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First-principle calculations of the electronic, elastic and thermoelectric properties of Ag doped $CuGaTe_2$

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ABSTRACT

To improve the performance of a thermoelectric material $CuGaTe_2$, element Ag is doped to replace element Ga and we investigate the electronic structure, phase stability, elastic and thermoelectric properties of $CuGa_{1-x}Ag_xTe_2$ (x = 0, 0.25 and 0.5) via first-principles method. The phase stability of $CuGa_{1-x}Ag_xTe_2$ is discussed by analyzing the formation energy, cohesive energy and elastic constants. The calculated sound velocities decrease with the increase of Ag content, which is favorable for reducing the lattice thermal conductivity. The analysis of band structures shows that the replacement of Ga by Ag makes $CuGaTe_2$ undergo a direct-indirect semiconductor transition. The Ag doping induces steep density of states in valence band edge, which is beneficial for increasing the carrier concentration and improving thermoelectric performance of $CuGaTe_2$.

1. Introduction

Thermoelectric (TE) material is a widely used functional material which can convert waste heat into useful electricity. It not only solves the energy shortage, but also effectively reduces environmental pollution. The ability of a TE material to produce thermoelectric power is characterized by a dimensionless figure of merit $ZT = S^2\sigma T/(\kappa_e + \kappa_l)$ [1,2], where σ is the electrical conductivity, S is the Seebeck coefficient, T is temperature, k_e and k_l are electronic and lattice contributions to thermal conductivity k, respectively. Obtaining a TE material with high ZT value is a challenging task, since a good TE material should satisfy some conflicting demands: high Seebeck coefficient and electrical conductivity, yet low thermal conductivity. Thus, the researchers are focus on seeking optimal TE materials and exploring new ways to improve their performance.

The compound $CuGaTe_2$ belongs to a group of I-III-VI_2 (I = Cu, Ag; III = Al, Ga, In; and VI = S, Se, Te) chalcopyrite semiconductors with analog zinc-blende lattices. Previous work has paid more attention to the study of ternary chalcopyrite semiconductor $CuGaTe_2$ due to its unique structural, electronic and optical properties [3]. Recently, $CuGaTe_2$ was reported to be a potential candidate for TE material with a large dimensionless figure of merit [4–6]. It shows outstanding thermoelectric properties and its maximum ZT value reaches 1.4 at 950 K, which stems from moderate performance of electrical properties and a rapid decrease of k with the increase of temperature [4]. However, $CuGaTe_2$ has relative high thermal conductivity k = 7.4 $Wm^{-1}K^{-1}$ at room temperature. Thus, its thermoelectric performance can be improved by a reduction of k by applying some optimization technique, for example through chemical doping, nanocrystallization, or imposing pressure. Zhang et al. [7] experimentally demonstrated that Ag doped compounds $CuGa_{1-x}Ag_xTe_2$ ($0 \le x \le 0.05$) can significantly increase the hole carrier concentration and reduce the thermal conductivity. However, there is no theoretical verification and no further investigation about higher Ag content system. In order to understand the crucial role of the atomic occupation of Ag in the host material $CuGaTe_2$, the first-principles density function calculations on the electronic, elastic and thermoelectric properties of $CuGa_{1-x}Ag_xTe_2$ (x = 0.25 and 0.5) materials are performed in this paper.

2. Computational details

The optimization of lattice structures was performed by using a plane wave pseudopotential method based on the density

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functional theory (DFT). The generalized gradient approximation of Perdew–Bueke–Ernzerhof (GGA-PBE) exchange correlation functional [8] was employed to relax the lattice constants and atoms positions, while the ultrasoft pseudopotential [9] was applied to model ion–electron interaction. Convergence tests showed that the plane wave cut-off energy of 500 eV and a k mesh of $5 \times 5 \times 3$ generated according to the Monkhorst–Pack scheme [10] in the irreducible Brillouin zone (IBZ) were sufficient. The states Cu $3d^{10}4s^1$, Ga $3d^{10}4s^24p^1$, Te $5s^25p^4$ and Ag $3d^{10}4s^1$ were treated as the valence states, respectively. Based on the Broyden–-Fletcher–Goldfarb–Shenno (BFGS) [11] minimization technique, the system was optimized via self-consistent calculation. The self-consistent convergence tolerance of the total energy, maximum force, maximum displacement and maximum stress were set as 5×10^{-6} eV/atom, 0.01 eV/Å, 5×10^{-4} Å, and 0.02 GPa, respectively.

