Structural, electronic, and thermoelectric properties of $\text{La}_2\text{CuBiS}_5$

Gui Yang^{1*}, Yanhong Yao² and Dongwei Ma¹

ABSTRACT The basic physical properties of $\text{La}_2\text{CuBiS}_5$ are studied by the first-principle calculations and the semiclassical Boltzmann theory. Charge density difference calculations show that electrons accumulate between Bi–S atoms, indicating considerable covalent bonding of Bi and S atoms. A similar charge density difference indicates that the Cu–S bonds also exhibit covalent character. The calculated minimum thermal conductivity of $\text{La}_2\text{CuBiS}_5$ is low, which is conducive to its use as a thermoelectric material. Owing to a bipolar effect, induced by thermal excitation, the material's Seebeck coefficient decreases sharply at $T = 800$ K. For the n-type and p-type doping conditions, the largest values of $S^2\sigma/\tau$ were calculated as -1.71×10^{11} and $1.837 \times 10^{11} \text{ W K}^{-2} \text{ ms}^{-1}$, respectively. The combination of a large dispersion and a high band degeneracy along the I – Y direction in the band structure simultaneously induces the highest S_y value and a high σ/τ_y value. Thus, the thermoelectric performance of $\text{La}_2\text{CuBiS}_5$ is anisotropic and most favorable along the y direction.

Keywords: chemical bond, electronic structure, thermoelectric properties

INTRODUCTION

The search for new rare-earth metal chalcogenides and their properties is an important area of research in materials science and technology. The unique lattice structures and unusual physical properties of these compounds have attracted the attention of many scientists. For example, the structure of $\text{Ba}_3\text{SmInS}_6$ [1] contains one-dimensional anionic chains of $[\text{SmInS}_6]^{6-}$ units; LaOBiS_2 crystallizes in a layered structure with La_2O_2 layers interleaved by layers of Bi_2S_4 [2]; La_2CuS_4 [3] has discrete anion triples $[\text{S}_3\text{Cu}\cdots\text{S}\cdots\text{CuS}_3]^{12-}$ in its lattice structure; the superconductivity of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [4–6] is, in part, a result of the

valence of copper ions and differences in their oxygen atom coordination environment; $\text{AgPb}_m\text{LaTe}_{m+2}$ [7] shows high electrical conductivity and a relatively small Seebeck coefficient.

In recent years, a large number of rare-earth metal chalcogenides compounds have been synthesized [1,8,9]. The structures of these compounds are chain or layered-type, similar to those of Zintl phase materials and polar intermetallic compounds. The promising thermoelectric performances of Zintl compounds (e.g., $\text{Ca}_5\text{Al}_2\text{Sb}_6$) [10–12] and intermetallic compounds (e.g., BiCuSeO) [13–15] have also drawn attention. However, rare-earth metal compounds have not been widely studied and their thermoelectric properties remain poorly understood. Recently, Bobev *et al.* [16] synthesized a new rare-earth metal compound $\text{La}_2\text{CuBiS}_5$ and analyzed its structure. To our knowledge, no theoretical studies on the chemical bonding and electronic and thermoelectric properties of $\text{La}_2\text{CuBiS}_5$ have been reported. This fundamental physical information would be useful for assessing its potential technological applications.

COMPUTATIONAL METHODS

The experimental lattice structure of $\text{La}_2\text{CuBiS}_5$ is used as the initial model and is relaxed by the general potential linearized augmented plane-wave (LAPW) method, as implemented in WIEN2K. The k -mesh is $10 \times 10 \times 10$ in the irreducible Brillouin zone (BZ), and the plane wave basis cut-off is $R_{\text{mt}} \times K_{\text{max}} = 7.0$, in terms of the smallest muffin-tin radius R_{mt} and the maximum plane wave vector K_{max} . Owing to the high mass of Bi and La atoms, spin orbit coupling is considered in our calculations. The electronic structure is calculated by the Tran–Blaha-modified Becke–Johnson

¹ College of Physics and Electrical Engineering, Anyang Normal University, Anyang 455000, China

² School of Mathematics and Statistics, Anyang Normal University, Anyang 455000, China

* Corresponding author (email: kui ziyang@126.com)

(TB-mBJ) exchange-correlation potential, which has been shown to yield accurate band gaps for most semiconductors [17–19].

On the basis of the electronic structure, the thermoelectric properties of $\text{La}_2\text{CuBiS}_5$ are obtained by semiclassical Boltzmann theory with a constant scattering time approximation as implemented in the BoltzTraP code [20]. In our calculations, the rigid-band approach is used to simulate the thermoelectric performance as a function of the doping level. This method has been used to successfully study many thermoelectric materials.

