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First principles study the luminescence mechanism of wurtzite $AgInS_2$ doped by zinc

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ABSTRACT

The electronic structure and optical property of wurtzite $AgInS_2$ with vacancy defects and doped by zinc have been investigated by the first principle to study the luminescence mechanism. The results show that the intrinsic silver vacancy and zinc vacancy may lead to the narrowing of bandgap, and it shows metallic characteristics after a indium atom is replaced by a zinc atom in the supercell of wurtzite $AgInS_2$. The dielectric property study indicates that the main peaks of imaginary part are red shift after the silver atom and the indium atom of wurtzite $AgInS_2$ are replaced respectively by zinc atoms. The optical property study indicates that the reflectivity and absorbility of $AgInS_2$ are improved after the silver atom and the indium atom are replaced respectively by the zinc atoms.

1. Introduction

As an I–III–VI ternary semiconductor compound, $AgInS_2$ is widely used in the fields of photovoltaic cells, photocatalysis, optoelectronics and nonlinear optics due to its excellent optical property and environmentally benign nature [1–3]. In general, $AgInS_2$ crystals have two different polymorphs: chalcopyrite and orthorhombic wurtzite. Orthorhombic wurtzite $AgInS_2$ has shown excellent photoelectrical and luminescent property, and it has attracted much concentration [4,5]. The experiment and simulated calculation of pure orthorhombic wurtzite $AgInS_2$ indicated that it was a direct bandgap semiconductor, and the bandgap is between 1.8 and 2.0 eV [6,7]. Yet, the luminescent property of pure orthorhombic wurtzite $AgInS_2$ has encountered limitations, and researchers have adopted various routes to improve the property. Metal ion doping is the most effective way to improve luminescent property of orthorhombic wurtzite $AgInS_2$. Recently, it is found that $AgInS_2$ has very excellent luminescent property, and the experiment results show that zinc doped $AgInS_2$ can exhibit multicolour in the visibleregion due to the adjustable band gap in the visible region [8–10]. But so far, the origin of the metal ion doped $AgInS_2$ hasn't been studied. It is necessary to study the electronic structure of metal doped $AgInS_2$ by simulated calculation to reveal the optical property change mechanism to guide experiments better.

The first principle which is based on density functional theory (DFT) can be used to calculate the band gap and optical property of a semiconductor [11–13]. It has been widely used in optical material calculation to explain the results of experiment of optical materials [14,15], and the standard DFT calculation the local density approximation (LDA) and general gradient approximation (GGA) are usually adopted by researchers for the convenient calculation mode and lower demand of computer performance. Using first principles predict the properties of multiple metal sulfides have been reported in a growing number of papers. For example, Walsh and his partners calculated structural, electronic, and defect properties of Cu_2ZnSnS_4 by the first principles [16,17]; Zeng and his partners calculated the instability of S vancancies in Cu_2ZnSnS_4 by the first principles [18]; Valakh and his coworkers studied the electronic, structural and optical properties of Cu_2ZnSnS_4 and relative compounds by the first principle [19–21].

In this work, both LDA and GGA are adopted to simulate the electronic structure and optical property of ternary sulfides $AgInS_2$ doped by zinc, and the purpose is to give a theory study example of $AgInS_2$ doped by metal ion to reveal the luminescent mechanism.

2. Computational details

The first principle calculation of $AgInS_2$ was carried out with the Cambridge Serial Tatal Energy Package module (CASTP) of material studio 6.0 version. The calculation adopts the supercell of wurtzite

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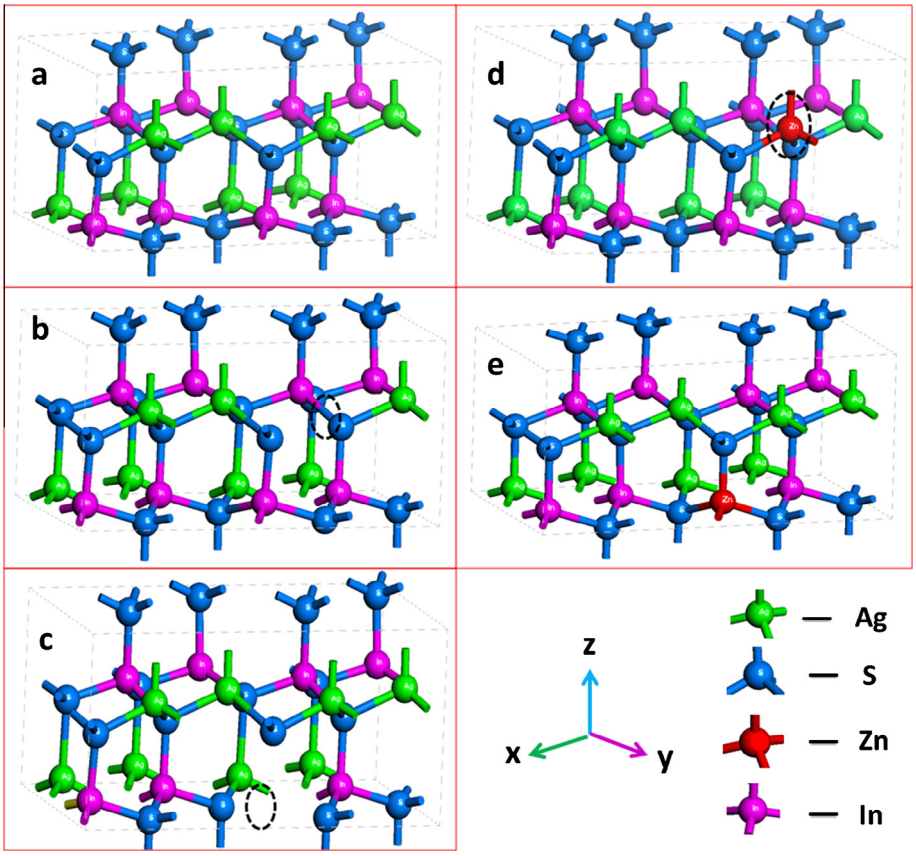

