Theoretical investigation of the thermoelectric transport properties of $BaSi_2$*

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(Received 15 August 2010; revised manuscript received 16 November 2010)

The full-potential linear augmented plane wave method based on density functional theory is employed to investigate the electronic structure of $BaSi_2$. With the constant relaxation time and rigid band approximation, the electrical conductivity, Seebeck coefficient and figure of merit are calculated by using Boltzmann transport theory, further evaluated as a function of carrier concentration. We find that the Seebeck coefficient is more anisotropic than electrical conductivity. The figure of merit of $BaSi_2$ is predicted to be quite high at room temperature, implying that optimal doping may be an effective way to improve thermoelectric properties.

Keywords: thermoelectric transport property, density functional theory, Boltzmann transport theory

PACS: 61.66.Dk, 71.20.–b, 71.15.–m **DOI:** 10.1088/1674-1056/20/4/046103

1. Introduction

Thermoelectric materials have attracted much interest because of their capability of converting heat directly into electricity or *vice versa*. The conversion efficiency of a thermoelectric device depends on a dimensionless figure of merit, $ZT = S^2\sigma T/\kappa$, where S is the thermoelectric power or Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity consisting of both the lattice ($\kappa_{\rm l}$) and the electronic ($\kappa_{\rm e}$) contribution, and T is the absolute temperature. So far, conventional thermoelectric materials, such as Bi_2Te_3, PbTe and SiGe, have optimal ZT values approximately 1.0 at room temperature.[1] Normally, these materials are costly and naturally rare, which is not in favour of large-scale industrial applications. In order to overcome these disadvantages, thermoelectric materials with both high conversion ability and environmental conscious are expected.

Semiconducting alkaline-earth metal silicides, such as Mg_2Si,[2–4] $FeSi_2$[5,6] and $BaSi_2$,[7,8] which are composed of elements that are in great abundance in the earth's crust and with economic prices, have attracted much attention also as environmentally friendly thermoelectric materials. Most importantly, a high thermoelectric conversion efficiency has been reported in these compounds. For example, alloy Mg_2(Si, Sn) of optimized composition exhibit large $ZT = 1.1$.[9] Recently, orthorhombic $BaSi_2$ has been studied as a potential candidate as a thermoelectric material owing to its quite large Seebeck coefficient and low thermal conductivity. The thermal conductivity κ is reported as low as 1.56 $\rm W{\cdot}m^{-1}{\cdot}K^{-1}$ at room temperature, and decreases gradually with increasing temperature and reaches the minimum value of 0.67 $\rm W{\cdot}m^{-1}{\cdot}K^{-1}$ at 873 K.[7] The remarkable low κ is comparable to, or lower than, those of typical thermoelectric materials, such as Bi_2Te_3. However, due to its low electrical conductivity, ZT is restricted to a quite low value, for example 0.01 at 954 K. The thermoelectric performance of $BaSi_2$ has been enhanced by modulating the composition[8] and the maximum ZT value of 0.07 at 970 K and has been obtained in the composition of $Ba_{0.98}La_{0.02}Si_2$.

On the theoretical side, the electronic band structure of $BaSi_2$ has been studied by several groups. Imai *et al.*[10] investigated the electronic properties of $BaSi_2$ using first-principle pseudopotential method, and an indirect band gap of 0.457 eV was obtained. Kishino and co-workers[11] calculated the electronic band structure of orthorhombic $BaSi_2$ using a local

*Project supported by the National Basic Research Program of China (Grant No. 2007CB607504) and Graduate Independent Innovation Foundation of Shandong University (Grant No. yzc09076).

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density approximation (LDA) in the all-electron full-potential linearized augmented plane wave (FLAPW) method. They predicted that $BaSi_2$ is an indirect semiconductor with a gap of 0.72 eV. The FLAPW result is closer to the experimental band gap of 1.1 eV[12] than the pseudopotential result. In our calculation, the FLAPW method is adopted. In addition, to obtain a more reliable value for the band gap, our calculations are performed with optimized lattice constants, while in the above two papers, experimental structure data were used. From the electronic structure of the material, thermoelectric transport properties such as σ, S and $\kappa_{\rm e}$ can be estimated, which can provide helpful information for understanding the thermoelectric performance of materials. Hence, to evaluate the doping effect on the thermoelectric transport properties of $BaSi_2$, we calculate its electronic structures. After the electron band structure is obtained, Boltzmann transport theory will be applied to obtain the transport properties.

2. Computational details

Three kinds of crystallographic structures of $BaSi_2$ have been reported,[13] i.e., orthorhombic, cubic, and trigonal structure at ambient conditions. Only the orthorhombic phase is stable, while the other two are in the metastable state. So in the following calculations, the electronic and thermoelectric transport property is studied for orthorhombic structure $BaSi_2$.

