First-Principles Study on the Thermoelectric Properties of FeAsS

Lin Zhu, Xia Jiang, Guoying Gao, Huahua Fu, and Kailun Yao

School of Physics and Wuhan National High Magnetic Field Center, Huazhong University of Science and Technology, Wuhan 430074, China

ABSTRACT: The electronic structure and thermoelectric properties of FeAsS are studied by the first-principles and the Boltzmann transport theory. The results show that FeAsS is a semiconductor with an indirect band gap of 0.73 eV. The dimensionless figure of merit (ZT) has obvious anisotropy, ZT value along the x- and y-directions is significantly larger than that along the z-direction, and p-type doping has better thermoelectric performance than n-type doping. The largest ZT value can reach 0.84, which is for p-type doping along the x-direction. The lattice thermal conductivity is extremely low, which is smaller than 1 W m\(^{-1}\) K\(^{-1}\). The results show that FeAsS is a promising candidate for thermoelectric applications.

1. INTRODUCTION

The environmental pollution and energy crisis are becoming more and more serious; therefore, it is of great significance to study novel thermoelectric materials.\(^1,2\) The dimensionless figure of merit \(ZT = S^2\sigma T/k\) is an important metrics for the conversion efficiency of thermoelectric materials;\(^3\) here, the \(S\), \(\sigma\), and \(T\) represent Seebeck coefficient, electrical conductivity, and the absolute work temperature, respectively. In addition, \(k\) is the sum of electrical thermal conductivity \(\left(k_e\right)\) and lattice (or phonon) thermal conductivity \(\left(k_l\right)\). The electrical conductivity \(\sigma\) and electrical thermal conductivity \(k_e\) are associated by the Wiedemann–Franz law: \(k_e = L\sigma T\), where \(L\) is the Lorentz number, its most typical value is \(2.45 \times 10^{-8}\) W \(\Omega\) K\(^2\) for metals and degenerate semiconductors.\(^4,5\) It is clear that a good thermoelectric material needs to have a large Seebeck coefficient \(S\) and electrical conductivity \(\sigma\) and also should have low thermal conductivity \(k = k_e + k_l\) at the same time. Theoretical and experimental results show that ZT can be improved by using band engineering and structure designs to increase \(S\sigma\) (often known as power factor and abbreviated as PF) and/or decrease \(k\).\(^6–8\)

FeAsS is a mineral sulfide with arsenic containing mineral on Earth. Previous studies show that FeAsS is a diamagnetic semiconductor with indirect band gap.\(^9–13\) It is crystallized in the monoclinic structure of space group p21/c with four formula units \((Z = 4)\) per unit, as shows in Figure 1a,b, and the lattice parameters are \(a = 5.74\) Å, \(b = 5.67\) Å, \(c = 5.76\) Å, which is consistent with previous result.\(^11\) The atomic positions of FeAsS are shown in Table 1.

2. RESULTS AND DISCUSSION

FeAsS is in the monoclinic structure of space group p21/c with four formula units \((Z = 4)\) per unit, as shows in Figure 1a,b, and the lattice parameters are \(a = 5.74\) Å, \(b = 5.67\) Å, \(c = 5.76\) Å, which is consistent with previous result.\(^11\) The atomic positions of FeAsS are shown in Table 1.

Figure 1c,d that FeAsS is a semiconductor with an indirect band gap of 0.73 eV and it is a little less than the value of 0.75 or 0.78 eV of previous studies.\(^9,10\) This moderate band gap means the thermoelectric performance can be optimized within a reasonable doping level. We note that the density of states (DOS) in the entire energy range mostly originate from the d orbital of the Fe atom, what is more, the valence bands exhibit much higher DOS than the conduction bands which is smaller than 1 W m\(^{-1}\) K\(^{-1}\). The results show that FeAsS is a promising candidate for thermoelectric applications.
implies that the p-type-doped thermoelectric performance is superior to that of n-type doped.