Fig. 1. The supercell crystal structural models of wurtzite $AgInS_2$ doped by zinc atom. (a) The supercell crystal structural model of pure wurtzite $AgInS_2$; (b) the supercell structural model of wurtzite $AgInS_2$ with silver atom vacancy; (c) the supercell structural model of wurtzite $AgInS_2$ with indium atom vacancy; (d) the supercell structural model of wurtzite $AgInS_2$ the silver atom of which is replaced by zinc atom; (e) the supercell structural model of wurtzite $AgInS_2$ the indium atom of which is replaced by zinc atom.

$AgInS_2$, which consists 32 atoms. The core electrons are optimized by the norm-conserving pseudopotentials and local density approximation (LDA) functional. The Perdew–Burke–Ernzerhof (PBE) of generalized gradient approximation (GGA) method was used as the exchange–correlation effects of valence electrons. The energy cutoff was chosen 720 eV, the Monkhorst–Pack scheme k-points grid sampling was set as $3 \times 3 \times 4$ for the irreducible Brillouin zone. The electronic configurations are $4s^2 4p^6 4d^{10} 5s^1$ for silver, $5s^2 5p^1$ for indium, $3s^2 3p^4$ for sulfur and $3s^2 3p^6 3d^{10} 4s^2$ for zinc.

3. Results and discussions

The space group of wurtzite $AgInS_2$ is $Pna2_1$ and the local symmetry is c_{2v}^9. The phase structure of $AgInS_2$ is chosen wurtzite orthorhombic structure which is stable even annealed at high temperatures [22]. The calculation adopts the supercell of wurtzite $AgInS_2$ which contains 32 atoms, including 8 silver atoms, 8 indium atoms and 16 sulfur atoms. The relaxed lattice constants of wurtzite $AgInS_2$ are $a = 7.041$ Å, $b = 8.196$ Å and 6.574 Å, which are consistent with the experiment results of $a = 6.977$ Å, $b = 8.273$ Å and $c = 6.695$ Å [23]. The defect structural models of silver and indium vacancy are respectively shown in Fig. 1(b) and (c), and the zinc substitution structural models of silver and indium atoms are shown in Fig. 1(d) and (e).

The diameter of zinc atom is 1.39 Å, which is smaller than that of silver atom (1.75 Å) and indium atom (2.00 Å), indicating that zinc atom can occupy less space in the supercell of wurtzite $AgInS_2$ after replacing silver and indium atoms. The calculated bond distances of Ag–S, In–S and Zn–S are 2.511 Å, 2.494 Å and 2.347 Å, respectively, showing that the bond length of Zn–S is the shortest and the bond energy is the largest.

The band structure of zinc doped wurtzite $AgInS_2$ along the high symmetry directions in the Brillouin zone is calculated based on the PBE, and the results are shown in Fig. 2. Fig. 2(a) shows the band structure of pure wurtzite $AgInS_2$, and the Fermi level indicated by a red[1] line is set to zero. Both of the valence bands maximum and the conduction bands minimum of wurtzite $AgInS_2$ are in G line, showing that wurtzite $AgInS_2$ is a direct band gap semiconductor. The simulated band gap is 1.215 eV, which is bigger than that of the results reported by the literature [22,23], but it is still less than the experiment value (1.8–2.0 eV) due to the simulated method adopted underestimate the results, but it doesn't affect the profile of band structure. Fig. 2(b)–(d) shows the band structure of silver vacancy defects, indium vacancy defects and the zinc substitution of silver, respectively. And the results show that the vacancy and zinc substitution of silver lead to the introduction of impurity levels, which can narrow the bandgap significantly, and this provides interpretation for the band gap adjustability and the luminescent mechanism of $AgInS_2$. Fig. 2(e) shows the band gap profile of zinc substitution of silver, and the impurity level bend across the Fermi level, which shows the metallic characteristics, which can enhance the electroconductivity. Therefore, the calculation results show that vacancy defects and zinc substitution of silver can lead to the narrow of the bandgap, and zinc substitution of indium can enhance the electroconductivity of $AgInS_2$ when it replaces indium.

[1] For interpretation of color in Figs. 2 and 4, the reader is referred to the web version of this article.