β -CsCu₅Se₃: A Promising Thermoelectric Material going beyond Photovoltaic Application

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Copper chalcogenides have attracted much attention in recent years because of their promising applications in thermoelectric conversion. However, many of them suffer from phase transformation at low temperature. Motivated by the synthesis of bulk β -CsCu_sSe₃ with high phase transformation temperature of 923 K for photovoltaic applications, its thermoelectric properties using first-principles calculations combined with Boltzmann transport theory are systematically studied. The results show that β -CsCu₅Se₂ possesses ultralow lattice thermal conductivities of 0.24, 0.41, and 0.25 W mK⁻¹ along the x, y, and z directions at room temperature, respectively, which are further reduced to 0.09, 0.15, and 0.09 W mK⁻¹ at 800 K. A detailed analysis of its group velocity, three phonon scattering rate, Grüneisen parameter and three phonon phase space reveals that the weak harmonicity and strong phonon anharmonic scattering are responsible for the ultralow lattice thermal conductivity, leading to a high figure of merit (ZT) value of 1.81 along the y direction at 800 K, which is three times higher than that of known thermoelectric materials o-CsCu₅S₃ (0.46 at 800 K) and t-CsCu₅S₃ (0.56 at 875 K). This study suggests that β -CsCu₅Se₃ is a multifunctional material promising for both photovoltaic and thermoelectric applications.

1. Introduction

Owing to the energy crisis and environmental problems, thermoelectric materials that can directly convert waste heat to electricity have attracted extensive interests,^[1,2] and especially much attention has been paid in recent years to the materials with low costs, nontoxicity, and earth abundance.^[3–8] Copper chalcogenides are such materials. For instance, the binary copper chalcogenide compounds, Cu₂X (X = S, Se), show good thermoelectric performances ($ZT\approx1.5$) at 1000 K,^[5,6] and the ternary chalcogenide semiconductors, Cu₃SbS₄ and *o*-CsCu₅S₃, exhibit excellent thermoelectric properties because of their low

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lattice thermal conductivities and large Seebeck coefficient.^[7,8] However, most of these materials possess low phase transformation temperature. It has been reported that both Cu₂S and Cu₂Se possess low phase transformation temperatures of 373 and 400 K,^[9,10] respectively, and for Cu₃SbS₄, phase transformation occurs at about 460 K,^[11] While phase transition would significantly affect the thermoelectric efficiency of thermoelectric materials,^[12] and result in poor device reliability.^[13,14] Therefore, it is highly desirable to find other materials with high thermal stability.

Recently, a new ternary chalcogenide compound, three-dimensional (3D) layered β -CsCu₅Se₃, was successfully synthesized via solvothermal methods, which shows a high phase transition temperature of 923 K.^[15] Since β -CsCu₅Se₃ is isostructural to the thermoelectric material *o*-CsCu₅S₃.^[8] and selenium is heavier and less electronegative than sulfur, so it is natural to expect that β -CsCu₅Se₃ would possess a lower lattice thermal conductivity, better electrical transport properties, and higher thermoelectric performance as compared to

o-CsCu₅S₃. Such a phenomenon has also been observed in many classic thermoelectric materials, including PbX, Bi₂X₃, Cu₂X, SnX (X = S, Se).^[16,17] Although β -CsCu₅Se₃ shows great performance in photovoltaic applications,^[15,18] the research on its lattice thermal conductivity and thermoelectric properties has not been reported yet, which motivates us to carry out this study. On the basis of density functional theory (DFT) combined with semiclassical Boltzmann transport theory, we do find that β -CsCu₅Se₃ possesses ultralow lattice thermal conductivities and a high *ZT* value, besides the reported photovoltaic features, exhibits high thermoelectric performance.