Figure 2a–c shows the electrical conductivity of p-type and n-type FeAsS along the x-, y- and z-directions as the function of carrier concentration at different temperatures of 300, 600, and 900 K. We noticed that the electrical conductivity increases with carrier concentration and temperature for both p-type and n-type of FeAsS. The electrical conductivity along the x- and y-directions is on the order of $10^6$; the electrical conductivity along the z-direction is an order of magnitude less than that along the x- and y-directions. We observe that the electrical conductivity of p-type FeAsS along the x- and y-directions is always greater than that of n-type FeAsS. For the z-direction at 600 and 900 K, the situation is opposite to that of the x- and y-directions. In the z-direction at 900 K, p-type is

Table 1. Atomic Positions of FeAsS

| atom  | x    | y    | z    |
|-------|------|------|------|
| S1    | 0.152028 | 0.367451 | 0.32275 |
| S2    | 0.847972 | 0.632549 | 0.67725 |
| S3    | 0.847972 | 0.867451 | 0.17725 |
| S4    | 0.152028 | 0.132549 | 0.82275 |
| Fe1   | 0.212072 | 0.00888 | 0.203029 |
| Fe2   | 0.787928 | 0.99112 | 0.796971 |
| Fe3   | 0.787928 | 0.50888 | 0.296971 |
| Fe4   | 0.212072 | 0.49112 | 0.703029 |
| As1   | 0.35375 | 0.632099 | 0.128119 |
| As2   | 0.64625 | 0.367901 | 0.871881 |
| As3   | 0.64625 | 0.132099 | 0.371881 |
| As4   | 0.35375 | 0.867901 | 0.628119 |

Figure 2. (a–c) Electrical conductivity of p-type and n-type FeAsS along the x-, y- and z-directions as the function of the carrier concentration at the temperatures of 300, 600, and 900 K. (d–f) Electrical thermal conductivity of p-type and n-type FeAsS along the x-, y-, and z-directions as the function of the carrier concentration at the temperatures of 300, 600, and 900 K.
higher when the carrier concentration is less than $3.5 \times 10^{21}$ cm$^{-3}$ and as the carrier concentration continues to increase, n-type will be greater.

The electrical conductivity is proportional to carrier concentration and inversely proportional to $(m^*)^{5/2}$; $m^*$ ($m^* = \hbar^2/(\partial^2 E/\partial k^2)$) is effective mass of carriers which is related to the flatness of the band.$^{15}$ Therefore, we can qualitatively analyze the electrical conductivity from the change trend of energy band. $^{16}$ The valence band is closer to Fermi level than the conduction band as displayed in Figure 1c,d. According to the Fermi–Drake distribution function, the closer to the Fermi level, the greater the carrier concentration. Therefore, the carrier concentration of the valence band is greater than the conduction band. The slope change of the valence band is more prominent than the conduction band along the high symmetric path of $Z-\Gamma$ and $\Gamma-Y$, but the slope change of the conduction band is more conspicuous along $Y-A$ (Figure 1c).

The effective mass of valence band is greater than that of conduction band of the $x$- and $y$-directions, but the situation is opposite for the $c$-direction. The analysis results are consistent with our calculations, which manifests that FeAsS has appropriate electrical conductivity.$^8$

Figure 2d–f displays the electrical thermal conductivity of p-type and n-type FeAsS along the $x$, $y$, and $z$-directions at the temperatures of 300, 600, and 900 K. The electrical conductivity ($\sigma$) and electrical thermal conductivity ($k_e$) are associated by the Wiedemann–Franz law: $k_e = L\sigma T$, where $L$ is the Lorentz number, its most typical value is $2.45 \times 10^{-8}$ W Ω K$^{-1}$ for metals and degenerate semiconductors$^{4,5}$ therefore, the change of electrical thermal conductivity is only slightly different from that of electrical conductivity.

From Figure 3, we can obtain that a phase transfer occurs by changing carrier concentration. Generally, the value of Seebeck coefficient should be larger than 200 $\mu$V K$^{-1}$ for promising thermoelectric materials.$^{17}$ Instructively, in our study, the average value of Seebeck coefficient for FeAsS in the whole temperature and carrier concentration range is almost larger than 200 $\mu$V K$^{-1}$, which indicates that there may be high values of PF and $ZT$ as we expect.

Take one-dimensional double atomic chain as the example,$^{18-20}$ the relationship between frequency and wave-number is given as follows

$$\omega^2 \langle \alpha_x^2 \rangle = \beta \frac{m + M}{mM} \left\{ 1 + \left( 1 - \frac{4mM}{(m + M)^2 \sin^2 \alpha q} \right)^{1/2} \right\}$$

(1)
From the above expression, we can obtain that the frequency gap between the acoustic phonon module and the optical phonon module is mainly determined by the atomic mass difference of the material components. In addition, the frequency range of phonon spectrum is related to the interaction between the atoms and the atomic mass difference in the material components. The one-dimensional double atomic chain analysis is also instructive for qualitative analysis of other three-dimensional multiaatomic chains.

