

Electrical characteristics and Thermoelectric Properties of LaZnSbO

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ABSTRACT

Using density functional theory calculations, the thermoelectric properties of LaZnSbO have been systematically investigated. The bulk LaZnSbO features a natural super lattice structure with low electrical conductivity and low thermal conductivity. The band structure reveals that it is a direct gap semiconductor having a band gap of 0.73eV. Doping can enhance its conductivity and thereby raise its ZT value. At a temperature of 900K, close to the carrier concentration $2.5 \times 10^{19}/\text{cm}^3$, the p-type doped system shows a Seebeck coefficient of $313 \mu\text{V}\text{K}^{-1}$, a conductivity of $2.06 \times 10^4 \text{Sm}^{-1}$ and a power factor of $0.78 \times 10^{-3} \text{Wm}^{-1}\text{K}^{-2}$. As a result, a thermoelectric figure of merit (ZT) reaches a maximum value of 1.43.

KEYWORDS

Electronic Structure; Thermoelectric properties; Figure of merit; Seebeck coefficient

1. INTRODUCTION

The thermoelectric energy conversion system has the remarkable capability of transforming waste thermal energy into useful electrical energy. This innovative system operates without the need for moving parts or liquids, which is a significant advantage in terms of both efficiency and environmental impact. Generators and refrigerators that are constructed using thermoelectric materials are not only environmentally friendly but also offer the added benefits of being quiet and stable in operation. Due to these desirable characteristics, thermoelectric materials have garnered extensive attention in recent years from both researchers and industry professionals.

In the realm of thermoelectric materials, researchers have identified that LaFeAsO, a specific compound, possesses a large Seebeck coefficient and power factor [1]. These properties make it particularly promising for potential applications in the field of thermoelectric refrigeration. Subsequent studies by Drago and others have highlighted a limitation of a broader class of materials known as RMChOs, which includes LaFeAsO. These materials are often constrained by their inherently low conductivity, which in turn leads to suboptimal thermoelectric characteristics. However, a breakthrough in this area has been the discovery that the thermoelectric performance of RMChOs can be notably enhanced through the process of doping, which serves to increase the carrier concentration within the material. One notable member of the RMChO family is LaZnSbO, which has been proven in recent years to exhibit outstanding thermoelectric properties. This is primarily attributed to the unique crystal structure of LaZnSbO, which consists of alternating layers of $[\text{La}_2\text{O}_2]^{2+}$ and $[\text{Zn}_2\text{Sb}_2]^{2-}$. Within this structure, the $[\text{La}_2\text{O}_2]^{2+}$ layers act as insulating charge storage areas, while the $[\text{Zn}_2\text{Sb}_2]^{2-}$ layers provide a conductive pathway for the transportation of charge carriers. By carefully controlling the conductive layers and optimizing the inter-layer phonon scattering, it is

possible to achieve high levels of conductivity while effectively reducing thermal conductivity. Another material that shares a similar structure with LaZnSbO and has shown excellent thermoelectric properties is BiCuSeO. In recent years, research has demonstrated that by increasing the conductivity of BiCuSeO while maintaining its inherently low thermal conductivity, the overall thermoelectric performance can be significantly improved. The focus of current research efforts lies in exploring whether the layered structure of these materials can alter the electronic structure of LaZnSbO, thereby enhancing its conductivity. Additionally, researchers are investigating methods to adjust the band structure of these materials to further optimize their thermoelectric performance, with the ultimate goal of developing more efficient and sustainable energy conversion technologies.

2. THEORY AND CALCULATION METHODS

The efficiency of thermoelectric materials is decided by their thermoelectric figure of merit, where S represents the Seebeck coefficient, T stands for temperature, σ denotes conductivity, and κ symbolizes thermal conductivity. The thermal conductivity consists of two parts: electronic thermal conductivity and lattice thermal conductivity. Hence, to get the thermoelectric optimal value of the system, it's essential to acquire the Seebeck coefficient S , electrical conductivity σ , and lattice thermal conductivity. For LaZnSbO, its Seebeck coefficient S and Lorenz number can be expressed by the following equation:

$$L = \left(\frac{k_B}{e} \right)^2 \left(\frac{(r+7/2)F_{r+5/2}(\eta)}{(r+3/2)F_{r+1/2}(\eta)} - \left[\frac{(r+5/2)F_{r+3/2}(\eta)}{(r+3/2)F_{r+1/2}(\eta)} \right]^2 \right) \quad (1)$$

$$S = \pm \frac{k_B}{e} \left(\frac{(r+5/2)F_{r+3/2}(\eta)}{(r+3/2)F_{r+1/2}(\eta)} - \eta \right) \quad (2)$$

