

First-principles study of defect formation in photovoltaic semiconductor Cu_2SnS_3

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Abstract

Formation energies of Cu, Sn and S vacancies in monoclinic Cu_2SnS_3 were calculated with first-principles pseudo-potential calculations using plane-wave basis functions. The calculations were performed in typical points in a schematic ternary phase diagram of a Cu-Sn-S system. The results were qualitatively similar to the case in CuInSe_2 . Cu_2SnS_3 is a preferable light-absorbing material for thin-film solar cells.

1. Introduction

A ternary copper chalcogenide Cu_2SnS_3 (CTS) has attracted considerable interest recently as a light absorbing material for thin-film solar cells such as $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) has, since both are comprised of earth-abundant materials. The crystal structure of CTS has been reported to be cubic, tetragonal, monoclinic or triclinic, where band-gap energies are found to be 0.98 to 1.15 eV, 1.35 eV, 0.93 eV, and 0.95 eV, respectively [1]. They are all derived from the zincblende-type structure. The monoclinic structure with the space group C1C1 shown in Fig.1 is most probable as the ground state structure, which contains two inequivalent Cu sites (Cu_1 and Cu_2), one Sn site and three inequivalent S sites (S_1 , S_2 and S_3), confirmed with first-principles calculations [1, 2]. The efficiency of fabricated CTS solar cells is 4.63% and they are appreciably smaller than those observed for CZTSSe (12.6%) or $\text{Cu}(\text{InGa})\text{Se}_2$ (21.7%) [3-5]. We report here theoretically calculated formation energies of neutral vacancies of Cu, Sn and S atoms in CTS by first-principles pseudopotential calculations and compare with those in CZTS and CuInSe_2 to see if there is a pronounced difference that may affect the efficiency of the solar cell.

2. Computational procedures

First-principles calculations were performed based on a density functional theory with the generalized gradient approximation (GGA) and the parametrization procedure by Perdew, Burke and Ernzerhof (PBE) using a plane-wave pseudopotential method. The code used is the Cambridge Serial Total Energy Package (CASTEP) ver. 7.02. Ultrasoft pseudopotentials were applied with a plane-wave cutoff energy of 500 eV. A specific $10 \times 10 \times 10$ k-point mesh was generated for a conventional CTS cell by the Monkhorst-Pack scheme for numerical integrations over the Brillouin zone. Self-consistent total energies were obtained by the density-mixing scheme in connection with the conjugate gradient

technique. Atomic positions were optimized by the quasi-Newton method with the Broyden-Fletcher-Goldfarb-Shanno scheme. The formation energy of point defect was calculated from the difference of total energy between imperfect crystal and perfect crystal. Calculations for the imperfect crystal were performed using a supercell with 96 atoms. The lattice constants were fixed at values optimized for the perfect crystal. Atomic arrangements around a vacancy were optimized allowing relaxation of the first and second nearest neighbor atoms.

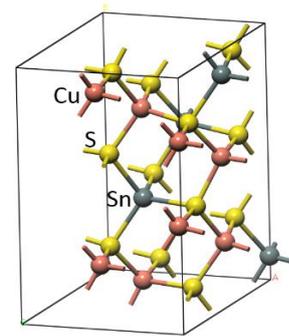


Fig. 1 Crystal structure of monoclinic Cu_2SnS_3 .

3. Results and discussion

The formation energy of a neutral vacancy in a compound depends on the atomic chemical potential μ in the system. The formation energy of Cu vacancy in CTS is expressed as

$$E_F(V_{\text{Cu}}) = E_t(\text{Cu}_{31}\text{Sn}_{16}\text{S}_{48}) - E_t(\text{Cu}_{32}\text{Sn}_{16}\text{S}_{48}) + \mu_{\text{Cu}},$$

where E_t is total energy of the supercell with or without a defect, and μ_{Cu} is the chemical potential of Cu. The chemical potential changes depending on the chemical environment of the system. As was reported in the literatures [5, 6], calculations of the formation energy of a Cu vacancy have been done for five points around the phase of CTS in a schematic ternary phase diagram of the Cu-Sn-S system shown in Fig.2. The five points shown in Fig.2 correspond to the vertices of the three-phase regions. For example, at point 1, CTS is in equilibrium with $\text{Cu}_{29}\text{S}_{16}$ and Cu metal. At point 3, CTS is in equilibrium with SnS_2 and S. Points 1, 2 and 5 correspond to Cu-rich conditions and the points 3 and 4 correspond to Cu-poor conditions. Chemical potentials for the bulk samples were obtained as total energies per formula by separate calculations. A compound Cu_2S is usually used in