After careful analysis of the calculated phonon dispersion shown in Figure 4a,b, we find the coupling existing in FeAsS between optical phonon modes and acoustic phonon modes. It implies that there is little difference in the mass of the constituent atoms and that the interactions between the atoms are relatively small. The weak interaction between atoms is not conducive to the transmission of phonons. However, the frequency range of phonon modules is relatively large, but the frequency range of acoustic branches is 0–5 THz which is relatively small and the slope of the phonon spectrum is larger along Z–G–Y. It’s worth noting that phonons have less state density in the frequencies of acoustic branches. Thus, we can conclude that FeAsS should have a small lattice thermal conductivity.

The intrinsic lattice thermal conductivity of FeAsS is calculated by using ShengBTE code. As shown in Figure 4c,d, the lattice thermal conductivity is anisotropic and the lattice thermal conductivity is largest along the z-direction, followed by the x-direction, and the smallest lattice thermal conductivity is along the y-direction. What is more in all directions, the lattice thermal conductivity is smaller than 1 W m$^{-1}$ K$^{-1}$, which is extremely low. (4) The thermoelectric figure of merit ZT has obvious anisotropy, and p-type doping has better thermoelectric performance than n-type doping. ZT for p-type doping along the x-, y-, and z-directions can reach 0.84, 0.82, and 0.63, respectively, ZT for n-type doping along the x-, y-, and z-directions can also reach 0.62, 0.71, and 0.59, respectively. These results show that FeAsS has potential application in thermoelectric material.

Figure 5 reveals that ZT for p-type is superior to that for n-type, which is consistent with previous analysis of energy band and DOS, where there is much higher DOS of the valence bands than that of the conduction bands around the Fermi level. In addition, we notice that there is only a slight difference between the ZT values along the x- and y-direction, the optimal ZT along the x- and y-directions for p-type are 0.84 and 0.82 and for n-type are 0.62 and 0.71, respectively. The optimal ZT along the z-direction for p-type and n-type are 0.63 and 0.59. ZT value along the x- and y-directions is significantly larger than that along the z-direction. The results show that FeAsS is a good thermoelectric material.

3. CONCLUSIONS

To summarize, we have adopted first-principles and Boltzmann transport theory to synthetically study the electronic structure and thermoelectric properties of FeAsS. The results show that FeAsS is a semiconductor with an indirect band gap of 0.73 eV. We also can draw conclusions from the results: (1) FeAsS has an appropriate electrical conductivity which is smaller than 5 × 10$^{-5}$ Ω$^{-1}$ m$^{-1}$. (2) The average value of Seebeck coefficient in the whole temperature and carrier concentration range is almost greater than 200 μV K$^{-1}$. (3) Lattice thermal conductivity is anisotropic. What is more, in all directions, the lattice thermal conductivity is smaller than 1 W m$^{-1}$ K$^{-1}$, which is extremely low. (4) The thermoelectric figure of merit ZT has obvious anisotropy, and p-type doping has better thermoelectric performance than n-type doping. ZT for p-type doping along the x-, y-, and z-directions can reach 0.84, 0.82, and 0.63, respectively, ZT for n-type doping along the x-, y-, and z-directions can also reach 0.62, 0.71, and 0.59, respectively. These results show that FeAsS has potential application in thermoelectric material.

4. COMPUTATIONAL APPROACH

The structure is optimized by using first-principles density functional theory in combination with projector-augmented-wave pseudopotentials, and the Perdew–Burke–Ernzerhof exchange correlation functional is used, which is implemented in Vienna ab initio simulation package (VASP). We choose a 13 13cho13 Monkhorst–Pack k-mesh. The plane-wave energy cutoff is set to 450 eV. The lattice parameters and the atomic positions are fully optimized until the maximum Hellmann–Feynman forces exerted on each atom less than 1 × 10$^{-6}$ eV/Å. The electronic band structure is calculated based on the optimized structure, and the k-grid is set to 31 × 31 × 31. After the structural optimization and the electronic band structure calculation, we carry out the electronic transport properties calculation by using BoltzTraP code. In addition, we adopt self-consistent single parabolic band (SCF-SPB) model to calculate electron relaxation time (τ) as detailed below.
Therefore, the best change of lattice thermal conductivity by less than 0.7%.

