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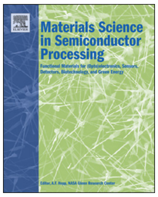

Phase equilibrium of a $CuInSe_2$–$CuInS_2$ pseudobinary system studied by combined first-principles calculations and cluster expansion Monte Carlo simulations

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ABSTRACT

We report the phase diagram of a $CuInSe_2$–$CuInS_2$ pseudobinary system calculated by a combination of first-principles calculations based on density functional theory, cluster expansion, and Monte Carlo simulations. All formation energies of $CuIn(Se_{1-x}S_x)_2$ (CISS) alloys are positive, indicating that CISS alloy is a miscibility gap system and has a tendency to phase separation. The phase diagram computed with conventional cluster expansion shows a miscibility gap with consolute temperature $T_C = 170$ K. The contribution of lattice vibrations lowers T_C to 130 K. The miscibility gaps for the $CuInSe_2$–$CuInS_2$ system are predicted to be asymmetric. The effect of lattice vibrations on the miscibility gap is found to be large, and the size mismatch mechanism can be used to explain the large vibrational effect in the $CuInSe_2$–$CuInS_2$ system.

1. Introduction

As one class of absorber layer materials of thin film solar cells, Cu based chalcopyrite semiconductors such as $CuInSe_2$ and its alloys with either $CuInS_2$ or $CuGaSe_2$ have received considerable attention due to their excellent optical and photovoltaic properties [1–4]. $CuInSe_2$ has a direct band gap energy of approximately 1.0 eV and a very high absorption coefficient (10^4–10^5 cm^{-1}) [2]. In order to obtain a closer match to the solar spectrum it is desirable to increase the band gap of the $CuInSe_2$ semiconductor thin film to 1.4–1.5 eV. This can be achieved by alloying of $CuInSe_2$ with $CuInS_2$, i.e. the formation of the quaternary alloys $CuIn(Se_{1-x}S_x)_2$ (CISS). Fig. 1 shows the crystal structure of CISS alloys. The CISS alloy film has proven to be a promising material for solar cells with high conversion efficiency [5,6].

Previous investigations of CISS have been mainly about the growth technology of CISS thin film [7–10], film morphology [1,11,12], structural, optical and electrical properties [12–15]. All these investigations are helpful for understanding CISS alloys and for developing higher efficiency solar cells. But, Sheppard et al. found that the formation of two distinct and stable $CuInSe_2$ and $CuInS_2$ ternary phases in the bulk of the CISS alloy is a typical reaction which occurs during the selenization and sulfurization of CuIn alloys [2]. Devices produced from these phase-separation absorber films exhibit inferior device

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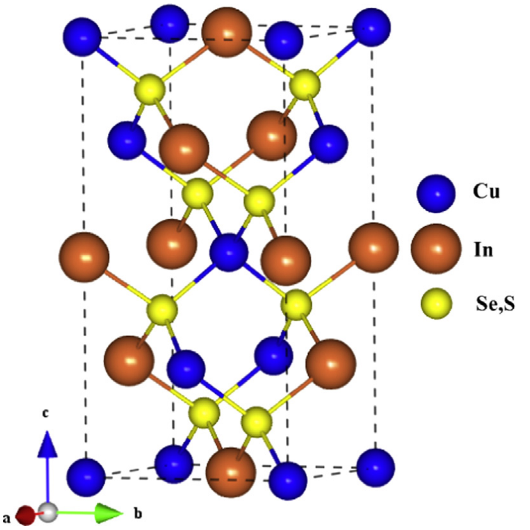

Fig. 1. Crystal structure of the chalcopyrite $CuIn(Se_{1-x}S_x)_2$ unit cell.

performances with low open-circuit voltages due to the limited band gap values [13]. Engelmann et al. found that the $CuInSe_2$ film can be converted to a graded $CuIn(Se_{1-x}S_x)_2$ film by reacting $CuInSe_2$ film in a flowing H_2S/Ar atmosphere, indicating that the CISS film is inhomogeneous [16]. For $Cu(In_{1-x}Ga_x)Se_2$ (CIGS) alloys which also have been proved to have the phase-separation behavior [17,18] and an inhomogeneity [19], the inhomogeneity can lead to the fluctuation of the band gap, and this is detrimental to the cell efficiency [20,21]. Werner et al. have showed that even small fluctuations in the composition unfavorably, which may be caused by the phase separation, can affect the electronic and optical properties of CIGS [21]. All of these means that the knowledge of the alloy phase equilibrium and homogeneity is essential for the effective design of the CISS alloy.