In this work, the VASP (Vienna *ab initio* simulation package) is employed for first - principles calculations [5]. The projector augmented plane wave (PAW) approach is utilized to simulate ion - electron interactions. The exchange - correlation can be characterized by the generalized gradient approximation (GGA), which is described by the Perdrew Burke Ernzerhof (PBE) functional. The thermoelectric properties of the material are computed by BoltzTraP [6]. During the calculation of the KS eigenvalue, the K - point sampling density of the bulk material is $19 \times 19 \times 7$.

3. RESULTS AND DISCUSSION

3.1. The Crystal Structure and Electronic Structure of LaZnSbO

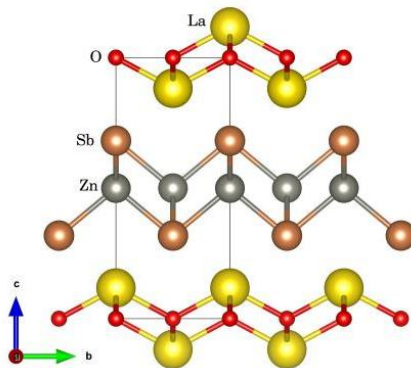


Figure 1. Crystal structure of LaZnSbO

Figure 1 depicts the crystal structure of bulk LaZnSbO, which consists of alternating $[\text{La}_2\text{O}_2]^{2+}$ layers and $[\text{Zn}_2\text{Sb}_2]^{2-}$ layers. In the $[\text{Zn}_2\text{Sb}_2]^{2-}$ layer, a tetrahedral arrangement is formed with Zn atoms at the center and four Sb atoms as vertices, creating a single tetrahedral layer. In the $[\text{La}_2\text{O}_2]^{2+}$ layer, O atoms are in the middle and La atoms are on both sides. With La atoms as the vertex, a square - pyramid structure is formed, where the four O atoms on the middle plane are arranged on both sides of the O - atom plane. This alternating stacking of different layers forms a natural super - lattice, leading to ultra - low thermal conductivity.

Even though it has extremely low thermal conductivity, it has the potential to be a good thermoelectric material. However, the issue is that the conductivity of bulk LaZnSbO is also quite low, which impacts its application in thermoelectric fields. Thus, by enhancing the conductivity of LaZnSbO, its thermoelectric efficiency can be significantly improved. Beginning with the band structure of bulk LaZnSbO, methods can be applied to boost its conductivity. In the band - structure calculation, the GGA + U method has been employed. Due to the presence of transition metal Zn, the band - gap width of LaZnSbO is severely underestimated when calculating its band structure using PBE functional theory (it is 0.24 eV calculated by PBE functional theory in this work). It's evident that the foundation for calculating the thermoelectric properties of the material is its electronic structure, meaning that only by obtaining an accurate electronic structure of LaZnSbO can its reliable thermoelectric properties be calculated. HSE06 hybrid functionals are commonly used to obtain accurate band structures [7]. However, in the calculation of thermoelectric properties, its accuracy depends greatly on the density of sampling points in the inverted space, which demands a very high density, usually hundreds or even thousands of times that of band calculations. Considering that HSE06 itself has a huge computational load, increasing the K - point density by several tens of times would require difficult estimation of computational resources. Therefore, to resolve this contradiction, this work uses the GGA + U method to handle the d orbitals of transition metal Zn [8]. Although the method of adding U is a semi - empirical approach, based on the U values in literature and testing, the author finally got reasonable results. The band - gap width obtained by using GGA + U in this chapter is 0.73 eV. It can be seen that the electronic structure obtained by the GGA + U method is reasonable and reliable.

