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First-principles study of thermoelectric and lattice vibrational properties of chalcopyrite $CuGaTe_2$

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ABSTRACT

The electronic structure of $CuGaTe_2$ has been investigated using first-principles calculations, and it was discovered that it has a mixture of heavy and light bands near the valence band maximum and a combination of electronically conducting and insulating units near the gap edges, highly desirable for good thermoelectric performance. Semi-classic Boltzmann transport theory was then used to calculate the thermoelectric properties of $CuGaTe_2$, and the optimal *p*- or *n*-type doping concentrations have been estimated based on the predicted maximum power factors. The phonon dispersion, phonon density of states, and specific heat of $CuGaTe_2$ were evaluated by density functional perturbation theory in combination with the quasi-harmonic approximation, and the calculated phonon frequencies at the Γ point as well as the specific heat are in agreement with experimental data. The relatively high thermal conductivity of $CuGaTe_2$ at low temperature is attributed to the lack of low-frequency vibrational modes, suggesting that its thermal conductivity can be reduced by introducing additional phonon scattering.

1. Introduction

Thermoelectric materials can convert waste heat into useful electrical energy, and have attracted great attentions in recent years [1,2]. The efficiency of a thermoelectric material at temperature T is evaluated by the dimensionless figure of merit $ZT = S^2\sigma T/\kappa$, where S is the thermopower, σ is the electrical conductivity, and κ is the thermal conductivity [1]. A ZT of 1, which corresponds to a heat-to-electricity conversion efficiency of several percents, is necessary for the practical applications of thermoelectric materials. To enhance ZT, phononic properties must be altered to reduce the thermal conductivity, and electronic structures must be engineered to maximize the thermopower and electrical conductivity [3]. These properties are intimately coupled, and it remains a challenge to search for new thermoelectric compounds with large ZT values.

The chalcopyrite semiconductors with the formula I–III–VI_2 (where I = Cu, Ag; III = Al, Ga, In; and VI = S, Se, Te) have found application in nonlinear optical devices [4–7] and solar cells [8] for many years. Recently, a number of crystals of this group have been investigated for thermoelectric applications because they exhibit excellent *p*-type thermoelectric performance in the middle-temperature range [9–16]. It was experimentally found that the bulk $CuGaTe_2$, one compound of this family, exhibits a high ZT value of 1.4 at the temperature about 950 K [9]. The thermopower and electrical conductivity of *p*-type $CuGaTe_2$ are both high, though it has a relatively high thermal conductivity at low temperature as well. It was reported that substitution with isoelectronic elements or introducing lattice defects can cause additional phonon scattering, and thus result in an overall reduction of the total thermal conductivity [13–15]. Furthermore, the power factor of $CuGaTe_2$ can be improved by doping to change the band structure. For example, Cui et al. have reported that the thermopower of $CuGaTe_2$ can be effectively enhanced by partial substitution of Ga by Sb [16]. In order to further enhance the thermoelectric performance of this compound, it is necessary to investigate and optimize its thermoelectric properties theoretically.

On the theoretical side, Zhang et al. have carried out a comparative study of the structural and electronic properties of Cu-based I–III–VI_2 semiconductors using first-principles with the Heyd–Scuseria–Ernzerhof functional and the Perdew–Burke–Ernzerhof functional, and observed the dual characteristics of Cu *d* orbitals in forming chemical bonds [17]. Parker et al. investigated the thermoelectric properties of $AgGaTe_2$ and related chalcopyrite structure materials [18], though $CuGaTe_2$ was not studied there. The doping and temperature dependence of thermoelectric properties of $AgGaTe_2$ have also been investigated by density functional theory (DFT) [19]. The vibrational properties of some crystals of I–III–VI_2 chalcopyrite semiconductors, such as $AgInSe_2$ [20], $AgInTe_2$ [20], $AgGaSe_2$ [21], and $AgGaTe_2$ [21], have been investigated by

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first-principles calculations. However, few studies have investigated the thermoelectric performance and vibrational properties of $CuGaTe_2$ compound. In this paper, the electronic structure and transport properties of $CuGaTe_2$ are investigated using first-principles calculations and semi-classical Boltzmann transport theory, and the optimal *p*- or *n*-type doping levels are calculated. In order to understand the origin of the relatively high thermal conductivity of $CuGaTe_2$, the lattice vibrational properties of $CuGaTe_2$ are also computed through density functional perturbation theory (DFPT) in combination with the quasi-harmonic approximation (QHA), and the results are compared with experimental data.

2. Computational method

The electronic structure calculations were performed within DFT using the projector augment wave method as implemented in Vienna *ab initio* Simulation Package (VASP) [22–24]. The exchange-correlation potential was treated by using the Perdew–Burke–Ernzerhof (PBE) [25] generalized gradient approximation (GGA). The energy convergence criterion was chosen to be 10^6 eV and the cutoff energy of the plane-wave was set at 400 eV. It is well known that the GGA cannot adequately describe the exchange-correlation effects of strongly localized Cu 3*d* electrons, and it underestimates the localization of Cu 3*d* electrons. The DFT + *U* can correct to some extend this problem, and we chose the PBE + *U* method for calculating electronic structure and transport properties. The effective Coulomb repulsion parameter *U* was set to be 4 eV based on the published literature of Cu-based ternary semiconductors [17].

The thermopower *S* and electronic conductivity over relaxation time σ/τ were obtained using the semi-classical Boltzmann theory in conjunction with rigid band and constant relaxation time approximations. All the calculations of transport properties were implemented in the BoltzTraP package [26], and the necessary crystal structure and eigen-energies for BoltzTraP calculation were obtained from *ab initio* results. In order to get reasonable transport properties, the Brillouin zones of the unit cells were represented by the Monkhorst–Pack special *k*-point scheme with 25 × 25 × 25 grid meshes.

