First-principles investigation of the effects of strain on elastic, thermal, and optical properties of $CuGaTe_2$*

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Based on the density functional theory, the influences of strain on structural, elastic, thermal and optical properties of $CuGaTe_2$ are discussed in detail. It is found that the tensile strain on $CuGaTe_2$ is beneficial to the decrease of lattice thermal conductivity by reducing the mean sound velocity and Debye temperature. Moreover, all strained and unstrained $CuGaTe_2$ exhibit rather similar optical characters. But the tensile strain improves the ability to absorb sunlight in the visible range. These research findings can give hints for designing thermoelectric and photovoltaic devices.

Keywords: elastic constants, thermal properties, optical properties, first-principles

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1. Introduction

The energy crisis and environmental pollution are increasingly serious. How to properly solve the energy shortage and environmental pollution is a worldwide concern. Photovoltaic and thermoelectric materials are both new energy materials, which can convert solar energy and industrial waste heat into available electric energy, respectively. It is most important and difficult to improve the conversion efficiencies of these new energy materials now.

Recently, the ternary chalcopyrite I–III–VI_2 (I = Cu, Ag; III = Al, Ga, In; and $VI = S$, Se, Te) has been of wide interest, since it is a kind of potential photovoltaic and thermoelectric (TE) material,[1–3] due to the unique structural properties. As a thermoelectric material, it shows excellent thermoelectric performance in the intermediate temperature range. For example, the maximum dimensionless figure of merit for $CuGaTe_2$ reached 1.4 experimentally[2] and 1.69 theoretically[3] at 950 K. In theory, Shen *et al.* proved that doping Zn and Mn at Ga sites can effectively tune carrier concentration and reduce the lattice thermal conductivity based on a single parabolic band approximation.[4] Rai *et al.* investigated the thermoelectric properties of bulk and surface (001) $CuInTe_2$ by the first principles calculation and suggested the key to improving their thermoelectric performance was to increase the Seebeck coefficient and electrical conductivity.[5] The ternary chalcopyrite is also extensively used in photovoltaic applications, especially $CuInSe_2$, due to its high conversion efficiency.[6] Zhang *et al.* employed the density functional theory (DFT) and discussed the structural and optical properties of $CuXTe_2$ (X = Al, Ga, In).[7] With recent development, the current best efficiency for sulfide thin film solar cell was 12.3%.[8] However, this efficiency is still much lower than the reported efficiency of other thin-film solar cells, such as 18.3% for CdTe.

It is reported that the semiconductor material, as a candidate used in photovoltaic or thermoelectric technology, is recognized by its energy band gap, optical and thermodynamic properties.[9,10] To our knowledge, many effective ways to adjust the electronic properties of semiconductors, such as doping,[11–13] pressure, and strain engineering have been proposed. Hinsche *et al.* focused on investigating the influence of strain on thermoelectric properties of Bi_2Te_3, Sb_2Te_3, and Si.[14,15] Our group studied the effect of strain on thermoelectric properties of $CuGaTe_2$.[16] In this paper, we estimate the Seebeck coefficient of $CuGaTe_2$, but do not discuss the effect on thermal conductivity. As far as we know, there are still no detailed theoretical studies on the influence of strain on optical and thermal properties up to now. Thus, we will focus on studying the effects of strain on elastic, thermal and optical properties of $CuGaTe_2$ by the first principles calculation in this work.

The rest of the paper is organized as follows. In Section 2, the crystal structure of $CuGaTe_2$ is described briefly. Then the details of parameter settings in the computational process are presented in Section 3. The results and discussion about the elastic, thermal and optical properties of $CuGaTe_2$ under strain are given in Section 4. Finally, some conclusions are drawn in Section 5.

2. Crystal structure

The ball-and-stick structure model of $CuGaTe_2$ is shown in Fig. 1. It possesses $I\bar{4}2d$ symmetry, where Cu atoms occupy the 4a (0 0 0) site, Ga atoms at the 4b (0 0 1/2) site, and the Te atoms at the 8d (u 1/4 1/8) site.[17] The ternary chal-

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copyrite with tetragonal distortions ($u \neq 1/4$, $\eta = c/2a \neq 1$, where a and c are the lattice parameters)[18] is not the perfect tetrahedral crystal structure. In this work, we define the strain to be biaxial in-plane and the specific forms can be expressed as $\Delta a/a = [(a-a_0)/a_0] \times 100\%$, where a_0 is the optimized in-plane lattice constant for the unstrained case, and a is the in-plane lattice constant for the strained case. The parameter a is intentionally compressed and elongated. The values of lattice constant c and atomic position u can be obtained after the lattice relaxation.