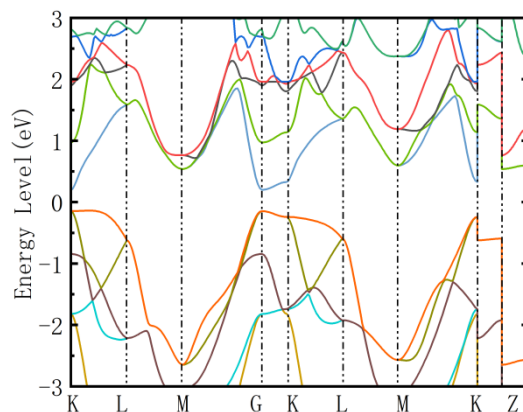


Figure 2. Band structure of bulk LaZnSbO with Fermi level set to 0 eV. The high symmetry points are K (0, 0.5, 0), G(0, 0, 0), M(0.5, 0.5, 0), X(0, 0.5, 0.5), L(0.5, 0.5, 0.5), Z(0, 0, 0.5)

Figure 2 provides a detailed illustration of the band structure associated with the bulk compound LaZnSbO. As can be observed, the electronic configuration of this material is characterized by the presence of an indirect band gap. Specifically, the conduction band minimum (CBM) is located at the point labeled Z. Additionally, it is noteworthy that the Gamma point, which is a high-symmetry point in the Brillouin zone, has an energy level that is nearly identical to that at point Z. Consequently, the Gamma point can also be considered as the position of the CBM within this electronic structure. On the other hand, the valence band maximum (VBM) is found along the path from point Z to point X, specifically at point A. Furthermore, along the path from point G to point M, there exists another

significant point, point B, whose energy level is very close to that of the VBM. It is important to note that the transition of the energy band at point A is relatively smooth, which implies that the effective mass of the holes at this point is comparatively large. In contrast, the band transition at point B is quite abrupt, indicating that the effective mass of the holes at this location is relatively small. Due to these characteristics, the holes at point A are commonly referred to as heavy holes, while those at point B are known as light holes. Ultimately, the effective mass of the carriers at the VBM is influenced by both the heavy holes at point A and the light holes at point B. The calculated effective mass of the hole in this material is approximately 0.53 times the mass of a free electron.

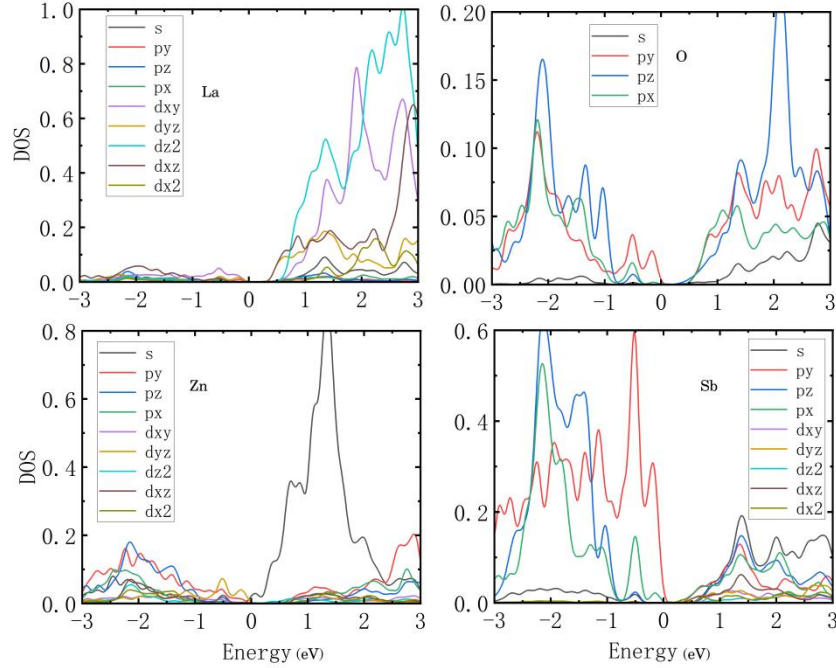


Figure 3. Projection density of states (PDOS) of each atom in bulk LaZnSbO, with the Fermi level set to 0 eV