RESULTS AND DISCUSSION

Lattice structure, bonding, and thermal conductivity

The lattice structure of $\text{La}_2\text{CuBiS}_5$ and its first BZ are shown in Fig. 1, as an orthorhombic system with the space group $Pnma$ (No. 62). The optimized equilibrium lattice constants are $a = 12.012 \text{ \AA}$, $b = 4.0103 \text{ \AA}$, and $c = 17.077 \text{ \AA}$. The calculations agree well with the experimental lattice constants. There are two inequivalent atomic positions for La, a single position for Cu and Bi each, five different positions for S. The CuS_4 tetrahedra and BiS_6 octahedra are formed in the lattice structure of $\text{La}_2\text{CuBiS}_5$.

The charge density difference (CDD) can directly display the transfer of electrons between different atoms, making it a useful method to judge the nature of chemical bonding in a system. CDD is calculated by the following equation:

$$\text{CDD} = \rho_{\text{sc}} - \rho_{\text{nsc}}, \quad (1)$$

where, ρ_{sc} represents the charge density of $\text{La}_2\text{CuBiS}_5$ from a self-consistent calculation (sc); ρ_{nsc} is the non-self-consistent calculation (nsc) for a superposition of atomic charge densities.

The CDD isosurface of $\text{La}_2\text{CuBiS}_5$ is shown in Fig. 2. Yellow and blue denote loss and gain of electrons, respectively. The Bi and S atoms devote their electrons to each other and electrons accumulate midway between the Bi and S atoms. Thus, the Bi–S bond has considerable covalent character. A similar electron accumulation exists between the center of Cu and S atoms. Hence, the Cu–S bond also exhibits covalent character. From Fig. 2, the loss of electrons around the La atoms suggests that La atoms provide electrons to the CuS_4 tetrahedra and BiS_6 octahedra. The coexistence of ionic and covalent bonding in $\text{La}_2\text{CuBiS}_5$ is similar to the bonding situation of Zintl phase compounds. Previous studies [21,22] showed that the complexity of the coexistence character often led to exceptionally low thermal conductivity, whereas the interconnected covalent substructures can lead to paths for high-mobility charge transport. Therefore, the covalent bond substructure (CuS_4 tetrahedra and BiS_6 octahedra) enables a high carrier mobility, and the complex lattice structure can effectively scatter phonons and reduce the thermal conductivity.

Recently, the ShengBTE method [23] has been used to calculate the thermal conductivity as a function of the temperature. In this method, its main inputs are set of second- and third-order interatomic force constants, which can be

Figure 1 (a) Lattice structure of $\text{La}_2\text{CuBiS}_5$. Green, blue, purple, and yellow balls represent La, Cu, Bi and S atoms, respectively. (b) Corresponding first Brillouin zone.

Figure 2 Calculated charge density difference of $\text{La}_2\text{CuBiS}_5$.

calculated using third-party *ab-initio* packages such as VASP and Wien2k.

In this paper, we tried to calculate the main inputs using the VASP. However, the calculations are strongly related to the atom numbers in the unit cell. Thirty-six atoms in $\text{La}_2\text{CuBiS}_5$ unit cell make the calculations difficult. Because the calculation of phonon scattering requires a developed understanding of the lattice dynamics and very long computational times are necessary to run these simulations. Therefore, we have to give up the calculations. Here, we use the Clarke model, which has been shown to be an effective method for assessing the minimum thermal conductivity [24]. The minimum thermal conductivity in the Clarke model is defined as [25]:

$$\kappa_{\min}^{\text{Clarke}} = 0.87k_{\text{B}} \left(\frac{N_{\text{A}} n \rho}{M} \right)^{2/3} \left(\frac{Y}{\rho} \right)^{1/2}, \quad (2)$$

where k_{B} is the Boltzmann's constant, N_{A} is Avogadro's number, n is the number of atoms per unit cell, M is the mass per unit cell, ρ is the density, and Y is the Young's modulus.

The value of Y is calculated from the bulk modulus B and

shear modulus G :

$$Y = 9BG / (3B + G). \quad (3)$$

The values of B and G are obtained from the calculations of the elastic properties of the materials and the results are listed in Table 1. Here, the elastic properties are calculated from the strain-stress method. A small, finite strain is applied to the stable structure and then the atomic positions are optimized. Elastic properties are obtained by fitting the stresses and strains of the strained structure. We compared the $\kappa_{\min}^{\text{Clarke}}$ of $\text{La}_2\text{CuBiS}_5$ with that of two other Zintl phase materials [21,26]. These results suggest that $\text{La}_2\text{CuBiS}_5$ has a low thermal conductivity.