2. Computational Methods

Based on density functional theory (DFT) and the projector augmented wave (PAW) method,^[19,20] we perform first-principles calculations using the Vienna Ab initio Simulation Package (VASP).^[21] The Perdew–Burke–Ernzerhof (PBE) functional^[22] within the generalized gradient approximation (GGA)^[23] is used to treat the interactions between ion cores and valence electrons. For structural relaxation, van der Waals interactions are taken into account by using the optB86b-vdW functional^[24] with the

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Figure 1. a) Optimized geometry and the building block (Cu₄Se₄ column) of β -CsCu₅Se₃. Cyan, green, and blue spheres stand for Cs, Se, and Cu atoms, respectively, and red is for Cu₃ atoms. b) Phonon spectra of β -CsCu₅Se₃. The three acoustic branches (TA, TA', and LA) are in red.

kinetic energy cutoff of 500 eV. The convergence criteria for total energy and atomic force components are set to 10^{-6} eV and 10^{-4} eV A⁻¹, respectively. Band structure is obtained by using the screened hybrid functional of Heyd–Scuseria–Ernzerhof (HSE06).^[25,26] The ab initio molecular dynamics (AIMD) simulations are carried out to examine the thermal stability. The first Brillouin zone is represented by *k* points sampled with a grid density of $2\pi \times 0.02$ Å⁻¹ by using the Monkhorst–Pack scheme.^[27]

The thermoelectric transport properties are studied based on semi-classical Boltzmann theory^[28] within the relaxation approximation as implemented in the BoltzTrap2 program.^[29] The phonon Boltzmann transport equation (BTE)^[30] is adopted to obtain the lattice thermal conductivity via the ShengBTE code.^[31] The required harmonic second-order interatomic force constants (IFCs) and anharmonic third-order IFCs are calculated with the cutoff radius of 4.2 Å (up to sixth nearest neighbors) using Phonopy package.^[32] It is worthy to mention that the DFT method has been proven to be one of the most accurate methods for the computation of the electronic structure of solids,^[33,34] and its combination with semi-classic Boltzmann transport theory for thermal transport properties is reliable with predicted power.^[35–37]

3. Results and Discussion

3.1. Geometric Structure and Stability

Bulk β -CsCu₅Se₃ crystallizes in the orthogonal space group Pmma (No. 51). As shown in **Figure 1a**, it is isostructural to the known thermoelectric material *o*-CsCu₅S₃.^[8] The β -CsCu₅Se₃ compound is formed by combining the Cu₅Se₃ layers with Cs⁺ ions, and the interactions between the Cu₅Se₃ layer and Cs⁺ ions are weak van der Waals (vdW) interactions. The unit cell of β -CsCu₅Se₃ consists of 2 Cs, 10 Cu, and 6 Se atoms with the lattice constants a = 10.00 Å, b = 4.05 Å and c = 8.98 Å, which are in good agreement with the experimental results (a = 9.99 Å, b = 4.10 Å, and c = 9.01 Å).^[15] The detailed atomic positions for the optimized structure are given in Table S1 (Supporting Information). In addition, β -CsCu₅Se₃ can also be considered as being constructed from the Cu₄Se₄ columnar building block, as shown in Figure 1a. These peculiar structural characteristics may lead to anisotropic electrical transport properties.

To verify the stability of β -CsCu₅Se₃, we first calculate its phonon spectra, and plot the results in Figure 1b. One can see that all vibrational modes are real in the entire Brillouin zone, confirming that β -CsCu₅Se₃ is dynamically stable. We note that the three acoustic branches have relatively low frequencies (<2 THz), implying low group velocities and low lattice thermal conductivity. Besides, there are strong hybridizations between the low frequency optical phonons and acoustic phonons, which would provide more phonon scattering channels, and result in strong phonon scattering.^[38,39] These features indicate that β -CsCu₅Se₃ may have a relatively low lattice thermal conductivity.

Next, we perform AIMD simulations at different temperatures to confirm the thermal stability of β -CsCu₅Se₃. Since the phase transition temperature is 923 K,^[15] we conduct AIMD at different temperatures from 300 to 800 K. The results at 800 K are plotted in Figure S1 (Supporting Information), which shows that the geometric structure does not suffer from any obvious structural distortions or transformations after heated for 10 picoseconds (ps). The total potential energy fluctuates within a constant range. Thus, we conclude that β -CsCu₅Se₃ is thermally stable and can withstand a high temperature of 800 K.