Figure 3 presents the projected density of states (PDOS) of bulk LaZnSbO, suggesting that the band VBM of it consists of Sb p orbitals and Zn d orbitals, whereas the primary components of CBM are La p orbitals and O p orbitals. The charge distribution maps of CBM and VBM reveal that the charges at VBM are focused on Sb and Zn atoms, while the charges on CBM are focused on La and oxygen atoms. Because of the alternate stacking of a layer of $[\text{La}_2\text{O}_2]^{2+}$ and a layer of $[\text{Zn}_2\text{Sb}_2]^{2-}$ in the structure of LaZnSbO, the charge of CBM is exactly concentrated in the $[\text{La}_2\text{O}_2]^{2+}$ layer, while the charge on VBM is concentrated in the $[\text{Zn}_2\text{Sb}_2]^{2-}$ layer. Electrons in LaZnSbO are excited to move into the conduction band, creating electron - hole pairs and thereby obtaining conductivity. This is equal to electrons transferring from the $[\text{Zn}_2\text{Sb}_2]^{2-}$ layer to the $[\text{La}_2\text{O}_2]^{2+}$ layer, leaving holes in the $[\text{Zn}_2\text{Sb}_2]^{2-}$ layer and surplus electrons in the $[\text{La}_2\text{O}_2]^{2+}$ layer. In this manner, carrier separation can be effectively realized in intrinsic LaZnSbO, where the majority carriers in the $[\text{Zn}_2\text{Sb}_2]^{2-}$ layer are holes and the majority carriers in the $[\text{La}_2\text{O}_2]^{2+}$ layer are electrons, respectively forming $[\text{Zn}_2\text{Sb}_2]^{2-}$ hole - conductive layer and $[\text{La}_2\text{O}_2]^{2+}$ electron - conductive layer.

3.2. The Thermoelectric Properties of LaZnSbO

Due to the indirect bandgap characteristics of the LaZnSbO semiconductor material, along with the complex process of electron inter-layer transfer that occurs during excitation, electron transitions within this material are quite challenging. This inherent difficulty in electron transitions results in the semiconductor exhibiting a low level of electrical conductivity. However, empirical research has demonstrated that by incorporating doping impurities into the LaZnSbO structure and creating impurity energy levels, electron transitions can be significantly facilitated. This enhancement in

electron transitions leads to the acquisition of a substantial number of charge carriers, thereby markedly improving the electrical conductivity of the material. Building upon the band structure of LaZnSbO, its thermoelectric properties can be determined by rigorously solving the Boltzmann transport equation. This mathematical approach allows for a detailed analysis of how charge carriers behave and contribute to the material's thermoelectric performance.

Figure 4 illustrates the intricate relationship curves that exist between the Seebeck coefficient, electrical conductivity, power factor, thermoelectric figure of merit (ZT), and carrier concentration for LaZnSbO semiconductor samples, across a temperature range of 400K to 900K. These curves are delineated separately for both electron (n-type) and hole (p-type) carrier types. Upon examining Figure 4, it becomes evident that the Seebeck coefficient for the n-type doped system exhibits negative values, whereas the p-type doped system yields positive values. As the concentration of carriers increases, there is a general trend of the Seebeck coefficient gradually decreasing. Typically, the Seebeck coefficient achieved through p-type doping is higher than that obtained from n-type doping. Interestingly, at elevated temperatures, the difference in the Seebeck coefficient between the two doping types tends to diminish, becoming less pronounced. This comprehensive analysis not only highlights the impact of doping on the electrical and thermoelectric properties of LaZnSbO but also provides valuable insights into how these properties can be optimized for potential applications in thermoelectric devices.