Electronic structure

Fig. 3 shows the electronic structure of $\text{La}_2\text{CuBiS}_5$ including the total and partial density of states (DOS) and band structure. As shown in Fig. 3a, there are three distinct regions in the valence bands. In the lowest energy region (-13.79 to -11.61 eV), the DOS is composed primarily of S 3s orbitals. From -10.25 to -8.83 eV, the DOS originates from the Bi 6s and S 3s states, and the strong hybridization between Bi and S atoms confirms the covalent bonding between Bi-S, discussed in relation to Fig. 2. The DOS just below the valence bands maximum (VBM) derives mainly from the Cu 3d states. For the conduction bands (1.31 to 2.42 eV), the La 5d states dominate the DOS. According to Equation (4), the DOS is related to the Seebeck coefficient S [27].

$$\begin{aligned} S &= \frac{\pi^2}{3} \left(\frac{\kappa_{\text{B}}^2 T}{q} \right) \left[\frac{d \ln \sigma(\varepsilon)}{d \varepsilon} \right]_{\varepsilon=\varepsilon_{\text{f}}} \\ &= \frac{\pi^2}{3} \left(\frac{\kappa_{\text{B}}^2 T}{q} \right) \left[\frac{1}{n} \frac{dn(\varepsilon)}{d \varepsilon} + \frac{1}{\mu} \frac{d \mu(\varepsilon)}{d \varepsilon} \right]_{\varepsilon=\varepsilon_{\text{f}}}, \end{aligned} \quad (4)$$

where $n(\varepsilon)$ is the carrier density, $\mu(\varepsilon)$ is the mobility, q is the electronic charge, and κ_{B} is the Boltzmann constant. Therefore, a high DOS near the Fermi level usually leads to a high Seebeck coefficient. A change of the distribution of electronic states near the VBM or CBM will improve the thermoelectric properties of the material.

Table 1 Calculated bulk modulus B , shear modulus G , Young's modulus Y , and the minimum thermal conductivity

	B (GPa)	G (GPa)	Y	$\kappa_{\min}$
$\text{La}_2\text{CuBiS}_5$	80.14	24.54	66.80	0.508
$\text{Ca}_5\text{Al}_2\text{Sb}_6^{\text{a}}$	40	25	62.07	0.479
$\text{Ca}_3\text{AlSb}_3^{\text{b}}$	37.66	25	61.41	0.484

a) Data from Ref. [21]; b) data from Ref. [26].

Figure 3 (a) Calculated total and partial DOS for $\text{La}_2\text{CuBiS}_5$. (b) The band structure of $\text{La}_2\text{CuBiS}_5$.

The band structure of $\text{La}_2\text{CuBiS}_5$ is shown in Fig. 3b. The maximum point in the valence band and the minimum point in conduction band are both located at the Γ point. Thus, $\text{La}_2\text{CuBiS}_5$ is a semiconductor with a direct band gap of 1.31 eV, which is consistent with the value 1.30 eV measured by optical diffuse reflection spectroscopy [28]. We plotted the band structure in the energy window -1.0 – 2.0 eV, because the thermoelectric properties were mainly determined by the energy bands near the Fermi level.

Thermoelectric properties

The thermoelectric conversion efficiency is defined by the dimensionless figure of merit $zT = S^2\sigma T / \kappa$. Here, S , σ , T , and κ represent the Seebeck coefficient, electrical conductivity, temperature, and thermal conductivity, respectively. The thermal conductivity κ is the sum of the electron thermal conductivity κ_e and the lattice thermal conductivity κ_l . In the rigid-band approach, a shift of the Fermi level indicates doping of the compound. For a doped semiconductor [21], the thermoelectric parameters can be expressed as follows:

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m_{\text{DOS}}^* T \left(\frac{\pi}{3n} \right)^{2/3}, \quad (5)$$

$$m_{\text{DOS}}^* = (m_1^* m_2^* m_3^*)^{1/3} N_v^{2/3}, \quad (6)$$

$$\sigma = ne\mu, \quad (7)$$

$$\mu \propto \frac{1}{(m_i^*)^{5/2}}, \quad (8)$$

$$m_i^* = \frac{\int e^{-dE(k)/k_B T} m_b^*(k) dk}{\int e^{-dE(k)/k_B T} dk}, \quad (9)$$

where e is the electronic charge, n is the carrier concentration, N_v is the band degeneracy, and μ is the carrier mobility. m_i^* ($i = x, y, z$) represents the mass components along three perpendicular directions. The parameters m_{DOS}^* and

$$m_b^* = \hbar^2 \left[\frac{\partial^2 E}{\partial k^2} \right]^{-1}$$

are the density-of-states effective mass with the wave vector k and the band mass, respectively.