The mechanical stability of β -CsCu₅Se₃ is examined by using Born-Huang criteria.^[40] For 3D materials, the elastic constant tensors form a 6 × 6 matrix with 36 tensor elements. Considering the symmetry in geometry of β -CsCu₅Se₃, the 36 elements are further reduced to nine independent components.^[41] The calculated elastic constants are presented in Table S2 (Supporting Information). From which, one can see that Born–Huang criteria are met, namely, $C_{11} > 0$, $C_{22} > 0$, $C_{33} > 0$, $C_{44} > 0$, $C_{55} > 0$, $C_{66} > 0$, $[C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})] > 0$, $(C_{11} + C_{22} - 2C_{12}) > 0$, $(C_{11} + C_{33} - 2C_{13}) > 0$, $(C_{22} + C_{33} - 2C_{23}) > 0$, $[^{40}$ confirming that β -CsCu₅Se₃ is mechanically stable.

3.2. Electronic Structure

We then calculate the electronic band structure of β -CsCu₅Se₃ at the HSE06 level for accurate results. The results plotted in **Figure 2**a show that β -CsCu₅Se₃ is an indirect-bandgap semiconductor as the valence band maximum (VBM) is located at the *Z* point whereas the conduction band minimum (CBM) is located at the Γ point. The value of bandgap is 1.07 eV, which is consistent with the previously calculated result (1.01 eV).^[15] It



Figure 2. a) Electronic band structure, and b) corresponding partial DOS of β -CsCu₅Se₃. The Fermi level is shifted to 0 eV.

is noteworthy that there are two nearly energetically degenerate VBMs, as the energy difference between the VBM1 and VBM2 is only 0.05 eV, and the top of the valence band is quite flat along the *Z*- Γ direction. As shown in Figure 2b, both the CBM and VBM are dominated by the Cu and Se atoms, and the high degeneracy of VBM and the flat band near the VBM lead to a large slope of density of states (DOS) near the band edges, which would be beneficial for achieving high Seebeck coefficient for holes.^[42]

3.3. Lattice Thermal Conductivity

To study the thermoelectric properties of β -CsCu₅Se₃, we first calculate the lattice thermal conductivity k_{lat} at different temperatures. According to the phonon Boltzmann transport equation (BTE), k_{lat} is the sum of contributions over all the phonon modes $\lambda(q, j)$ with the wave vector q and branch index j, and the microscopic expression of lattice thermal conductivity can be written as

$$k_{\rm lat} = \frac{1}{N} \sum_{\lambda} C_{\rm ph,\lambda} v_{\alpha,\lambda} v_{\beta,\lambda} \tau_{\lambda}$$
(1)

where α and β denote the three directions (*x*, *y*, or *z*), λ is the phonon mode consisting of both wave vector q and branch index *j*, and *N* is the volume of the unit cell. $C_{\text{ph},\lambda}$, $v_{\alpha,\lambda}$, and τ_{λ} refer to the phonon specific heat, phonon velocity, and phonon lifetime. By solving the phonon BTE, the lattice thermal conductivities at room temperature along the x, y, and z directions are calculated to be 0.24, 0.41, and 0.25 W mK⁻¹, respectively, while decrease rapidly with temperature increasing. At 800 K, the corresponding lattice thermal conductivities further reduce to 0.09, 0.15, and 0.09 W mK^{-1} , which are much lower than that of its isostructural materials o-CsCu₅S₃ (0.30 W mK⁻¹ at 800 K),^[8] and lower than that of many other bulk copper-based materials, including Cu_{1.97}S (0.35 W mK⁻¹ at 1000 K), [16] Cu_{2.6}Se (around 0.4– 0.6 W mK⁻¹ at high temperature),^[6] CuSbS₂ (0.46 W mK⁻¹ at 300 K),^[43] and α -CuSCN (0.5 W mK⁻¹ at 800 K).^[44] The variation of lattice thermal conductivity with temperature is plotted in Figure 3a. Because of the ultralow lattice thermal conductivity, β -CsCu₅Se₃ is likely to be an ideal thermoelectric material. Also, we fit the relationships of lattice thermal conductivities with temperatures along the three directions, and present in Figure S2 (Supporting Information). The lattice thermal conductivities are approximately proportional to 1/T, suggesting that anharmonic phonon–phonon interactions are predominant in the phonon scattering, as is the case in SnSe.^[45]