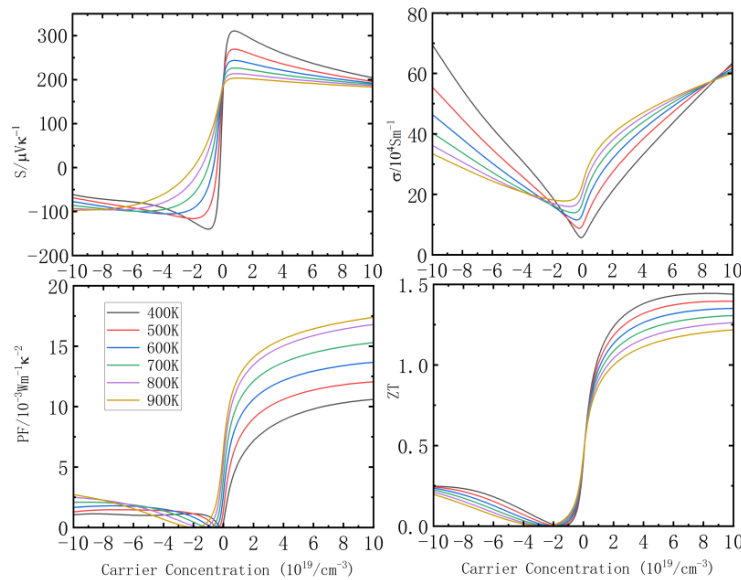


Figure 4. Shows the relationship curve between the Seebeck coefficient, conductivity, power factor, thermoelectric figure of merit, and carrier concentration of bulk LaZnSbO

Regarding conductivity, it's clear that as the carrier concentration goes up, the conductivity of both n - type and p - type doped systems also increases. At the same temperature, it can be noted that the conductivity of n - type doped systems is far higher than that of p - type doped systems, which is associated with the band structure of LaZnSbO. Due to the existence of heavy holes, the effective mass of holes is larger than that of electrons, causing a huge disparity in conductivity; Likewise, the higher the temperature, the greater the conductivity. For the power factor, it can be seen that because of the high conductivity of the n - type doping system, it reaches its peak value at lower carrier concentrations. As the carrier concentration keeps increasing, the S value drops, and the power factor is related to the square of S . So, even though the conductivity increases, the power factor still decreases. Finally, the thermoelectric figure of merit ZT can be acquired. As the doping concentration and impurity concentration increase, phonon scattering becomes more intense, leading to a decrease in lattice thermal conductivity; Meanwhile, due to the increase in conductivity, the electronic thermal conductivity rises rapidly. Therefore, when the carrier concentration is high, the electronic thermal conductivity in the n - type doped system is much higher than that in the p - type doped system.

Consequently, at high doping concentrations, the thermal conductivity in the n - type doped system is higher than that in the p - type doped system, resulting in a decrease in the ZT value. Thus, as the carrier concentration increases, the n - type system reaches the maximum ZT value earlier than the p - type doped system. From the figure, it can be seen that at a temperature of 900K, near the carrier concentration $2.5 \times 10^{19}/\text{cm}^3$, the p - type doped system reaches a maximum ZT value of approximately 1.43, which is in line with the experimental results.

4. CONCLUSION

The thermoelectric characteristics of the bulk LaZnSbO material have been thoroughly investigated through the application of density functional theory-based computational methods. This bulk compound exhibits a unique natural superlattice structure, which is characterized by its notably low thermal conductivity and reduced electrical conductivity. Detailed analysis of its band structure reveals that bulk LaZnSbO can be conceptualized as a layered arrangement where electron-conducting $[\text{La}_2\text{O}_2]^{2+}$ layers and hole-conducting $[\text{Zn}_2\text{Sb}_2]^{2-}$ layers alternate with each other. The conduction mechanism within this material involves the transfer of electrons from the $[\text{Zn}_2\text{Sb}_2]^{2-}$ layers to the $[\text{La}_2\text{O}_2]^{2+}$ layers, a process that is essential for the establishment of electrical conductivity. To enhance the overall conductivity of bulk LaZnSbO and thereby improve its thermoelectric performance, as measured by the figure of merit ZT, doping techniques can be employed. Doping introduces impurities into the material's lattice, which can facilitate the movement of charge carriers and thus increase the electrical conductivity. At an elevated temperature of 900K, which is a typical operating condition for many thermoelectric applications, the p-type doped system demonstrates particularly promising results. Specifically, when the carrier concentration is adjusted to approximately $2.5 \times 10^{19}/\text{cm}^3$, the doped system achieves a peak ZT value of approximately 1.43. This significant enhancement in ZT highlights the potential of bulk LaZnSbO as a viable candidate for efficient thermoelectric energy conversion technologies.

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