Fig. 4 shows the thermoelectric properties of $\text{La}_2\text{CuBiS}_5$ as functions of the carrier concentration and the temperature. The positive and negative values denote p-type and n-type doping respectively. In Fig. 4a, S increases with increasing temperature and decreases with increasing carrier concentration. The results are consistent with Equation (5). According to Equation (5), S is proportional to the temperature T and is inversely proportional to the carrier concentration n . At $T = 800$ K, the sharp decrease of S indicates a bipolar effect owing to thermal excitation. A Seebeck coefficient influenced by a bipolar effect can be written as:

$$S = \frac{S_n \sigma_n + S_p \sigma_p}{\sigma_n + \sigma_p}, \quad (10)$$

where S_n is the Seebeck coefficient of electrons and σ_n is the electrical conductivity of electrons; S_p is the Seebeck coefficient of holes and σ_p is the electrical conductivity of holes. The thermal excitation becomes stronger with increasing temperature and consequently the carrier concentration increases. Therefore, the contribution to the Seebeck coefficient S from minor carriers increases with increasing temperature. At low temperature, the contribution is negligible, whereas the contribution cannot be ignored at high temperature. Thus, S is suppressed at $T = 800$ K owing to

Figure 4 Calculated thermoelectric transport coefficients of $\text{La}_2\text{CuBiS}_5$ as a function of carrier concentration. (a) Seebeck coefficients S , (b) electrical conductivity with respect to relaxation time σ/τ . (c) Power factor with respect to relaxation time $S^2\sigma/\tau$.

the bipolar effect. Comparing the Seebeck coefficients, the highest value of S is $717 \mu\text{V K}^{-1}$ for the p-type doping conditions and the highest value of S is equal to $-654 \mu\text{V K}^{-1}$ for the n-type doping.

From Equation (7), σ/τ is proportional to the carrier concentration. Therefore, σ/τ increases with increasing n in Fig. 4b, whereas the variation of σ/τ at different temperatures is small. The σ/τ value for the n-type doping condition becomes much larger than that of p-type doping as n increases. The contribution from S combined with that from σ/τ gives the largest value of $S^2\sigma/\tau$ for the n-type doping, close to that of the p-type doping, as shown in Fig. 4c. The largest $S^2\sigma/\tau = -1.71 \times 10^{11} \text{ W K}^{-2} \text{ ms}^{-1}$ appears at $n = 3 \times 10^{20} \text{ cm}^{-3}$ for n-type doping, and at $n = 8 \times 10^{20} \text{ cm}^{-3}$ for p-type doping with $S^2\sigma/\tau = 1.837 \times 10^{11} \text{ W K}^{-2} \text{ ms}^{-1}$. Therefore, the thermoelectric performance of the n-type doped materials is comparable to that of the p-type doped ones.

The Anisotropic thermoelectric property

The calculated anisotropic thermoelectric properties are similar at all temperatures. Thus, we plotted only the results of $\text{La}_2\text{CuBiS}_5$ at $T = 600 \text{ K}$, as shown in Fig. 5. In Fig. 5, we obtain $S_y > S_x > S_z$, $\sigma/\tau_y \approx \sigma/\tau_x > \sigma/\tau_z$ for the p-type doping, and $S_y \approx S_x > S_z$, $\sigma/\tau_y > \sigma/\tau_x > \sigma/\tau_z$ for the n-type doping. Thus, $(S^2\sigma/\tau)_y > (S^2\sigma/\tau)_x > (S^2\sigma/\tau)_z$ (Fig. 5c) for both the n-type and p-type doping conditions. The anisotropic thermoelectric behaviors are related to the band structure. Refer to Fig. 3b, S_i and σ_i ($i = x, y, z$) are dominated by the bands along the Γ - i direction, which is marked by the arrow. From Equations (3)–(7), a high band degeneracy N_v

means a large m_{DOS}^* which contributes to S_i . The bands dispersion corresponds to the average band mass m_i^* , where Equation (7) is used [24]. A smaller dispersion band implies a larger m_i^* , whereas a larger dispersion band suggests a smaller m_i^* . To consider the contribution of the bands near the CBM or VBM, we first fitted the bands along the Γ - i direction by fourth-order polynomial expressions of the form $E(k) = A + B1 \times k + B2 \times k^2 + B3 \times k^3 + B4 \times k^4$. In this way we determined the band mass