To further explore the origin of the ultralow lattice thermal conductivity, we calculate the contributions of each acoustic branch to the lattice thermal conductivity. At room temperature, the contributions to thermal conductivity from the three acoustic branches (TA, TA', and LA) are 26%, 20%, and 16%, respectively, while the contribution from the optical branches accounts for 38%. These results show that the acoustic phonons are the main heat carriers.

The group velocity and Debye temperature are the key parameters to describe the strength of harmonicity. As shown in Figure 3b, the calculated group velocities of the acoustic and optical branches are very low, and all of them are lower than 4 km s⁻¹, implying a weak harmonicity and low lattice thermal conductivity of this system. The Debye temperatures $\theta_{\rm D}$ of the three acoustic branches along the x, y, and z directions are obtained from the formula, $\theta_{\rm D} = h v_{\rm m} / k_{\rm B}$, here *h*, $v_{\rm m}$, and $k_{\rm B}$ stand for Planck's constant, the highest frequency of each corresponding phonon branch, and Boltzmann constant, respectively. The calculated results are summarized in Table 1. One can see that the highest Debye temperature of the three acoustic modes is 77.26 K, which is comparable to that of many copper-based materials, such as CuSbS₂ (70.1, 81.8, and 87.9 K for TA, TA', and LA, respectively),^[43] CuBiS₂ (63.4, 62.8, and 78.1 K for TA, TA', and LA)^[43] and α -CsCu₅Se₃ (229.83 K),^[46] leading to the low lattice thermal conductivity of β -CsCu₅Se₃. Also, we find that the Debye temperature along the y direction is higher than that along the x and z directions, which is responsible for the higher thermal conductivity in the y direction.

We then consider the lowest order of anharmonic scattering, namely three phonon scattering, which depends on two factors: the strength of each scattering channel and the number of scattering channels for the phonons. The three phonon scattering rates (the reciprocal of the phonon lifetimes $1/\tau$) and the Grüneisen parameter (γ) are related to the intensity of phonon anharmonic scattering during heat conduction, and a higher scattering rate and a larger Grüneisen parameter imply a stronger phonon scattering, leading to a higher anharmonicity and lower lattice thermal conductivity. As shown in Figure 3c, β -CsCu₅Se₃ exhibits a higher three phonon scattering rate, as compared to the thermoelectric material β -CuSCN.^[44] The average value of the Grüneisen parameters of β -CsCu₅Se₃ for



Figure 3. Variations of a) the lattice thermal conductivity (k_{lat}) with temperature, b) the group velocity (V_g), c) three phonon scattering rate ($1/\tau$), d) Grüneisen parameter (γ), e) weighted phase space (WP_3) with frequency, and f) the atomic displacement parameter (ADP) with temperature for β -CsCu_SSe₃.

Table 1. Calculated Debye temperature $\theta_{\rm D}$ (in K) for the three acoustic branches of $\beta\text{-}{\rm CsCu_5Se_3}.$

Direction	ТА	TA′	LA
Г-Х	32.15	36.47	44.63
Г-Ү	48.46	56.63	77.26
Г-Z	23.06	39.35	58.55

all the phonon modes is calculated to be 1.72, which is comparable to that of many excellent thermoelectric materials with low lattice thermal conductivity, such as PbTe (1.45),^[47] SnSe (1.79),^[47] α -CsCu₅Se₃ (1.90),^[46] and AgSbTe₂ (2.05).^[48] The number of phonon scattering channels in the heat transport process is quantified by the three phonon phase space *WP*₃ as displayed in Figure 3e, and a relatively large three-phonon phase space means more scattering channels in the material, leading to large thermal resistance. Compared with β -CuSCN,^[44] we find that the acoustic and optical branches of β -CsCu₅Se₃ are coupled with each other, making it much easier to satisfy the energy and momentum conservation, thus β -CsCu₅Se₃ possesses a larger WP_3 , indicating higher three phonon anharmonic scattering and higher thermal resistance. The large three phonon scattering rates, Grüneisen parameter, and three phonon phase space suggest a strong three phonon anharmonic scattering.