After optimizing, the electronic structures were investigated via the full-potential all-electron linearized augmented plane wave (FP-LAPW) method implemented in the WIEN2K code [12]. We employed a modified version of the exchange potential proposed by Becke and Johnson, known as a modified Becke Johnson (mBJ) potential [13]. The well converged basis sets with $R_{mt}K_{max} = 8.5$ were used, where R_{mt} and K_{max} are the smallest muffin-tin (MT)

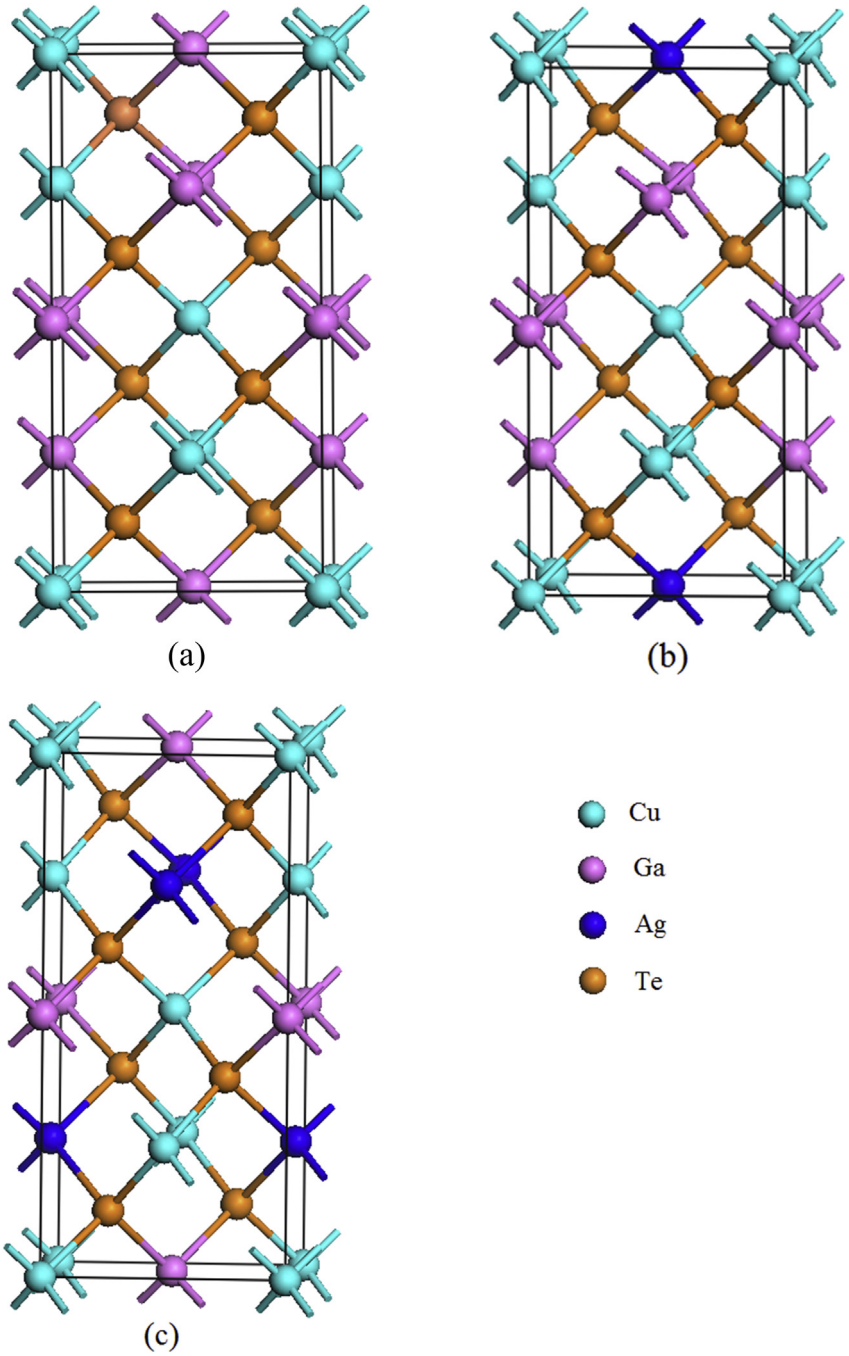

Fig. 1. The crystal structure of (a) chalcopyrite compounds $CuGaTe_2$, (b) $CuGa_{0.75}Ag_{0.25}Te_2$, (c) $CuGa_{0.5}Ag_{0.5}Te_2$.