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Study on the Thermoelectric Properties of NdZnSbO

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ABSTRACT

The thermoelectric properties of NdZnSbO have been systematically studied using density functional theory calculations. The bulk NdZnSbO is a natural super lattice structure with low thermal conductivity and low electrical conductivity. The band structure indicates that it is a direct gap semiconductor with a band gap of 0.68eV. Its conductivity can be improved by doping and thus increase its ZT value. At a temperature of 800K, near the carrier concentration 2.1E19/cm3, the p-type doped system presents a Seeback coefficient of 382μVκ^{-1}, a conductivity of 1.48×10^{4}Sm^{-1} and a power factor of 0.66×10^{-3}Wm^{-1}κ^{-2}. As a result, a thermoelectric figure of merit (ZT) reaches a maximum value of 1.12.

KEYWORDS

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

1. INTRODUCTION

The thermoelectric energy conversion system can convert waste thermal energy into electrical energy because it does not require moving parts and liquids. Generators and refrigerators made of thermoelectric materials are not only environmentally friendly but also quiet and stable. Therefore, thermoelectric materials have received widespread attention in recent years.

Some members of RMChO (R=Bi, Ce Dy; M=Cu, Ag; Ch=S, Se, Te) were gradually discovered in the 1990s [1]. Researchers found that LaFeAsO have a large Seebeck coefficient and power factor, which is expected to be used in the field of thermoelectric refrigeration. Afterwards, Dragoe found that RMChOs are limited by their low conductivity, resulting in poor thermoelectric properties, but their thermoelectric performance can be significantly improved by doping to increase carrier concentration. As a member of RMChO, NdZnSbO has been shown to have excellent thermoelectric properties in recent years [2]. This is due to the unique crystal structure of NdZnSbO, which is composed of alternating stacking of $[Nd_2O_2]^{2+}$ layers and $[Zn_2Sb_2]^{2-}$ layers (as shown in Figure1). Among them, $[Nd_2O_2]^{2+}$ serves as an insulating charge storage region, while $[Zn_2Sb_2]^{2-}$ provides a conductive channel for carrier transport. In this way, high conductivity can be achieved by controlling the conductive layer, while inter-layer phonon scattering can effectively reduce thermal conductivity. BiCuSeO, which presents the same structure with NdZnSbO, has been shown to have excellent thermoelectric properties in recent years [3, 4]. By increasing the conductivity of BiCuSeO while maintaining its low thermal conductivity, its thermoelectric performance can be greatly improved. The research focus on whether such layered sheets can change the electronic structure of NdZnSbO, improve its conductivity, and whether there are methods to adjust its band structure and thermoelectric performance.

2. THEORY AND CALCULATION METHODS

The efficiency of thermoelectric materials is determined by their thermoelectric figure of merit, where S is the Seebeck coefficient, T is temperature, σ is conductivity, and κ is thermal conductivity. The thermal conductivity is composed of two contributions: electronic thermal conductivity and lattice thermal conductivity. Therefore, to obtain the thermoelectric optimal value of the system, it is necessary to obtain the Seebeck coefficient S, electrical conductivity σ, and lattice thermal conductivity. For NdZnSbO, its Seebeck coefficient S and Lorenz number can be given by the following equation:

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

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

The VASP (Vienna *ab initio* simulation pakage) package is used for first principles calculations in this work [5]. The projector augmented plane wave (PAW) method is used to simulate ion electron interactions; Exchange correlation can be described using generalized gradient approximation (GGA), described by Perdrew Burke Ernzerhof (PBE) functional. The thermoelectric properties of the material are calculated by BoltzTraP [6]. When calculating the KS eigenvalue, the K-point sampling density of the bulk material is 19×19×7.