Another parameter for characterizing the anharmonicity is atomic displacement parameter (ADP), which measures the square displacement of atoms near their equilibrium positions, and a large ADP means a weak bonding and large vibration, resulting in strong phonon scattering.^[49–51] For β -CsCu₅Se₃, the ADP values of Cs and Cu atoms are calculated to be 0.025 and 0.021 Å², respectively, at room temperature, which are larger www.advancedsciencenews.com

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Figure 4. a–c) Seebeck coefficient (S), d–f) electrical conductivity (σ), and g–i) power factor (PF) as a function of the chemical potential along the *x*, *y*, and *z* directions, respectively, for β -CsCu₅Se₃.

than that of many materials with low thermal conductivities, including CuSbS₂ (0.015 Å²)^[43] and Cu₃SbS₄ (<0.02 Å²).^[50] Generally, low lattice thermal conductivity can be attributed to: (i) complex crystal structure, (ii) large average atomic mass, (iii) strong anharmonicity, and (iv) weak interatomic bonding.^[52,53] These factors can be used to understand the mechanisms of the ultralow lattice thermal conductivity exhibited in β -CsCu₅Se₃.

3.4. Thermoelectric Properties

The performance of thermoelectric material is evaluated by its figure of merit (*ZT*), $ZT = S^2 \sigma T/k$, where *S*, σ , and *k* represent Seebeck coefficient, electrical conductivity, and thermal conductivity, respectively. Considering the fact that β -CsCu₅Se₃ possesses an ultralow thermal conductivity, we then study its thermoelectric properties. Since the temperature of phase transformation is about 923 K,^[15] we choose 300, 500, and 800 K to conduct the thermoelectric calculations. We first calculate Seebeck coefficient (*S*) as a function of chemical potential (μ), aiming to examine the ability to produce voltage from temperature difference. As shown in **Figure 4**a–c, at 800 K, the Seebeck coefficient of p-type β -CsCu₅Se₃ in the γ direction reaches its maximum of 278 μ V K⁻¹, which is larger than that of β -Cu₂Se (230 μ V K⁻¹)^[6] and α -CsCu₅Se₃ (about 150 μ V K⁻¹)^[46] at the same temperature.

We next calculate the electrical conductivity of β -CsCu₅Se₃. In general, for heavily doped semiconductors, electron relaxation time (τ_e) is usually in the range of 1–10 femtosecond (fs).^[54] We

use the minimum $\tau_e = 1$ fs for a conservative estimation, and the obtained electrical conductivity as a function of chemical potential is plotted in Figure 4d-f. Unlike Seebeck coefficient, the electrical conductivity is less sensitive to temperature. It is notable that the electrical conductivity shows strong anisotropy, which results from its structural characteristics. In β -CsCu₅Se₃, the interactions between alternately stacked Cu₅Se₃ layers and Cs⁺ ions are weak van der Waals (vdW) interactions, therefore the *z* direction is poor in conduction and has a minimal σ .^[55] In addition, we also calculate the carrier mobility by using the deformation potential approximation method,^[56] and summarized the results in Table S3 (Supporting Information) to better understand the electrical transport property of β -CsCu₅Se₃. The high carrier mobility along the y direction corresponds to the high σ along this direction. We note that the absolute values of Seebeck coefficient and the electrical conductivity show opposite trends when the chemical potential changes. Therefore, in order to get an excellent power factor (PF = $S^2\sigma$), an optimum chemical potential is needed. As shown in Figure 4g-i, the power factor peak appears at a doping concentration where neither the Seebeck coefficient nor the electrical conductivity reaches the maximum, indicating that doping is an efficient way to tune the thermoelectric performance of this material. The anisotropy of Seebeck coefficient and electrical conductivity leads to the anisotropy of power factor. The maximum PF values for p-type β -CsCu₅Se₃ at 800 K along the x, y, and z directions are 0.40, 0.79, and 0.20 mW mK⁻², respectively, while those for n-type β -CsCu₅Se₃ are 0.59, 0.59, and 0.47 mW mK⁻², respectively, which are larger



