ISSN: 2710-0588

Electric Structure and Thermoelectric Performance in Cs_2O Crystal

Jian Liu[1,*]

[1] School of Mathematical Sciences and Statistics, Baise University, Baise, China

[*] Corresponding Author

Abstract

In this work, first principles DFT calculations has been employed with anharmonic phonon scatter theory and Boltzmann transport method to perform a exhaustive study on the thermoelectric properties as electronic and phonon transport of layered Cs_2O crystal. The results indicate that Cs_2O crystal represents a flat-and-dispersive type band structure, which returns a high power factor. In the other hand, low lattice thermal conductivity is discovered in Cs_2O semiconductor, combined with its high power factor, the Cs_2O crystal is considered a promising thermoelectric material. It is demonstrated that p-type Cs_2O could be optimized to exhibit outstanding thermoelectric performance with a maximum *ZT* value of 0.71 at 500K. Explored by density functional theory calculations, the high *ZT* value is due to its high Seebeck coefficient *S*, high electrical conductivity σ, and low lattice thermal conductivity κ_L.

Keywords

Seebeck coefficient, DFT calculations, Boltzmann transport method, *ZT*.

1. Introduction

Thermoelectric (TE) materials offer an opportunity to reduce the energy consumption and enhance the energy utilization efficiency by realizing the direct conversion between heat and electricity. This two-way technology has very promising applications such as solid state refrigerators, space power, solar thermoelectric device, and waste heat recuperation. However, for a wide application, the efficiency of TE material needs to be improved significantly. The efficiency of TE materials is evaluated by the dimensionless figure of merit $ZT = S^2\sigma T / (\kappa_e + \kappa_L)$, where S, σ, T, κ_e, and κ_L are the Seebeck coefficient, the electrical conductivity, the absolute temperature, the electronic thermal conductivity and the lattice thermal conductivity. Therefore, the effective method to improve ZT is to reduce the lattice thermal conductivity, either by exploring novel materials presenting intrinsically disharmony, or by phonon scatter engineering. Likewise, another way to enhance power factor(PF) is searching materials with a desirable band structure with small band effective mass and high valley degeneracy. However, it is challenging that Seebeck coefficient and electrical conductivity are inversely related. Therefore, exploring and discovering new materials with low thermal conductivity and high power factor ($S^2\sigma$) provides an effective way to achieve high TE performance ZT.

Recent theoretical work and experimental work suggest that the dimension reducing of materials could significantly improves the TE performance. Due to the quantum confinement effect, the electronic density of state of low dimensional materials is significantly increased, thus the PF is improved, and the interface/surface can effectively scatter the thermal phonon thus inhibit thermal conductivity. Transition metal *bi*-chalcogenide generally provide complicated atomic structure and therefore more convoluted phonon paths by incorporating X_2^{2-} dimers (X=S and Se) in their crystal structures. For instance, the lattice thermal conductivity of WSe_2 is about 40 $Wm^{-1}K^{-1}$ at 300K, which both W and Se atoms have small atomic masses[1,2].

ISSN: 2710-0588

Here, we use first principles DFT calculations, anharmonic phonon scatter theory and Boltzmann transport method, to predict a comprehensive study on the thermoelectric properties as electronic and phonon transport of layered Cs_2O crystal. The results indicate that p-type Cs_2O present an intrinsic low thermal conductivity and a high ZT value larger than 0.7.

2. Methods

The band structure of Cs_2O was calculated using Quantum Expresso (QE) based on density functional theory (DFT)[3,4]. The Perdew-Burke-Ernzerhof (PBE) with generalized gradient approximation (GGA) was used to describe the exchange-correlation energy[5,6]. Based on the calculated energy band structure, the electronic transport properties (including S, σ / τ, κ_e / τ, where τ is the relaxation time) were determined by employing the semiclassical Boltzmann theory within the relaxation time approximation as implemented in the BoltzTraP code[7]. To figure out the electron and hole relaxation time, the deformation potential theory proposed by Bardeen and Shockley was applied, where the relaxation time can be expressed as[8]:

$$\tau = \frac{2(2\pi)^{1/2}\hbar^4 C_l}{3E_l^2(k_B T)^{3/2} m^{*3/2}} \quad (1)$$