A unit cell containing eight formulae of $BaSi_2$ with space group *Pnma* is adopted in our calculations. Electronic structure calculations are performed in the WIEN2K[14] code. Exchange and correlation effects are accounted for by the generalized gradient approximation parameterized by Perdew, Burke, and Ernzerhof.[15] We have converged all of our calculations with respect to the $R_{\rm MT} * K_{\rm max}$ up to 8, corresponding to 29181 plane waves; the muffin-tin radii are chosen to be 2.2 a.u. for Si and 2.5 a.u. for Ba.

From the calculated band structure, the thermoelectric transport tensors can be evaluated using the standard Boltzmann kinetic transport theory and the rigid band approach.[16] The doping levels can be evaluated by shifting the Fermi level to simulate n- or p-doped materials. The electrical conductivity and Seebeck coefficient tensors as a function of temperature T and chemical potential μ are expressed as

$$\sigma_{\alpha\beta}(T;\mu) = \frac{1}{\Omega}\int \sigma_{\alpha\beta}(\varepsilon)\left[-\frac{\partial f_\mu(T;\varepsilon)}{\partial\varepsilon}\right]{\rm d}\varepsilon, \quad (1)$$

$$S_{\alpha\beta}(T;\mu) = \frac{1}{eT\Omega\sigma_{\alpha\beta}(T;\mu)}\int \sigma_{\alpha\beta}(\varepsilon)(\varepsilon-\mu) \times \left[-\frac{\partial f_\mu(T;\varepsilon)}{\partial\varepsilon}\right]{\rm d}\varepsilon, \quad (2)$$

where

$$\sigma_{\alpha\beta}(\varepsilon) = \frac{e^2}{N}\sum_{i,\boldsymbol{k}} \tau_{i,\boldsymbol{k}} v_\alpha(i,\boldsymbol{k}) v_\beta(i,\boldsymbol{k})\delta(\varepsilon-\varepsilon_{i,\boldsymbol{k}}), \quad (3)$$

where α and β are tensor indices, e is the electron charge, Ω is the volume of the unit cell, $\varepsilon(\boldsymbol{k})$ is the band energy, N is the number of $\boldsymbol{k}$-points sampled, $v(\boldsymbol{k})$ is the band velocity, $\tau(\boldsymbol{k})$ is the relaxation time and f is the Fermi function. Transport properties are calculated using the BoltzTrap program,[16] which relies on a well tested smoothed Fourier interpolation to obtain an analytical expression of bands. As τ cannot be determined from band structure calculations, in our approach the relaxation time is assumed to be a constant, based on the consideration that the electrons contributing to transport are in a narrow energy range due to the delta-function like Fermi broadening. The relaxation time is nearly the same for the electrons in such a narrow energy range. The validity of this method has been tested earlier, and the method actually turns out to be a good approximation.[16,17] The temperature dependence of the energy band structure is neglected. For the transport tensor calculation, eigen-energies of 6000 $\boldsymbol{k}$-points on a non-shifted mesh in the Brillouin zone (BZ) are calculated.

3. Results and discussion

First, the electronic properties of $BaSi_2$ are obtained in the optimized crystal structure. The calculated lattice parameters are $a = 8.92$ Å (1 Å=0.1 nm), $b = 6.68$ Å, and $c = 11.45$ Å, which are consistent with the experimental data.[18] The electronic band structure is shown in Fig. 1, which is plotted with 80 $\boldsymbol{k}$-points along the high symmetry directions in the BZ. The conduction band minimum (CBM) resides at the T point, while the valence band maximum (VBM) lies between Y and Γ. Hence, $BaSi_2$ is an indirect band gap semiconductor with a band gap of 0.78 eV from our calculation. This value is in close agreement with the experimental result estimated from the temperature dependence of the resistivity, 1.1 eV,[12] and also with that of the previously published DFT calculation, 0.72 eV.[11]

From Fig. 1, we also notice that the bands along different directions have different slopes, showing a strong anisotropic behaviour. At the CBM, the electron bands near the Fermi level along the T–Z (010)

symmetry line are more dispersive than that along the R–T (100) symmetry line, indicating that the electrons in the $\boldsymbol{k}_x$-direction are more localized than those of the $\boldsymbol{k}_y$-direction. At the VBM, however, flat band dispersions exist along the X–S (010) symmetry line, while bands along the Γ–X (100) symmetry line are more dispersive. Since the electrical transport properties rely on the band structure, the anisotropic energy band structure of the crystal implies significant anisotropy in the electrical transport properties.