3. RESULTS AND DISCUSSION

3.1. The Crystal Structure and Electronic Structure of NdZnSbO

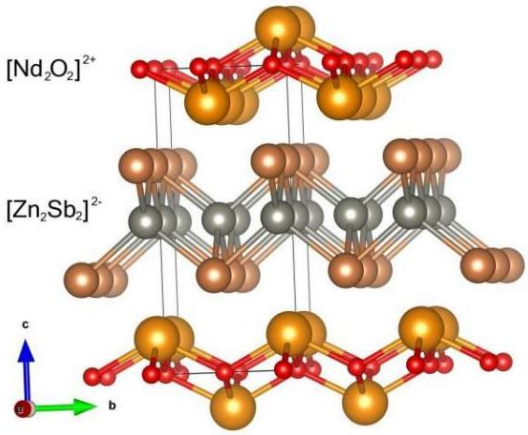

Figure 1. Crystal structure of NdZnSbO

The crystal structure of bulk NdZnSbO is shown in Figure 1, which is composed of alternating layers of $[Nd_2O_2]^{2+}$ layers and $[Zn_2Sb_2]^{2-}$ layers. In the $[Zn_2Sb_2]^{2-}$ layer, a tetrahedral arrangement is formed with Zn atoms as the center and four Sb atoms as vertices, forming a single tetrahedral layer; In the $[Nd_2O_2]^{2+}$ layer, O atoms are in the middle and Nd atoms are on both sides, with Nd atoms as the vertex, forming a square pyramid structure with the four O atoms on the middle plane arranged on both sides of the O atom plane. This alternating stacking of different layers forms a natural super-lattice, resulting in ultra-low thermal conductivity.

Although it has a very low thermal conductivity, it has the potential to become a good thermoelectric material. However, the problem is that the conductivity of bulk NdZnSbO is also very low, which

affects its application in thermoelectric fields. Therefore, by improving the conductivity of NdZnSbO, its thermoelectric efficiency can be greatly enhanced. Starting from the band structure of bulk NdZnSbO, the methods could be applied to improve its conductivity. In the calculation of band structure, the GGA+U method has been adopted. Due to the presence of transition metal Zn, the bandgap width of NdZnSbO is greatly underestimated when calculating its band structure using PBE functional theory (it is 0.23 eV calculated using PBE functional theory in this work, while the experimental value was 0.78 eV). It can be seen that the basis for calculating the thermoelectric properties of the material is its electronic structure, which means that only by obtaining an accurate electronic structure of NdZnSbO, its reliable thermoelectric properties can be calculated. HSE06 hybrid functionals were commonly used to obtain accurate band structures [7]. However, in the calculation of thermoelectric properties, its accuracy relies heavily on the density of sampling points in the inverted space, which requires a very high density, usually hundreds or even thousands of times that of band calculations. Given that HSE06 itself has a very large computational load, increasing the K-point density by several tens of times would require difficult estimation of computational resources. Therefore, in order to resolve the contradiction here, this work adopts the GGA+U method to deal with 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 ultimately obtained reasonable results. The bandgap width obtained by using GGA+U in this chapter is 0.68eV, while other calculated values for bulk NdZnSbO are about 0.70eV. It can be seen that the electronic structure obtained by the GGA+U method is reasonable and reliable.

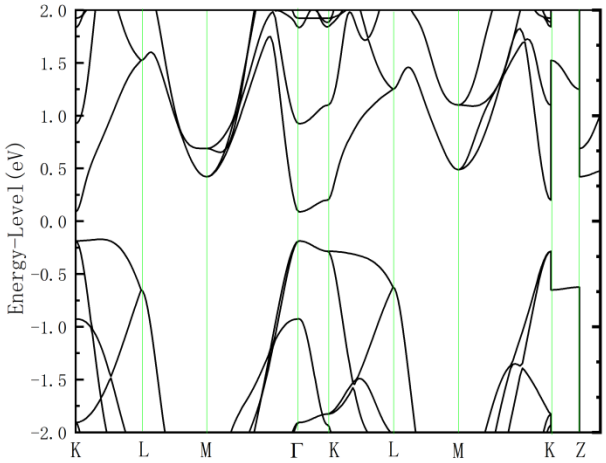

Figure 2. Band structure of bulk NdZnSbO with Fermi level set to 0 eV. The high symmetry points are K (0, 0.5, 0), G (0, 0, 0), M (0.5, 0.5, 0), X (0, 0.5, 0.5), L (0.5, 0.5, 0.5), Z (0, 0, 0.5)

The band structure of bulk NdZnSbO is shown in Figure 2. It can be seen that its electronic structure is an indirect band gap, where CBM is located at point Z, and Gamma point is almost equal to point Z, which can also be considered as the position of its CBM; On the other hand, its VBM is located at point A on the path from point Z to point X, while on the path from point G to point M, there is also point B that is very close to the value of VBM. Obviously, the band change at point A is relatively gentle, and the corresponding hole effective mass is relatively large, while the band change at point B is drastic, and the hole mass at this location is relatively small. Therefore, the holes at point A are called heavy holes, and the holes at point B are called light holes. Ultimately, the carrier effective mass at VBM is determined by both the heavy holes at point A and the light holes at point B. The effective mass of the hole obtained is approximately $0.6m_0$.