In this formula, the deformation potential constant is expressed as $E_l = \Delta E/(\Delta l/l_0)$, where l_0 is the lattice constant along the transport direction, Δl is the distortion of l_0, ΔE is the energy change of the band (value band maximum for hole and conduct band minimum for electron) with proper strain; m^* is the effective mass, which is obtained near the CBM (electron) and the VBM (hole) by using $m^* = \hbar^2 \left(\frac{\partial^2 E}{\partial k^2}\right)^{-1}$; the elastic modular can be calculated by using $C_l = \frac{2\partial E_{tot}}{V_0(\partial l/l_0)^2}|_{l=l_0}$, where the E_{tot} is the total energy of the system, V_0 is the lattice volume at equilibrium.

The κ_e was calculated employing the Wiedemann-Franz law ($\kappa_e = L\sigma T$) with $L = 2.45 \times 10^{-8} WK^{-2}$. The lattice thermal conductivity κ_L was calculated employing ShengBTE code by solving the Boltzmann transport equation of phonons[9]. The input of ShengBTE are the second order and third order atomic force constants, which were calculated by phonopy code using a $5 \times 5 \times 1$ supercell and a $3 \times 3 \times 1$ k point sampling.

3. Results and Discussion

3.1. The Crystal Structure and Electronic Structure of Cs_2O

The crystal structure of Cs_2O is the point group of P1 with an inversion center, as can be seen in Figure 1. And the lattice parameters calculated by first principle DFT are 4.269 Å, 4.269 Å and 22.087 Å. As shown in Figure 1, the O atom and Cs1 atom have formed a square-planar coordination and alternately layered with Cs2. It is universal among transition-metal compound with such a coordination geometry. The d^{11} electronic configuration of Cs_2O demonstrates that the oxidation state of Cs is 1+. Therefore, the existence of both $[Cs1]^+$ and $[Cs2]^+$ cations results in the oxidation states of the stoichiometry of the complexes as $Cs^+Cs^+O^{2-}$. The electron localization function (ELF) calculated by DFT has explored the formation of the Cs^{1+} and O^{2-} dimers, a covalent nature of bonding has observed where the attractors in the midpoint of two atoms Cs1 and Cs2 layers. The calculated Cs-O bond length of 2.89 Å. There are four factors according to Slack's theory that results to a low lattice thermal conductivity: a intricate compound structure, high atomic masses, weak inter-atomic bond, and anharmonicity. As discussed above, the crystal structure of Cs_2O presents all these key features, a strong phonon blocking from the inter-layer especially.

ISSN: 2710-0588

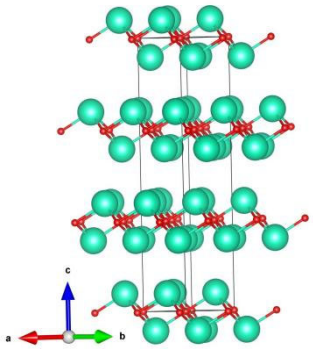

Figure 1. The Crystal Structure of Cs_2O

The band structure is illustrated in Figure 2, The value band maximum (VBM) is located at L point and a second maximum is found at M point with a very tiny energy difference. This multi-valley feature in VBM of Cs_2O indicating a large density of states (DOS) efficient mass which usually leads to a large Seebeck coefficient S. As shown in Figure 3, the DOS of VBM is much larger than those of CBM of Cs_2O, resulting a larger S in p-type Cs_2O as observed in Figure 2. The VBM and the CBM are composed primarily of O atoms as shown in Figure 3, therefore, an effective way to enhance the thermopower of p-type Cs_2O is to adjust the amounts of O atoms. It is seen that the overlap of the Cs dxy orbital and the px and py orbitals of the nearest O anion is negligible, therefore a comparatively flat band is anticipated between the layers.