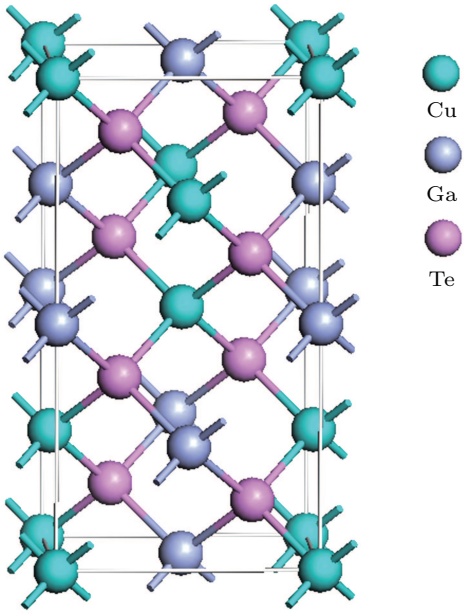


Fig. 1. (color online) Ball-and-stick structure model of $CuGaTe_2$.

3. Computational parameter settings

In this paper, we will focus on discussing the influence of strain on elastic, thermal and optical properties of $CuGaTe_2$. For this purpose, the employed computational approach is the first-principle calculations based on the density functional theory (DFT).[19] The calculations are performed with the CASTEP code. The details of parameter settings during the computational process are shown below. The exchange correlation functional is selected as the generalized gradient approximation of Perdew–Burke–Ernzerhof (GGA-PBE);[20] pseudo-potential is chosen as the ultrasoft pseudo-potential; the cut-off energy and a k mesh are set to be 500 eV and 5×5×3, respectively. The self-consistent convergence tolerance of the total energy, maximum force, maximum displacement and maximum stress are set to be 5×10^{-6} eV/atom, 0.01 eV/Å, 5×10^{-4} Å, and 0.02 GPa, respectively.[21] The electronic configurations are regarded as Cu $3d^{10}4s^1$, Ga $3d^{10}4s^24p^1$, and Te $5s^25p^4$ during the calculations.

4. Results and discussion

4.1. Structural and elastic properties

In experiment, the strain may be caused by depositing $CuGaTe_2$ thin film on the tops of different substrates. In order to simulate this situation, the strain ratio $\Delta a/a$ is taken in a range from −2% (compressive strain) to 2% (tensile strain). The calculated values of lattice constant c and unit-cell volume V of strained and unstrained $CuGaTe_2$ are shown in Fig. 2. It can be found that the lattice constant c and the deformation parameter η decrease linearly with the increase of lattice constant a, which means that the parameter c is strongly dependent on a. But the unit-cell volume V is expanded linearly with the increase of lattice constant a. This is because the reducing rate of the parameter c is slower than the increasing rate of the parameter a.

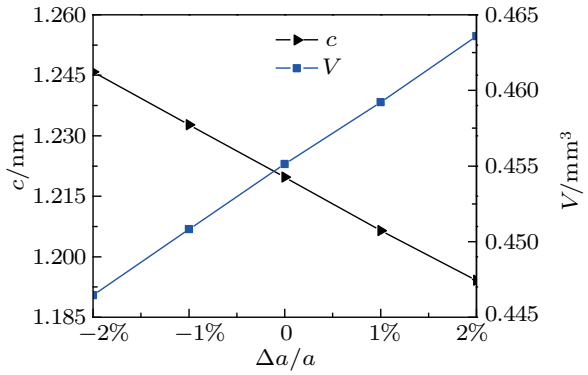


Fig. 2. (color online) Optimized lattice constant c and unit-cell volume V of $CuGaTe_2$ versus strain ratio $\Delta a/a$.

Generally, elastic properties of a solid are very important because they conduce to understanding the mechanical stability and mechanical properties.[22] For a tetragonal crystal, six elastic constants are independent,[23] that is, C_{11}, C_{12}, C_{13}, C_{33}, C_{44}, and C_{66}.[22] The mechanical stability for a tetragonal crystal makes the following restrictions on the elastic constants:[24]

$$C_{11} > 0,\ C_{33} > 0,\ C_{44} > 0,\ C_{66} > 0,\ (C_{11} - C_{12}) > 0,$$
$$(C_{11} + C_{33} - 2C_{13}) > 0,\ [2(C_{11} + C_{12}) + C_{33} + 4C_{13}] > 0. \quad (1)$$

Table 1. Values of elastic constants C_{ij} and elastic moduli B, G (in unit GPa) for strained $CuGaTe_2$.