place of $\text{Cu}_{29}\text{S}_{16}$ in the literature, however, the formation enthalpy of Cu_2S is found to be positive, making Cu_2S unstable, by the present method of calculation, and the recently analyzed compound $\text{Cu}_{29}\text{S}_{16}$ [7] has been chosen for theoretical consistency in this study. Calculated vacancy formation energies for inequivalent sites of Cu_1 , Cu_2 , Sn, S_1 , S_2 and S_3 are plotted in Fig.3 for the five points in Fig. 2. The formation energy of Cu_1 vacancy, which is nearly the same as that of Cu_2 vacancy, takes the minimum at points 3 and 4, which are in Cu-poor conditions. The formation energy of S_1 vacancy, which is nearly the same as that of S_2 or S_3 vacancy, takes the minimum at point 5 which is in S-poor condition. Similarly, the formation energy of Sn vacancy takes the minimum at point 2 which is in Sn-poor condition. The minimum formation energy of Cu vacancy is smaller than that of S or Sn, showing easy creation of Cu vacancies in CTS compared with S or Sn vacancies. These features are qualitatively similar to the case of CuInSe_2 , if In and Se atoms are replaced with Sn and Sn atoms respectively.

Displacement of near-neighbor atoms around a vacancy of Cu, Sn or S are also studied. Relative changes of the distances between a Cu_1 vacancy and the four nearest-neighbor S atoms of S_1 , and another S_1 , S_2 and S_3 from the original arrangement without the vacancy were calculated to be -0.81%, -0.33%, -0.88% and +0.17%, respectively. The positive change corresponds to the case of S_3 , which is bonded by two Sn and two Cu atoms. Calculated relative changes of the distances between the S atoms and their nearest-neighbor Cu or Sn atoms range from -0.85% to -1.45% for S-Cu bonds, and from -1.63% to -1.96% for S-Sn bonds. Relative changes of the distances between a Cu_1 vacancy and the four nearest neighbor S atoms are similar to the case of Cu_2 , and the directions of the displacements are shown in Fig.4. These behaviors are similar to the case of CuInSe_2 , except for the existence of the positive change. This positive change and more shortening of the S-Sn bonds seem to indicate that S-Sn bonds are stronger than the S-Cu bonds in this atomic arrangement.

In summary, formation energies of Cu, Sn and S vacancies in monoclinic Cu_2SnS_3 were calculated in typical points in a schematic ternary phase diagram. The results are qualitatively similar to the case in CuInSe_2 . Viewing also a calculated similarity in partial density of states in Cu_2SnS_3 and CuInSe_2 [1], and the calculated high optical absorbing coefficient of Cu_2SnS_3 [6], Cu_2SnS_3 is concluded to be a preferable light-absorbing material for thin-film solar cells.

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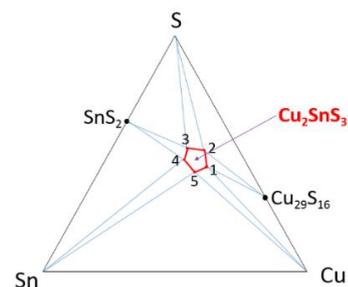


Fig. 2 Schematic ternary phase diagram of Cu-Sn-S system.

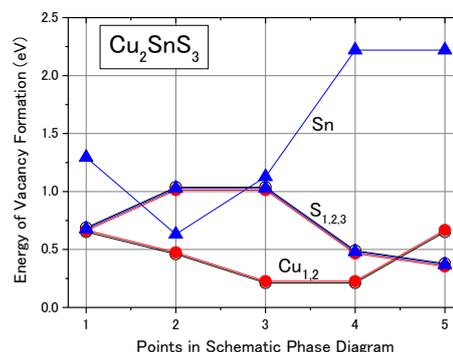


Fig. 3 Calculated vacancy formation energies of inequivalent Cu_1 , Cu_2 , Sn, S_1 , S_2 and S_3 sites in Cu_2SnS_3 plotted at five points in Fig.2.

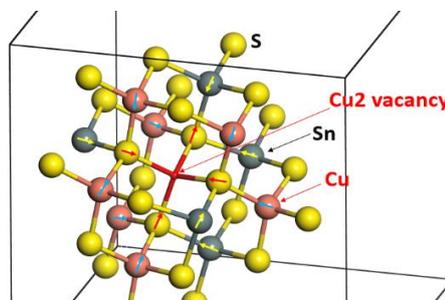


Fig. 4. Directions of displacements of near-neighbor atoms around a Cu_2 vacancy in Cu_2SnS_3 are shown with arrows.

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