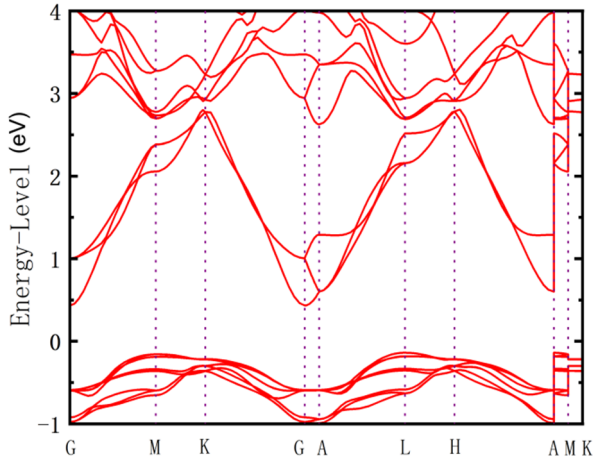

Figure 2. The band Structure of Cs_2O

As seen in Figure 2, the valence band maximum (VBM) along the M-K and L-H is comparatively flat, providing a high density of states (DOS) around the Fermi energy level. On the other side as shown in Figure 3, the overlap between Cs dz2 and dxy orbitals results in a very distributed band along the M-G direction, which means a small band effective mass and therefore high carrier mobility. This flat-and-dispersive type band structure has been found in many high performance thermoelectric materials such as BiCuSeO, PdSe, and some other oxide compounds. Therefore, the flat-and-dispersive type band structure of Cs_2O indicating it has a high thermoelectric performance as well. It is considered to find novel thermoelectric conductor , in which the carriers energy distribution of should be as narrow as possible, and in the direction of applied electric field, carriers velocity as high as possible. Near the Fermi level, An enormously decentralized band with a small effective mass leads to a large electrical conductivity, in the meanwhile, a flat band with large carrier effective masses (where presents a high densities of charges) normally brings about a high Seebeck coefficient. In the case of the

ISSN: 2710-0588

Cs_2O compound, the calculated hole effective masses along the M-K direction is about 2.35 m_0 and for the M-G direction is 0.62 m_0, which indicating a large Seebeck coefficient and electrical conductivity along the Cs_2O layer .