$\Delta a/a$	C_{11}/GPa	C_{33}/GPa	C_{44}/GPa	C_{66}/GPa	C_{12}/GPa	C_{13}/GPa	B/GPa	G/GPa
−2%	77.16	79.23	36.23	36.66	46.18	40.50	54.20	27.14
−1%	73.47	74.81	36.64	36.96	41.84	39.56	51.52	26.81
0	70.04	70.02	35.12	35.50	37.04	37.73	48.34 51.5[2]	25.54
1%	69.77	65.96	35.20	27.93	34.82	36.59	46.83	24.64
2%	65.72	57.06	35.72	18.59	26.65	31.60	40.89	22.89

The elastic constants of $CuGaTe_2$ with no strain have been reported in Ref. [25]. The calculated results for the strained cases are listed in Table 1, together with the available experimental data. Obviously, the computed elastic constants of the strained and unstrained cases obey the mechanical stability conditions. It can be seen that the ratios of C_{11}/C_{33} and C_{12}/C_{13} decrease with the increase of the biaxial in-plane strain from -2% to 2% slowly, while the ratio of C_{44}/C_{66} increases rapidly. It suggests that the pseudo-cubic nature is destroyed by the biaxial in-plane strain, which makes the bond strength along the [100] direction more affected than ones along the [010] and [001] directions. Table 1 also shows the calculated values of bulk modulus B and shear modulus G by the Voigt–Reuss–Hill approximation.[26] It is found that the values of B and G decrease with the biaxial in-plane strain varying from -2% to 2%, which may be relevant to the expansion of the lattice volume. The ratio of B/G can be used to predict the brittle or ductile behavior of material.[27] If $B/G > 1.75$, the material is ductile, otherwise, it is brittle. All the values of B/G for strained $CuGaTe_2$ are larger than 1.75, belonging with ductile materials. But when the strain is increased from -2% to 2%, the value of B/G decreases gradually.

Table 2. Values of the mean sound velocity v_s, Debye temperature T_D, and minimum thermal conductivity k_{min} for strained $CuGaTe_2$.

$\Delta a/a$	-2%	-1%	0	1%	2%
v_s/ms^{-1}	2416.03	2411.05	2363.66	2331.99	2255.07
T_D/K	237.09	235.84	230.47 229[2]	226.70	218.53
k_{min}/W·m^{-1}·K^{-1}	0.50	0.49	0.48	0.47	0.45

From the Navier's equation,[28] the transverse sound velocity v_t and longitudinal sound velocity v_l can be derived. The mean sound velocity v_s can be obtained from

$$v_s = \left[\frac{1}{3}\left(\frac{2}{v_t^3} + \frac{1}{v_l^3}\right)\right]^{-1/3}. \tag{2}$$

The calculated values of mean sound velocities v_s are listed in Table 2. It is found that the effect of tensile strain on the reduction of the average sound velocity is primarily pronounced.

4.2. Thermal properties

The heat capacity is an important parameter for a substance, since it not only provides an essential insight into the vibrational properties but is also involved with many applications.[29] Applying the Debye approximation, the expression of constant-volume heat capacity C_v is given by

$$C_v(T/T_D) = 9R\left(\frac{T}{T_D}\right)^3 \int_0^{T_D/T} \frac{\xi^4 e^\xi}{(e^\xi - 1)^2} \mathrm{d}\xi, \tag{3}$$

where $\xi = \hbar\omega/k_B T$, k_B and R are the Boltzmann's constant and gas constant, respectively. Besides, T_D is the Debye temperature, which can be expressed as

$$T_D = \frac{h}{k_B}\left[\frac{3n}{4\pi}\left(\frac{N_A\rho}{M}\right)\right]^{1/3} v_s, \tag{4}$$

where h and N_A are Plank's and Avogadro's constant, respectively; M is the relative molecular weight; n is the number of atoms in the molecule. The calculated values of Debye temperature T_D are listed in Table 2. One can see that the calculated Debye temperature of unstrained $CuGaTe_2$ is close to the experimental result (229 K). With the increase of applied strain, the Debye temperature decreases linearly, which means that the thermal vibration frequency of atoms in $CuGaTe_2$ varies with strain. As pointed out previously, the relatively low Debye temperature would lead to the small Hall mobility μ_H and low thermal conductivity.[2,21] Thus, the application of the tensile strain to $CuGaTe_2$ is expected to reduce the thermal conductivity and enhance its figure of merit.

From the point of view of kinetic theory, the thermal conductivity is expressed as[30]

$$\kappa = \frac{1}{3}C_v l v_s = \frac{1}{3}C_v \tau v_s^2, \tag{5}$$

where C_v is the constant-volume heat capacity, l is the phonon mean free path, and τ is the average phonon lifetime. It is clearly indicated that the item $C_v v_s^2$ directly determines thermal conductivity from Eq. (5). To qualitatively highlight the effect of strain on thermal conductivity, we plot each item $C_v v_s^2$ as a function of temperature shown in Fig. 3, which demonstrates once again the effect tensile strain contributes to reducing the thermal conductivity.