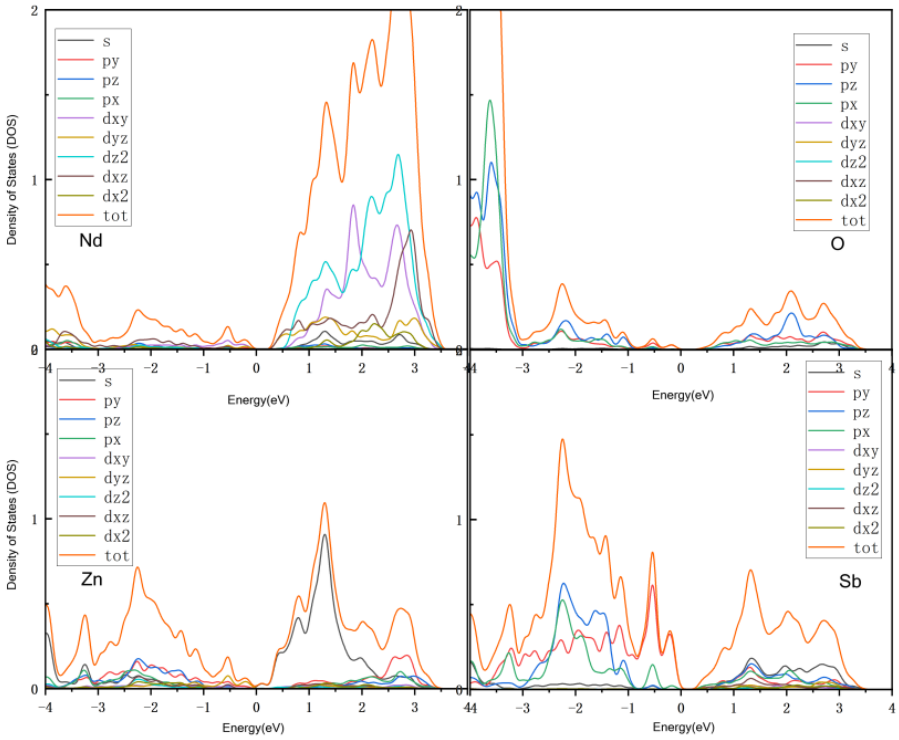

Figure 3. Projection density of states (PDOS) of each atom in bulk NdZnSbO, with the Fermi level set to 0 eV

Figure 3 shows the projected density of states (PDOS) of bulk NdZnSbO, indicating that its band VBM is composed of Sb p orbitals and Zn d orbitals, while the main components of CBM are Nd p orbitals and O p orbitals. The charge distribution maps on CBM and VBM show that the charges at VBM are concentrated on Sb and Zn atoms, while the charges on CBM are concentrated on Nd and oxygen atoms. Due to the alternating stacking of a layer of $[Nd_2O_2]^{2+}$ and a layer of $[Zn_2Sb_2]^{2-}$ in the structure of NdZnSbO, the charge of CBM is precisely concentrated in the $[Nd_2O_2]^{2+}$ layer, while the charge on VBM is concentrated in the $[Zn_2Sb_2]^{2-}$ layer. Electrons in NdZnSbO are excited to transition into the conduction band, forming electron hole pairs and thus gaining conductivity. This is equivalent to electrons transferring from the $[Zn_2Sb_2]^{2-}$ layer to the $[Nd_2O_2]^{2+}$ layer, leaving holes in the $[Zn_2Sb_2]^{2-}$ layer and excess electrons in the $[Nd_2O_2]^{2+}$ layer. In this way, carrier separation can be effectively achieved in intrinsic NdZnSbO, where the multi carriers in the $[Zn_2Sb_2]^{2-}$ layer are holes and the multi carriers in the $[Nd_2O_2]^{2+}$ layer are electrons, forming $[Zn_2Sb_2]^{2-}$ hole conductive layer and $[Nd_2O_2]^{2+}$ electron conductive layer, respectively.

3.2. The Thermoelectric Properties of NdZnSbO

Due to the indirect bandgap of NdZnSbO semiconductor and the interlayer transfer of electrons during excitation, electron transitions are relatively difficult, resulting in its low conductivity. Experimental results have shown that doping impurities into NdZnSbO and introducing impurity energy levels can effectively enhance electron transitions and obtain a large number of charge carriers, thereby improving its conductivity. Based on the band structure of NdZnSbO, its thermoelectric properties are obtained by solving the Boltzmann transport equation.