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Figure 5. a–c) Electronic thermal conductivity (k_e), and d–f) figure of merit (*ZT*) as a function of the chemical potential along the *x*, *y*, and *z* directions, respectively, for β -CsCu₅Se₃.

than that of Cu₂S (0.11 mW mK⁻² at 823 K)^[8] but comparable with that of Cu₂Se (about 0.50 mW mK⁻² at 800 K).^[16]

The total thermal conductivity of a material includes the electronic contribution (k_e) and phonon contribution (k_{lat}). The part of electronic contribution (k_e) can be estimated from the Wiedemann–Franz law,^[57] $k_e = L\sigma T$, here, *L* is the Lorenz number, which is usually chosen to be 1.5×10^8 W Ω K⁻² for a non-degenerate semiconductor.^[58,59] The calculated electronic thermal conductivities k_e for β -CsCu₅Se₃ at different chemical potentials and temperatures are plotted in Figure 5a–c. One can see that although the variation of the electronic thermal conductivity k_e with chemical potential μ has a similar trend to that of the electrical conductivity σ (Figure 4d–f), the electronic thermal conductivity k_e increases rapidly with temperature, especially in the γ direction.

Based on above results, we calculate the *ZT* value of β -CsCu₅Se₃ as a function of chemical potential at 300, 500, and 800 K. As shown in Figure 5d–f, the *ZT* value increases with increasing temperature. At 800 K, the maximum *ZT* value of p-type β -CsCu₅Se₃ is 0.42, 1.81, and 0.57 along the *x*, *y*, and *z* directions, respectively, while that of n-type β -CsCu₅Se₃ is 1.71, 0.99, and 1.10. In brief, at 800 K, a satisfactory *ZT* value of 1.81 is achieved at the chemical potential μ = -0.19 eV along the *y* direction, which is larger than that of many reported thermoelectric materials, including *o*-CsCu₅S₃ (0.46 at 800 K),^[8] *t*-CsCu₅S₃ (0.56 at 875 K),^[8] Cu₂Se (1.5 at 1000 K),^[6] Cu₂S (about 0.31 at 800 K),^[16] Cu_{1.98}S (1.4 at 1000 K),^[16] Cu_{1.97}S (1.7 at 1000 K),^[16] α -CsCu₅Se₃ (1.03 at 980 K),^[46] and CsAg₅Te₃ (1.5 at 727 K),^[60] implying that β -CsCu₅Se₃ is promising in thermoelectric applications.

4. Conclusions

On the basis of the recently experimental findings of β -CsCu₅Se₃ for photovoltaic application with a high phase transformation temperature of 923 K, we have performed a comprehensive study on the thermal transport properties of β -CsCu₅Se₃ by using density functional theory (DFT) and semi-classical Boltzmann

transport theory. The intrinsic lattice thermal conductivities at 800 K are calculated to be 0.09, 0.15, and 0.09 W mK⁻¹ along the *x*, *y*, and *z* directions, respectively, which are lower than that of many other copper-based materials. The underlying reasons for the ultralow thermal conductivity are due to the unique geometry with complicated crystal structure, large average atomic mass, weak interatomic bonding, and the strong phonon–phonon scattering, leading to the weak harmonicity and strong phonon anharmonic scattering. These features make β -CsCu₅Se₃ promising for thermoelectric applications with a high *ZT* value of 1.81 at 800 K. Our study suggests that besides the outstanding photovoltaic properties, the newly synthesized β -CsCu₅Se₃ is also a potential material for thermoelectric applications with high performance in a wide working temperature range.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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