The cell containing 96 atoms based on the optimized structure is used. The third-order anharmonic IFCs are calculated from the atomic vibrations.

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Lin Zhu: 0000-0003-0336-8209

E-mail: linzh@hust.edu.cn. Phone/Fax: +86 027-87556264.

**ORCID**

Lin Zhu: 0000-0003-0366-8209

Huahua Fu: 0000-0003-3920-6324

**Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the National Natural Science Foundation of China under the Grant No. 11374111 and 11874159.

**REFERENCES**

(1) Yang, L.; Chen, Z.-G.; Dargusch, M. S.; Zou, J. High Performance Thermoelectric Materials: Progress and Their Applications. Adv. Energy Mater. 2017, 8, 1701979.

(2) Zhu, L.; Li, R.; Yao, K. Temperature-controlled colossal magnetoresistance and perfect spin Seebeck effect in hybrid graphene/boron nitride nanoribbons. Phys. Chem. Chem. Phys. 2017, 19, 4085–4092.

(3) Jiang, X.; Zhu, L.; Yao, K. L. Thermoelectric properties of TeX2(X=S, Se, Te). J. Alloys Compd. 2018, 764, 505–511.

(4) Jonson, M.; Mahan, G. D. Mott’s formula for the thermopower and the Wiedemann-Franz law. Phys. Rev. B: Condens. Matter Mater. Phys. 1980, 21, 4223–4229.

(5) Stojanovic, N.; Matihrpala, D. H. S.; Berg, J. M.; Holtz, M. Thermal conductivity in metallic nanostructures at high temperature: Electrons, phonons, and the Wiedemann-Franz law. Phys. Rev. B: Condens. Matter Mater. Phys. 2010, 82, 075418.

(6) He, J.; Kanatzidis, M. G.; Dravid, V. P. High performance bulk thermoelectrics via a panoscopic approach. Mater. Today 2013, 16, 166–176.

(7) Chen, G.; Dresselhaus, M. S.; Dresselhaus, G.; Fleurial, J.-P.; Caliart, T. Recent developments in thermoelectric materials. Int. Mater. Rev. 2003, 48, 45–66.

(8) Sootsman, J. R.; Chung, D. Y.; Kanatzidis, M. G. New and Old Concepts in Thermoelectric Materials. Angew. Chem., Int. Ed. 2009, 48, 8616–8639.

(9) Silva, J. C. M.; De Abreu, H. A.; Duarte, H. A. Electronic and structural properties of bulk arsenopyrite and its cleavage surfaces - a DFT study. RSC Adv. 2015, 5, 2013–2023.

(10) Li, Y.-Q.; He, Q.; Chen, J.-H.; Zhao, C.-H. Electronic and chemical structures of pyrite and arsenopyrite. Mineral. Mag. 2015, 79, 1779–1789.

(11) Kuvandikov, O. K.; Shakarov, K. O.; Shodiev, Z. M.; Rabbimova, G. R. Analysis of the paramagnetic properties of pyrite, arsenopyrite, and chalcopyrite at high temperatures. J. Commun. Technol. Electron. 2007, 52, 1062–1064.

(12) Yang, H.; Downs, R. T. Crystal structure of glaucodot, (Co,Fe)AsS, and its relationships to marcasite and arsenopyrite. Am. Mineral. 2008, 93, 1183–1186.

(13) Telkes, M. Thermoelectric Power and Electrical Resistivity of Minerals. Am. Mineral. 1950, 35, 536–555.

(14) Guo, S.-D.; Qiu, L. Thermoelectric properties of topological insulator BaSn2. J. Phys. D: Appl. Phys. 2017, 50, 015101.

(15) Guo, S.-D.; Wang, Y.-H.; Lu, W.-L. Elastic and transport properties of topological semimetal ZrTe. New J. Phys. 2017, 19, 113048.

(16) Tan, G.; Zhao, L.-D.; Kanatzidis, M. G. Rationally Designing High-Performance Bulk Thermoelectric Materials. Chem. Rev. 2016, 116, 12123–12149.

(17) Li, G.; Ding, G.; Gao, G. Thermoelectric properties of SnSe2monolayer. J. Phys.: Condens. Matter. 2017, 29, 015001.

(18) Callaway, J. Quantum Theory of the Solid State; Academic Press: New York, 1976.

(19) Born, M.; Huang, K. Dynamical Theory of Crystal Lattices; Oxford University Press: Oxford, 1954.