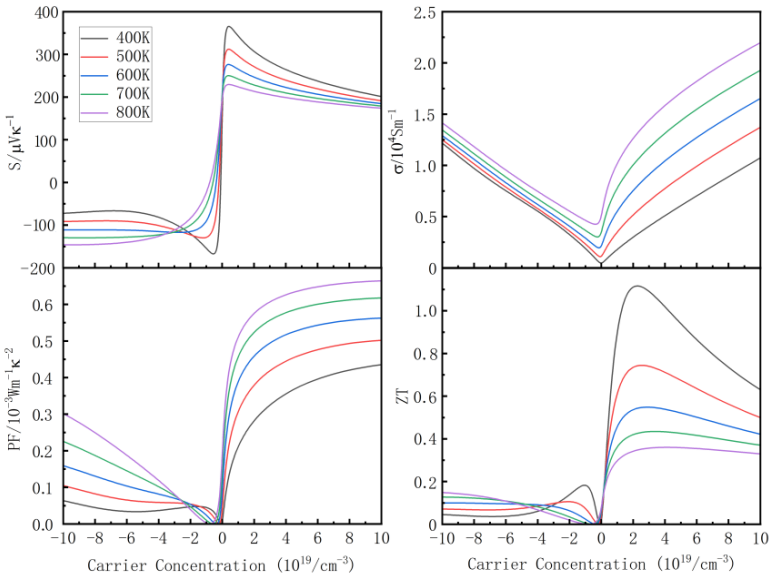

Figure 4. shows the relationship curve between the Seeback coefficient, conductivity, power factor, thermoelectric figure of merit, and carrier concentration of bulk NdZnSbO.

Figure 4 shows the relationship curves between the Seeback coefficient, conductivity, power factor, thermoelectric figure of merit (ZT), and carrier concentration of NdZnSbO at temperatures from 400K to 800K, respectively, with electron (n) and hole (p) carrier types. From Figure 4, it can be seen that the Seeback coefficient of the n-type doped system is negative, while the Seeback coefficient of the p-type doped system is positive. As the carrier concentration increases, the S value gradually decreases. Overall, the Seeback coefficient obtained by p-type doping is higher than that of n-type doping, and the Seeback coefficient is not significantly different at high temperatures. For conductivity, it is evident that as the carrier concentration increases, the conductivity of both n-type and p-type doped systems also increases. At the same temperature, it can be seen that the conductivity of n-type doped systems is much higher than that of p-type doped systems, which is related to the band structure of NdZnSbO. Due to the presence of heavy holes, the effective mass of holes is greater than that of electrons, resulting in a huge difference in conductivity; Similarly, the higher the temperature, the greater the conductivity. For the power factor, it can be seen that due to the high conductivity of the n-type doping system, it reaches its maximum value at lower carrier concentrations. As the carrier concentration continues to increase, the S value decreases, and the power factor is square related to S. Therefore, although the conductivity increases, the power factor still decreases. Finally, the thermoelectric figure of merit ZT can be obtained. As the doping concentration and impurity concentration increase, phonon scattering intensifies, resulting in a decrease in lattice thermal conductivity; Meanwhile, due to the increase in conductivity, the electronic thermal conductivity rapidly increases. 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. As a result, at high doping concentrations, the thermal conductivity in the n-type doped system is higher than that in the p-type doped system, leading to a decrease in ZT value. Therefore, as the carrier concentration increases, the n-type system reaches the maximum ZT value before the p-type doped system. From the figure, it can be seen that at a temperature of 800K, near the carrier concentration 2.1E19/cm^3, the p-type doped system reaches a maximum ZT value of about 1.12, which is consistent with the experimental results.

4. CONCLUSION

The thermoelectric properties of bulk NdZnSbO have been systematically studied using density functional theory calculations. The bulk NdZnSbO is a natural superlattice structure with low thermal

conductivity and low electrical conductivity. The band structure indicates that it can be seen as an alternating stack of $[Nd_2O_2]^{2+}$ electron conductive layers and $[Zn_2Sb_2]^{2-}$ hole conductive layers. Its electrons need to be transferred from the $[Zn_2Sb_2]^{2-}$ layer to the $[Nd_2O_2]^{2+}$ layer to form conductivity, which can be improved by doping to enhance its conductivity and thus increase its ZT value. at a temperature of 800K, near the carrier concentration 2.1E19/cm^3, the p-type doped system reaches a maximum ZT value of about 1.12.

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