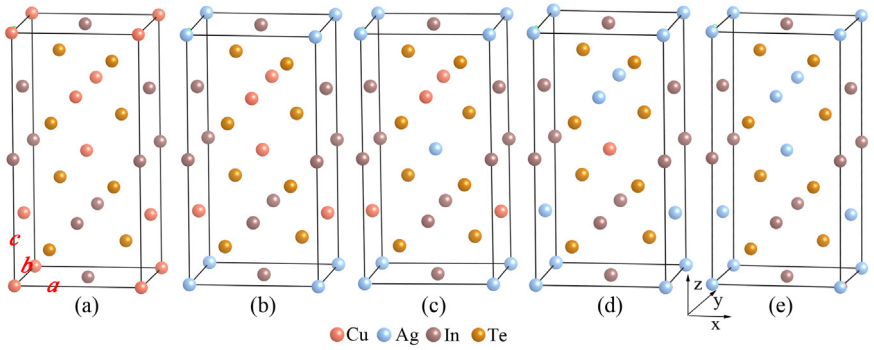

Fig. 1. Illustrations of $Cu_{1-x}Ag_xInTe_2$ (x = 0, 0.25, 0.5, 0.75 and 1) compounds. (a) $CuInTe_2$, (b) $Cu_{0.75}Ag_{0.25}InTe_2$, (c) $Cu_{0.5}Ag_{0.5}InTe_2$, (d) $Cu_{0.25}Ag_{0.75}InTe_2$ and (e) $AgInTe_2$.

we have made a study on their electronic structures and optical properties by using the first-principles approach based on density functional theory (DFT). We expect to provide some meritorious theoretical information for the promising applications of these materials.

2. Structure models and computational methods

2.1. Structure models

$CuInTe_2$ crystal has a chalcopyrite-type structure with the space group I-42d (NO.122) in the tetragonal system, and its experimental lattice constants are $a = b = 6.310$ Å, $c = 12.581$ Å and $\alpha = \beta = \gamma = 90°$. The unit cell of $CuInTe_2$ contains four Cu atoms, four In atoms and eight Te atoms, while the crystal models of Ag-doped $CuInTe_2$, namely $Cu_{1-x}Ag_xInTe_2$ (x = 0.25, 0.5, 0.75 and 1), are formed by replacing Cu atoms in $CuInTe_2$ with 1, 2, 3 or 4 Ag atoms, respectively. Accordingly, as shown in Fig. 1, their chemical formulas are respectively denoted as $CuInTe_2$, $Cu_{0.75}Ag_{0.25}InTe_2$, $Cu_{0.5}Ag_{0.5}InTe_2$, $Cu_{0.25}Ag_{0.75}InTe_2$ and $AgInTe_2$. All $Cu_{1-x}Ag_xInTe_2$ compounds are tetragonal for different values of x. However, their space groups are I-42d (No.122) for x = 0 and 1, $I-4$ (No.82) for x = 0.5 and P-4 (No. 81) for x = 0.25 and 0.75, respectively.

2.2. Computational methods

In the current work, the first-principle calculations were performed based on the plane-wave pseudopotential DFT by using the Cambridge Sequential Total Energy Package (CASTEP) simulation software. The electronic exchange-correlations were treated by the Perdew-Burke-Ernzerhof (PBE) under generalized gradient approximation (GGA) [17], and the ion-electron interactions were described by the norm-conserving pseudo potential (NC-PP) [18]. The electronic configurations during calculations were $3d^{10}4s^1$, $4s^24p^64d^{10}5s^1$, $5s^25p^1$ and $5s^25p^4$ for Cu, Ag, In and Te, respectively. For solids, especially doped solids, the fully relaxed structures with highly converged total energies, forces and stresses play crucial roles in the studies of their electronic structures as well as optical properties. Accordingly, geometry optimization is essential to obtain their stable states of the relaxed structures, meaning that strict convergence criteria must be satisfied in the relaxation of atomic positions and lattice parameters. As for the convergence criteria in the current calculations, a cutoff energy of 920 eV for a plane-wave basis and a 8 × 8 × 4 k-point mesh in the first Brillouin zone were used during the structural optimization based on the Broyden-Fletcher-Goldfarb-Shanno (BFGS) method [19,20]. The atomic relaxation was stopped when the total energy converged to 5×10^{-6} eV/atom, the ionic force was within 0.01 eV/Å, the residual stress of the unit cell was less than 0.02 GPa and the displacement deviation was below 5.0×10^{-4} Å. After geometry optimization, the relaxed structures were used in the calculations of electronic structures and dielectric functions to obtain the optical properties of $Cu_{1-x}Ag_xInTe_2$ compounds.

3. Results and discussion

3.1. Crystal structures

The calculated lattice constants (namely a, c and V) of $Cu_{1-x}Ag_xInTe_2$ compounds, as well as other experimental results [21–23], are plotted in Fig. 2. The calculated values coincide well with the experimental ones, indicating that the current computational methods are reliable. We can also see from Fig. 2 that the theoretical lattice constants of $Cu_{1-x}Ag_xInTe_2$ monotonically increase with the increasing Ag-doped concentration, due to the larger radius of Ag atoms.

3.2. Electronic structures

The energy band structures of $Cu_{1-x}Ag_xInTe_2$ compounds along the high symmetry points in the first Brillouin zone are presented in Fig. 3. The Fermi energy is set to zero. Both the valence band maximum (VBM) and the conduction band minimum (CBM) of each $Cu_{1-x}Ag_xInTe_2$ crystal are located at the symmetry point G in the first Brillouin zone, showing that all of them are direct-gap semiconductors. The theoretically calculated band gaps, 1.128, 1.086, 1.053, 1.029 and 1.01 eV, of $Cu_{1-x}Ag_xInTe_2$ (x = 0, 0.25, 0.5, 0.75 and 1) coincide well with the experimental results (1.06 eV for $CuInTe_2$ [24] and 1.02 eV for $AgInTe_2$ [25]). To put it another way, after doping Ag atoms, the band gaps of $Cu_{1-x}Ag_xInTe_2$ compounds decrease. This is consistent with the phenomenon in Fig. 3 that the conduction bands get closer to the Fermi level (i.e., the top of the valence band) with x increasing. It means that the electron transitions from valence bands to conduction bands can get easier after doping Ag atoms, which may induce intense light absorption of $Cu_{1-x}Ag_xInTe_2$ and improve their photocatalytic properties.

The total and partial density of states for $Cu_{1-x}Ag_xInTe_2$ compounds

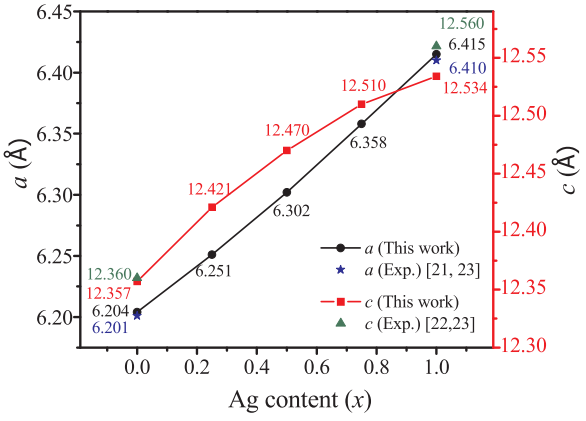

Fig. 2. The lattice constants (a and c) of $Cu_{1-x}Ag_xInTe_2$ compounds as a function of x.