$$m_b^* = \hbar^2 \left[\frac{\partial^2 E}{\partial k^2} \right]^{-1}.$$

Finally, the average band mass m_i^* can be obtained by Equation (9) [21]. The results are listed in Table 2. The value of m_i^* is inversely proportional to the mobility μ and consequently $m_i^* \propto (\sigma/\tau)^{-1}$. Therefore, the smallest $m_{\Gamma-Y}^*$ in n-type or in p-type doping conditions leads to the largest value of σ/τ_y . Fortunately, the combination of the large dispersion and high band degeneracy along the Γ - Y direction causes the largest S_y and a high σ/τ_y to occur simultaneously, which gives rise to the largest $(S^2\sigma/\tau)_y$ for the n-type doping conditions (Fig. 5c). Therefore, the thermoelectric performance along the y direction is better than that along x and z directions.

SUMMARY

In this paper, the electronic structure and thermoelectric properties of $\text{La}_2\text{CuBiS}_5$ are studied by the first principles and semiclassical Boltzmann theory. CDD is used to judge the nature of chemical bonding between different atoms in

Figure 5 Anisotropic thermoelectric transport of $\text{La}_2\text{CuBiS}_5$ as a function of carrier concentration. (a) Seebeck coefficients S , (b) electrical conductivity with respect to relaxation time σ/τ . (c) Power factor with respect to relaxation time $S^2\sigma/\tau$.

Table 2 Coefficients of the fitted fourth-order polynomial expressions and calculated m_i^*

Valence (conduction) band	Γ -X	Γ -Y	Γ -Z
A	-0.0012 (1.37687)	2.45229 (21.22725)	131.14774 (-235.34838)
B1	0.42725 (0.4069)	-5.31698 (-105.42005)	-513.06998 (832.59862)
B2	-35.0041 (-20.18438)	-6.01159 (211.71008)	740.99899 (-1094.88508)
B3	366.94451 (254.98329)	16.67497 (-184.41308)	-469.38366 (637.83555)
B4	-1140.69688 (-817.73662)	-7.87385 (58.33838)	110.21779 (-138.8431)
m_i^*	-55.0223 (32.17831)	-27.5565 (8.56748)	-75.6670 (130.1639)

$\text{La}_2\text{CuBiS}_5$. The results show that Bi-S and Cu-S exhibit covalent character. From our analysis of the band structure, the calculated thermoelectric properties of materials with n-type doping are comparable to those of p-type doping. Furthermore, the anisotropic thermoelectric performance exhibits the relationship $(S^2\sigma/\tau)_y > (S^2\sigma/\tau)_x > (S^2\sigma/\tau)_z$ for both n-type and p-type doping conditions.

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Gui Yang received his PhD in physics from Shanghai University in 2008. He is currently an associate professor in the College of Physics and Electrical Engineering at Anyang Normal University, China. His scientific research focuses on the thermoelectric properties of materials.

Dongwei Ma received his PhD degree in physics from Fudan University in 2012. He is currently a professor in the College of Physics and Electrical Engineering at Anyang Normal University, China. His scientific research focuses on the theoretical studies on the electronic structures of the solid materials and its correlation with the materials' properties.

La₂CuBiS₅化合物的电子结构和热电特性研究

杨葵^{1*}, 姚艳红², 马东伟¹

摘要 本文采用第一性原理和半经典玻尔兹曼理论相结合的方法研究了La₂CuBiS₅的基本性质. 电荷差分密度图显示电子积聚在Bi-S原子之间, 这意味着Bi和S之间成共价键. Cu和S之间的电荷差分密度与Bi-S的相似, 表明Cu-S之间成共价键. 计算表明La₂CuBiS₅的最小热导率非常小, 这有利于材料的热电特性. 受热激发引起的双极化效应的影响, 材料的塞贝克系数在 $T = 800$ K时明显下降, n型和p型掺杂对应的最大 $S^2\sigma/\tau$ 值分别是 -1.71×10^{11} 和 $1.837 \times 10^{11} \text{ W K}^{-2} \text{ ms}^{-1}$. 沿 T - Y 方向上能带的大的弥散性和较高简并度有利于 S_y 和 σ/τ_y . 因此, La₂CuBiS₅展现出各向异性的热电特性, 并且沿 y 方向上的热电特性最佳.