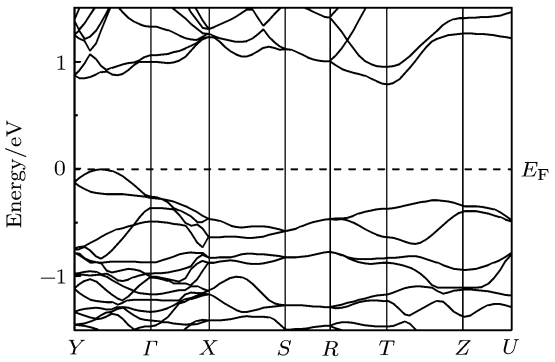


Fig. 1. Calculated electronic band structure of $BaSi_2$. The reciprocal coordinates of high-symmetry points are Y=(0, 0.5, 0), Γ=(0, 0, 0), X=(0.5, 0, 0), S=(0.5, 0.5, 0), R=(0.5, 0.5, 0.5), T=(0, 0.5, 0.5), Z=(0, 0, 0.5), U=(0.5, 0, 0.5). The energy of the valence band edge is set as the zero energy reference.

Partial electronic density of states (DOS) of $BaSi_2$ is shown in Fig. 2. The orbital resolved partial density of states (PDOS) implies that the states in the energy range between −3 eV to 0 eV are mostly contributed by the 3p states of Si atom, while those in the conduction band mainly come from the hybridization of the 5d states and 3s, 3p states of Si atom. Since the transport properties are largely related to the DOS around the Fermi level, the 3p states of the Si and 5d states of Ba are responsible for the transport properties of $BaSi_2$ predominantly.

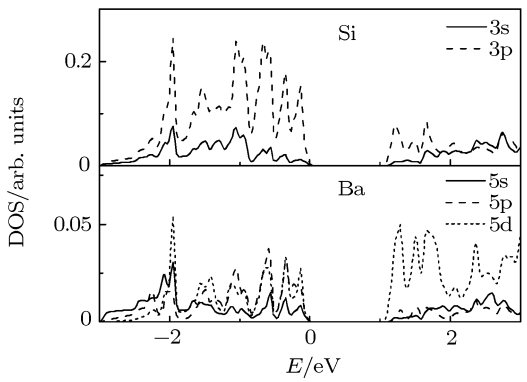


Fig. 2. Partial density of states for Si and Ba and total density of states for $BaSi_2$.

The transport properties as a function of the carrier concentration are evaluated using the Boltzmann transport theory with the results of the electronic band structure calculated above. The calculated properties are given at 300 K without considering the specific dopant element. Figure 3 shows the calculated electrical conductivity versus the relaxation time (σ/τ) along three principle crystal axes for p- and n-doped $BaSi_2$. We can see that as the carrier concentration increases, the electrical conductivity increases for both p- and n-type systems. The anisotropic behaviour also can be easily seen from Fig. 3, i.e., σ/τ along the $\boldsymbol{x}$ direction for p-doped $BaSi_2$ is larger than that in other directions, while for n-doped system the value of σ/τ is reduced from $\boldsymbol{x}$ then $\boldsymbol{y}$ to the $\boldsymbol{z}$ direction.

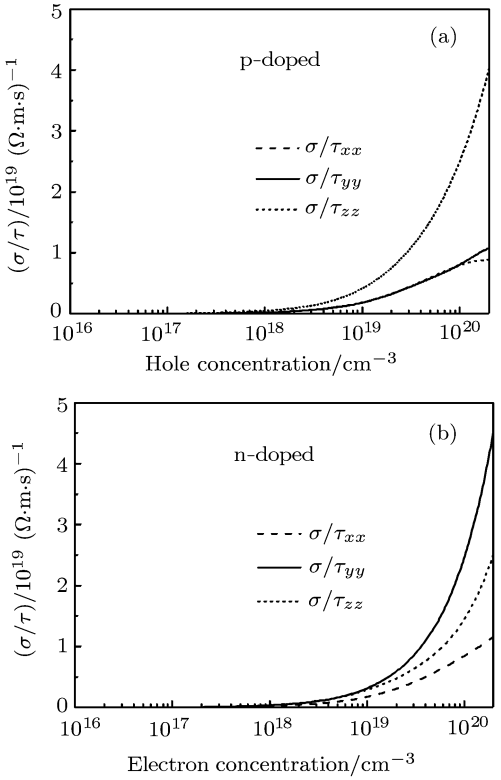


Fig. 3. Calculated (a) p- and (b) n-type electrical conductivities for $BaSi_2$ along the $\boldsymbol{x}$, $\boldsymbol{y}$ and $\boldsymbol{z}$ crystal axes as functions of carrier concentration at 300 K.

The Seebeck coefficient is calculated without any fitting parameter under the assumption of a constant relaxation time, and is plotted as a function of the carrier concentration in Fig. 4. The Seebeck coefficient decreases with increasing carrier concentration. The isotropic character of the Seebeck coefficient is not as obvious as that of electrical conductivity. This can be understood from Eq. (2) that the Seebeck coefficient

is the ratio of the 0th and 1st moments of the electrical conductivity,[17] which results in the cancellation of the anisotropy.