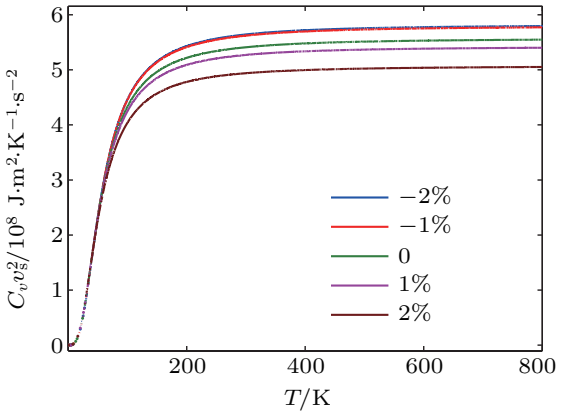


Fig. 3. (color online) Plots of temperature-dependent item $C_v v_s^2$ of $CuGaTe_2$ for the various strained cases.

In addition, to quantitatively measure the effect of strain on thermal conductivity, the minimum thermal conductivity k_{min} is estimated using Cahill model.[31] Its specific expression can be written as

$$\kappa_{min} = \frac{k_B}{2.48} n^{2/3}(v_l + v_{t1} + v_{t2}), \tag{6}$$

where k_B is the Boltzmann constant, v_l and v_s are longitudinal sound velocity and transverse sound velocity, and $v_{t1} = v_{t2} =$

v_t. The calculated values of minimum thermal conductivities for strained $CuGaTe_2$ are listed in Table 2. It can be seen that the change of k_{min} with strain is consistent with the change of T_D and $C_v v_s^2$. Thus, the tensile strain is helpful for enhancing the phonon scattering and reducing the lattice thermal conductivity.

4.3. Optical properties

A photovoltaic material should satisfy some requirements: it should be a direct-gap semiconductor, have a band gap preferably large enough (close to 1.4 eV), large absorption coefficient to absorb the essential part of the visible light spectrum and small reflectance.[7] We have studied the energy bands of $CuGaTe_2$ at various in-plane lattice parameters (-2%, -1%, 0, 1%, 2%) in Ref. [16] previously. Our results indicated that their energy bands are direct band gaps. The calculated value of band gap for unstrained $CuGaTe_2$ is 0.095 eV. However, the experimental value is 1.23 eV.[32] So we set a scissor operator of 1.135 eV to overcome such a discrepancy. To model the broadening effect, the instrumental smearing of 0.25 eV is used in all cases.

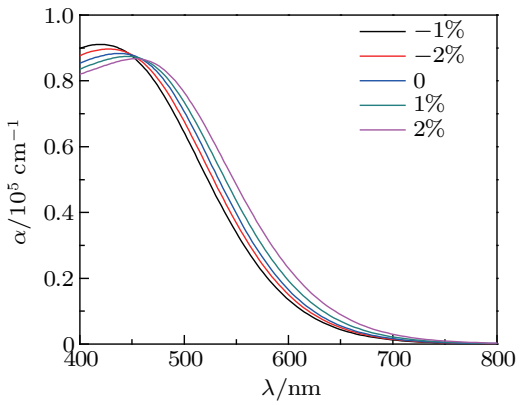


Fig. 4. (color online) Obtained plots of absorption coefficient α versus wavelength λ of $CuGaTe_2$ for the various strained cases.

The absorption coefficient is a main optical characteristic of photovoltaic material to measure how far light can penetrate the material. The absorption coefficient α can be computed using the following equation:

$$\alpha(\omega) = 2\omega \left\{ \frac{\left[\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)\right]^{1/2} - \varepsilon_1(\omega)}{2} \right\}^{1/2}, \quad (7)$$

where ω is the frequency, $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real part and imaginary part of the dielectric function, respectively. The absorption coefficient-dependence of the wavelength λ is shown in Fig. 4. One can see that the behaviors of all strained and unstrained $CuGaTe_2$ are rather similar. In the visible spectrum, the values of absorption coefficient for $CuGaTe_2$ under tensile strain are obviously higher than those under compressive strain. These findings show that the tensile strain is helpful to improve the ability to absorb the $CuGaTe_2$, which make it have the potential to be used as an important photovoltaic material.

5. Conclusions

We mainly discuss the influence of strain on structural, elastic, thermal and optical properties of $CuGaTe_2$ based on the density functional theory in this work. The optimized out-of-plane lattice constant c decreases linearly with the increase of in-plane lattice constant a. But the unit-cell volume V is expanded. The calculated elastic constants for the strained and unstrained cases satisfy the mechanical stability. The values of sound velocities and Debye temperature are estimated by the obtained elastic constants. It is found that they both decrease with the increase of tensile strain. This means that applying tensile strain to $CuGaTe_2$ is beneficial to reducing the thermal conductivity. Moreover, the tensile strain is helpful for improving the absorption of sunlight. These results give hints for designing the $CuGaTe_2$ into good thermoelectric and photovoltaic materials.

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