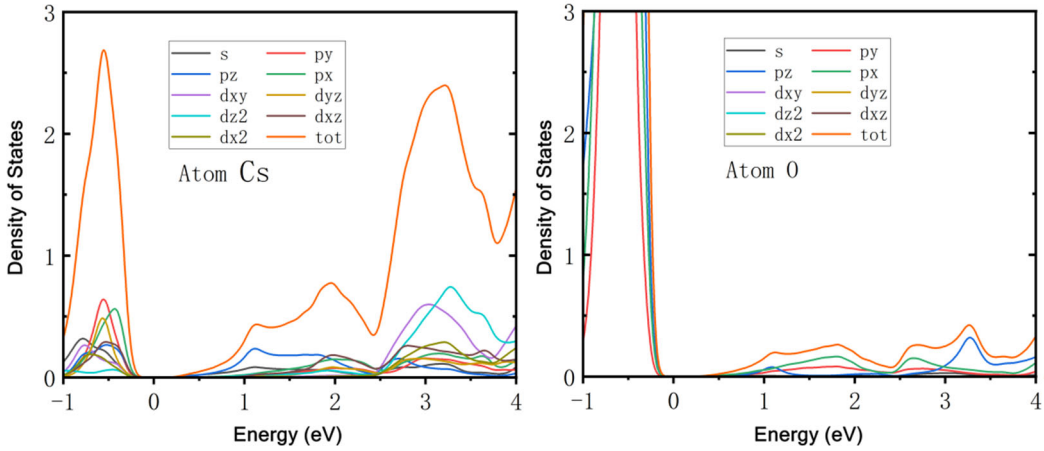

Figure 3. The calculated density of States of atom Cs and O

3.2. The Thermoelectric Properties of Cs_2O

As demonstrated in Figure 4, the highest value of S at 500K is 648.3 $\mu V/K$ for p-type Cs_2O and -512.6 $\mu V/K$ for n-type Cs_2O. The value of S decreases gradually with the increasing carrier concentration. For the carrier concentration of $10^{18}/cm^{-3}$, the value of S is 326.9 $\mu V/K$ and 265.7 $\mu V/K$ at 900K for p-type and n-type Cs_2O respectively. As demonstrated in Figure 4, the value of σ increases gradually with the increasing carrier concentration, and the value of σ for p-type Cs_2O is larger than that of n-type Cs_2O. Therefore, the power factor ($S^2\sigma$) of p-type Cs_2O should be larger than p-typeCs_2O due to its larger S and σ.

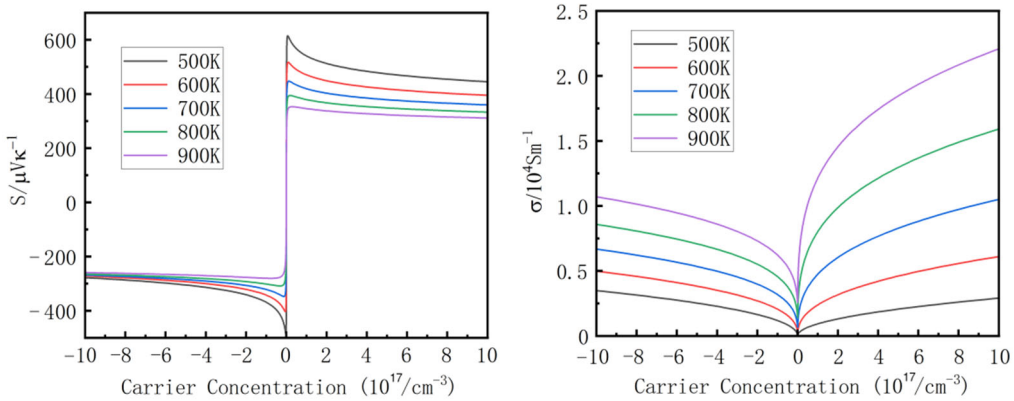

Figure 4. The calculated Seebeck coefficient and electrical conductivityof Cs_2O

As shown in Figure 5, low lattice thermal conductivity κ_L of 5.34 $Wm^{-1}K^{-1}$ at 300K is obtained, and it decreases to 1.68 $Wm^{-1}K^{-1}$ as temperature increases to 900K. In Figure 5, the electronic transport coefficients of p-type and n-type Cs_2O compound at varying temperatures calculated by Boltzmann transport equation is demonstrated. The calculated power factor along the layers for both p-type and n-type Cs_2O, assuming a constant relaxation time, are respectively 21.2 and 6.1 mW/mK^2. Between the Cs_2O layers, the power factor of p-type Cs_2O is large (20.6 mW/mK^2), while the n-type Cs_2O is very small (5.2mW/mK^2). Therefore, a large power factor anisotropy is determined with a noticeable power factor along the layers in the p-type Cs_2O semiconductor.

ISSN: 2710-0588

With the constant electron relaxation time approximation, the maximum power factor for MoS_2, $MoSe_2$ and WSe_2 at 300K are about 1.75 mW/mK^2 0.81 mW/mK^2 and 1.68 mW/mK^2 respectively. The power factors of Cs_2O semiconductor, which are 3.63 mW/mK^2 for p-type and 2.31 mW/mK^2 for n-type, are comparable to these transition metal chalcogenides. Finally, the figure of merit (ZT) is evaluated by $ZT = S^2\sigma T / (\kappa_e + \kappa_L)$, which is demonstrated in Figure 2(d). For the carrier concentration of $10^{18}/cm^{-3}$, it is found that the highest ZT value is 0.71 at 500K, and 0.52 at 600K.