The phonon calculations were carried out within the framework of the force-constants method. Real-space force constants of the supercell were calculated in the DFPT as implemented in the VASP code. The phonon frequencies were computed from the force constants using the Phonopy code [27]. For the phonon dispersion and the heat capacity, local density approximation (LDA) [28] generally yields a better agreement with experiments than GGA, and more discussions about this can be found in [29,30], thus the exchange-correlation effects were taken into account in the framework of the LDA. For the QHA calculations, a 2 × 2 × 2 supercell with a total of 128 atoms was created and seven non-symmetry equivalent displacements were applied to the structure in order to determine the force constants.

3. Results and discussion

3.1. Crystal lattice and electronic structure

$CuGaTe_2$ is crystallized in the body-centered-tetragonal chalcopyrite structure with the space group $I\bar{4}2d$, and the structure of $CuGaTe_2$ is shown in Fig. 1. The calculations were carried out on the primitive cell of $CuGaTe_2$ containing two Cu, two Ga, and four Te atoms. The calculated lattice parameters of $CuGaTe_2$ are $a = 0.6121$ nm and $c = 1.2122$ nm, which overestimate the lattice constants within 1.7% compared with experimental reported data at room temperature ($a = 0.6024$ nm and $c = 1.1924$ nm) [31]. It is well known that GGA often overestimates lattice constants of solids [25], though the difference here is rather small. The calculated electronic band structure of $CuGaTe_2$ is shown in Fig. 2. It can be seen from Fig. 2a that the band structure of $CuGaTe_2$ has a direct gap at the Γ point. The calculated band gap is 0.41 eV, while the experimental measured gap is 1.24 eV [32]. And indeed, the shape of the band structure is correct and the problem of band gap can be amended by a rigid shift of the conduction band, as previously reported for some semiconductors [33,34]. In order to obtain more realistic thermoelectric properties, we correct this problem using a scissors operator by moving the conduction band upward to match the experiment value of band gap in the transport properties calculations. Since experimental works to date have found that $CuGaTe_2$ tends to form *p*-type semiconductors, we focus our discussion on the valence band maximum (VBM). As shown in Fig. 2a, the valence band maximum (VBM) is located at the Γ point, and the dispersion along the Γ–Z direction is greater than the Γ–X

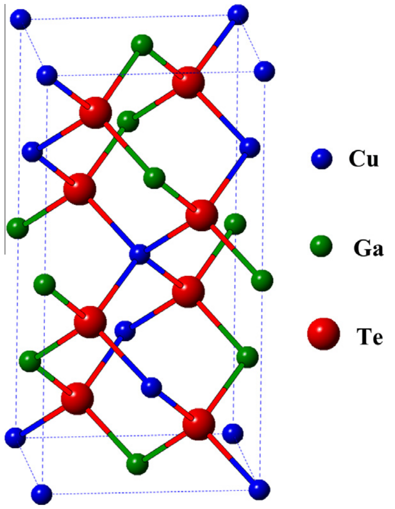

Fig. 1. Crystal structure of $CuGaTe_2$.

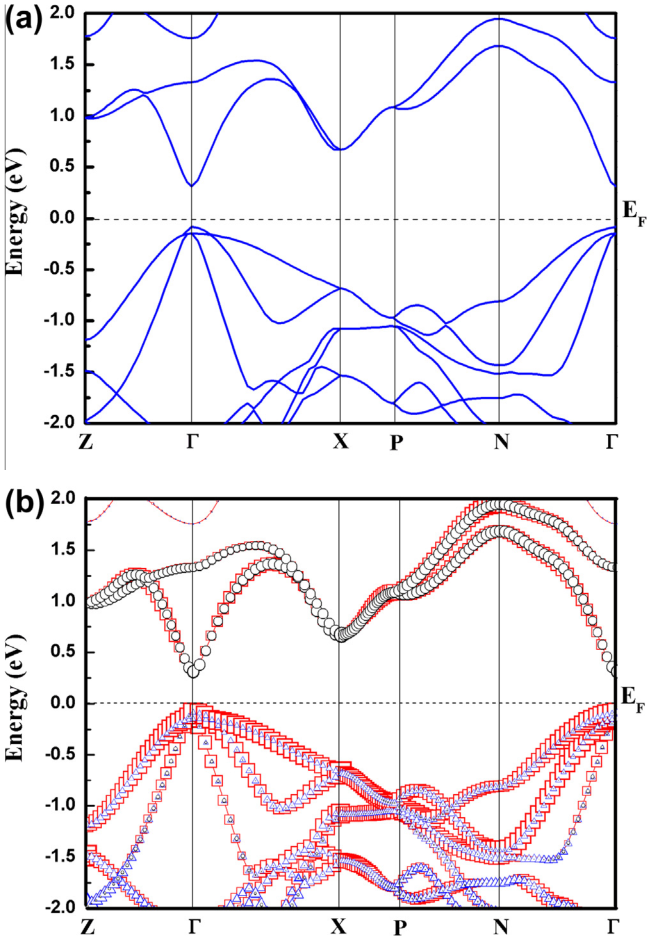

Fig. 2. (a) Electronic band structure of $CuGaTe_2$. (b) The contribution of each atom in the band structure of $CuGaTe_2$: including the *d*-orbital of Cu (blue triangles), the *s*-orbital of Ga (black circles), and the *p*-orbital of Te (red squares). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)