(20) Kittel, Ch. Introduction to Solid State Physics, 5th ed.; J. Wiley and Sons: New York, 1976.

(21) Li, W.; Carrete, J.; Katcho, N. A.; Mingo, N. ShengBTE: A solver of the Boltzmann transport equation for phonons. Comput. Phys. Commun. 2014, 185, 1747–1758.

(22) Gonze, X.; Amadon, B.; Anglade, P.-M.; Beuken, J.-M.; Bottin, F.; Boulangier, P.; Bruneval, F.; Caliste, D.; Caracas, R.; Cote, M.; Deutsch, T.; Genovese, L.; Ghosez, P.; Giantomassi, M.; Goedecker, S.; Hamann, D. R.; Hermet, P.; Jollet, F.; Jomard, G.; Leroux, S.; Mancini, M.; Mazevet, S.; Oliveira, M. J. T.; Onida, G.; Pouillon, Y.; Rangel, T.; Rignanese, G.-M.; Sangalli, D.; Shaﬁaf, R.; Torrent, M.; Verstraete, M. J.; Zerah, G.; Zwanziger, J. W. ABINIT: first-principles approach to material and nanosystem properties. Comput. Phys. Commun. 2009, 180, 2582–2615.

(23) Gonze, X.; Beuken, J.-M.; Caracas, R.; Detraux, F.; Fuchs, M.; Rignanese, G.-M.; Sindic, L.; Verstraete, M.; Zerah, G.; Jollet, F.; Torrent, M.; Roy, A.; Mikami, M.; Ghosez, P.; Raty, J.-Y.; Allan, D. C. First-principles computation of material properties: the ABINIT software project. Comput. Mater. Sci. 2002, 25, 478–492.

(24) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the norm-conserving approximation. Phys. Rev. B: Condens. Matter Mater. Phys. 1999, 59, 1758–1775.

(25) Ernzerhof, M.; Scuseria, G. E. Assessment of the Perdew-Burke-Ernzerhof exchange-correlation functional. J. Chem. Phys. 1999, 110, 5029–5036.

(26) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 1996, 77, 3865–3868.
(27) Kresse, G.; Hafner, J. Ab initio molecular dynamics for liquid metals. Phys. Rev. B: Condens. Matter Mater. Phys. 1993, 47, 558–561.
(28) Kresse, G.; Hafner, J. Ab initio molecular-dynamics simulation of the liquid-metal-amorphous-semiconductor transition in germanium. Phys. Rev. B: Condens. Matter Mater. Phys. 1994, 49, 14251–14269.
(29) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B: Condens. Matter Mater. Phys. 1996, 54, 11169–11186.
(30) Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. Comput. Mater. Sci. 1996, 6, 15–50.
(31) Madsen, G. K. H.; Singh, D. J. BoltzTraP. A code for calculating band-structure dependent quantities. Comput. Phys. Commun. 2006, 175, 67–71.
(32) Ding, Y.; Xiao, B.; Tang, G.; Hong, J. Transport Properties and High Thermopower of SnSe2: A Full Ab-Initio Investigation. J. Phys. Chem. C 2016, 121, 225–236.
(33) Zhang, L.-C.; Qin, G.; Fang, W.-Z.; Cui, H.-J.; Zheng, Q.-R.; Yan, Q.-B.; Su, G. Tinselenidene: a Two-dimensional Auxetic Material with Ultralow Lattice Thermal Conductivity and Ultrahigh Hole Mobility. Sci. Rep. 2016, 6, 19830.
(34) Bardeen, J.; Shockley, W. Deformation Potentials and Mobilities in Non-Polar Crystals. Phys. Rev. 1950, 80, 72–80.
(35) Guo, R.; Wang, X.; Kuang, Y.; Huang, B. First-principles study of anisotropic thermoelectric transport properties of IV-VI semiconductor compounds SnSe and SnS. Phys. Rev. B: Condens. Matter Mater. Phys. 2015, 92, 115202.
(36) Wu, L.-J.; Zhao, Y.-Q.; Chen, C.-W.; Wang, L.-Z.; Liu, B.; Cai, M.-Q. First-principles hybrid functional study of the electronic structure and charge carrier mobility in perovskite CH3NH3SnI3. Chin. Phys. B 2016, 25, 107202.
(37) Togo, A.; Tanaka, I. First principles phonon calculations in materials science. Scr. Mater. 2015, 108, 1–5.