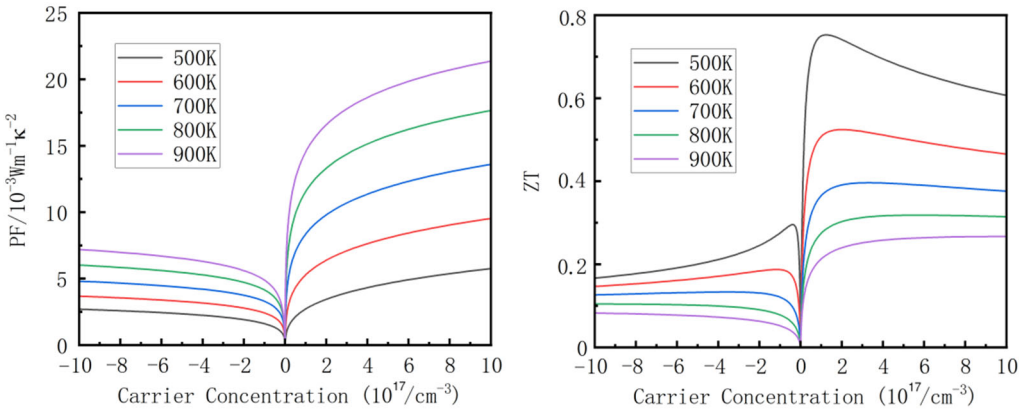

Figure 5. The calculated power factor (PF) and figure of merit (ZT) of Cs_2O

4. Conclusion

To summarise, the electronic structure, electron and phonon transport properties and thermoelectric performance of the recently synthesized Cs_2O semiconductor have been studied through the methods of first-principles DFT calculations and Boltzmann transport theory. The results indicate that the lattice thermal conductivity of Cs_2O semiconductor is much lower than some transition metal chalcogenides, such as MoS_2, $MoSe_2$, WSe_2. The third-order force constants discussed in detail reveals that the phonon scatter in the Cs_2O layers are the reason for the low lattice thermal conductivity. In the meanwhile, the flat-and-dispersive type band structure provides a high power factor. In the case of low lattice thermal conductivity together with high power factor, Cs_2O semiconductor is considered a promising thermoelectric material with a high ZT for both hole and electron doping. First principle calculations reveal that p-type Cs_2O processes high Seebeck coefficient S, high electrical conductivity σ, and low lattice thermal conductivity κ_L, which leads to outstanding thermoelectric performance of p-type Cs_2O with a maximum ZT value of 0.71 at 500K.

References

[1] Chiritescu C , Cahill D G , Nguyen N ,et al.Ultralow thermal conductivity in disordered, layered WSe2 crystals. Science, 2007, 315(5810):351-353.

[2] Sun M B M ,emailprotected, Emailprotected E ,et al.Modulating Thermoelectric Properties of the MoSe2/WSe2 Superlattice Heterostructure by Twist Angles. ACS Applied Materials And Interfaces, 2024, 16(3):3325-3333.

[3] Giannozzi P , Baroni S , Bonini N ,et al.Quantum ESPRESSO: a modular and open-source software project for quantum simulations of materials. J Phys Condens Matter, 2009, 21(39):395502.

[4] Giannozzi P , Baseggio O ,Pietro Bonfà,et al.Q uantum ESPRESSO toward the exascale. The Journal of Chemical Physics, 2020, 152(15):154105.

[5] Perdew J P , Burke K , Ernzerhof M .Generalized Gradient Approximation Made Simple. Physical Review Letters, 1998, 77(18):3865-3868.

ISSN: 2710-0588

[6] Kresse G G ,J.J. Furthmüller.Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. Physical review. B, Condensed matter, 1996, 54:11169.

[7] Madsen G K H , Singh D J .BoltzTraP. A code for calculating band-structure dependent quantities. Computer Physics Communications, 2006, 175(1):67-71.

[8] Bardeen J , Shockley W S .Deformation Potentials and Mobilities in Non-Polar Crystals. Physical Review, 1950, 80(1):72-80.

[9] Li W ,Carrete, Jesús, A. Katcho N ,et al.ShengBTE: A solver of the Boltzmann transport equation for phonons. Computer Physics Communications, 2014, 185(6):1747-1758.