Recent first-principles study of phase equilibrium of similar pseudobinary alloys, $CuInSe_2$–$CuGaSe_2$ and $CuInSe_2$–$CuAlSe_2$, has predicted the miscibility gap and consolute temperature of these alloys [22], though the available phase diagrams show complete miscibility in the solid state [23,24]. However, for the $CuInSe_2$–$CuInS_2$ system, first-principles study of phase equilibrium does not exist in the literature. Therefore, the aim of this work is to corroborate and complement the experimental observations by precisely locating the position of the miscibility gap in the $CuInSe_2$–$CuInS_2$ system using first-principles calculations combined with the cluster expansion (CE) and Monte Carlo (MC) techniques.

2. Computational methodology

2.1. Cluster expansion

In principle, the computation of phase equilibrium and ground-state structure of the $CuIn(Se_{1-x}S_x)_2$ pseudobinary alloy requires the calculation of total energy for all possible configurations of placing atoms S and Se on N sites. Since the number of possible configurations 2^N is enormous even for a suitable number of sites N, calculating the total energies solely by first-principles is unfeasible for an exhaustive set of configurations. The cluster expansion (CE) method constructs an Ising-like Hamiltonian for the energies of the different atomic configurations, and can be considered as a compact representation of the configurational total energy of the alloy. In the $CuInSe_2$–$CuInS_2$ pseudobinary system, each alloy configuration is described by a set of "spin" occupation variables σ_i, which take values $\sigma_i = -1$ when site-i is occupied by S atom and $\sigma_i = +1$ when site-i is occupied by Se atom.

The CE parameterizes the configurational energy (per exchangeable anion), as a polynomial in "spin" occupation variables:

$$E(\sigma) = \sum_{\alpha} m_\alpha J_\alpha \langle \prod_{i \in \alpha'} \sigma_i \rangle, \tag{1}$$

where α is a cluster (a set of lattice sites i). The sum is taken over all clusters α that are not equivalent by a symmetry operation of the space group of the parent lattice, while the average is taken over all clusters α' that are equivalent to α by symmetry. The coefficient J_α in this polynomial embodies the information regarding the energetics of the alloy and is called the effective cluster interaction (ECI). The multiplicity m_α indicates the number of clusters that are equivalent to α by symmetry. It is seen that when all clusters α are considered in the sum, the cluster expansion is able to represent the energy $E(\sigma)$ of any configuration σ by an appropriate selection of the values of J_α. The unknown parameters of the cluster expansion (the ECIs) are then determined by fitting them to the energies of a relatively small number of configurations obtained by first-principles calculations [25]. The CE can be improved by increasing the number of clusters and/or the number of energies used in the fit when necessary. Detailed illustrations of the CE method can be found in many literatures [26–30]. The CE method was performed with the Alloy Theoretic Automated Toolkit (ATAT) which can automate most of the tasks associated with the construction of the CE Hamiltonian and the calculation of thermodynamic properties [25,31,32]. ATAT proceeds by gradually increasing the number of clusters included in the cluster expansion until the desired accuracy is achieved.

The cross-validation (CV) score is used as a criterion that shows the predictive power of the cluster expansion. For a given set of structural energies, the optimal set of clusters is determined by minimizing the CV score. A cluster expansion can be considered satisfactory when the CV score is small, typically less than 0.025 eV. The CV score is similar to the root mean square error and defined as

$$CV = \left(\frac{1}{N} \sum_{i=1}^{N} \left(E_i - \hat{E}_i \right)^2 \right)^{1/2}, \tag{2}$$

where E_i is the calculated energy of structure i, and $\hat{E}_i$ is the predicted value of the energy of structure i obtained from a least-squares fit to the $(N-1)$ other structural energies [25]. The CV score is an improvement relative to the standard mean square error criterion that only minimizes the error for structures included in the fit.

2.2. Density functional theory calculations

The electronic-structure total-energy calculations of ordered structures, which are required for the construction