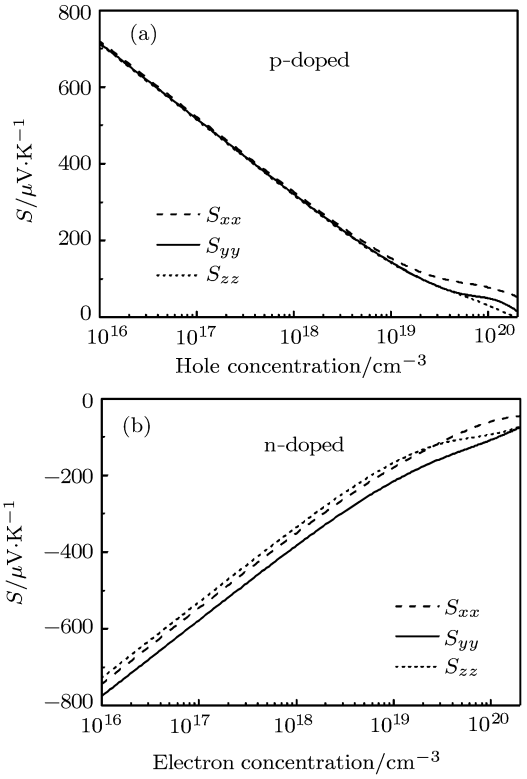


Fig. 4. Carrier concentration dependence of Seebeck coefficients for (a) p- and (b) n-doped $BaSi_2$ at 300 K.

To evaluate ZT of $BaSi_2$, lattice thermal conductivity and the relaxation time have to be supplied as parameters. The relaxation time is derived by fitting the available experimental data. The electron mobility is about 800 cm^2/V·s at 300 K, while the electron concentration is 4.8×10^{15} cm^{-3}.[19] If the measuring direction is assumed to be along the $\boldsymbol{x}$, $\boldsymbol{y}$ and $\boldsymbol{z}$ directions, the relaxation times τ we obtain are about 6.14×10^{-14} s, 3.72×10^{-14} s and 3.43×10^{-14} s, respectively. Since there is no available data on the thermal conductivity of the $BaSi_2$ single crystal, the polycrystalline lattice thermal conductivity of $\kappa_{\rm l} = 1.38$ W·m^{-1}·K^{-1} is used.[7] Generally, the value of $\kappa_{\rm l}$ of the polycrystal sample is smaller than that of a single crystal. Using the experimental value of $\kappa_{\rm l}$, we estimate the ZT values for different carrier concentrations, as shown in Fig. 5. Here we assume that τ and $\kappa_{\rm l}$ are independent of structures and doping level. The predicted ZT values have large anisotropic character, and the ZT components possess different peak positions. For the n-doped system along the $\boldsymbol{y}$ crystal direction, the maximum value of ZT is above 0.7 at the carrier concentration of 1.0×10^{19} cm^{-3}. For the p-doped system, the maximum ZT value can also reaches 0.7 along the $\boldsymbol{x}$ crystal direction at the carrier concentration of 3.2×10^{18} cm^{-3}.

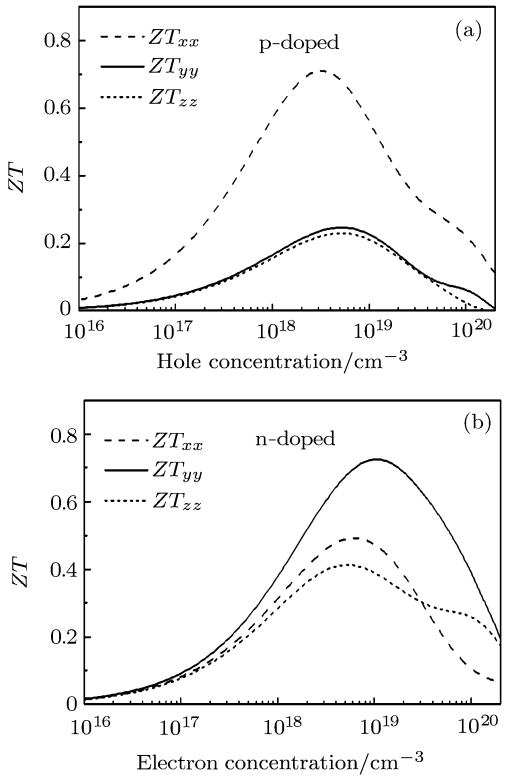


Fig. 5. Calculated ZT values as a function of carrier concentration for (a) p- and (b) n-doped $BaSi_2$ at 300 K.

The calculated maximum ZT and its corresponding carrier concentration and the optimal doping level of $BaSi_2$ at 300 K are listed in Table 1. The optimal doping concentration is about (0.015–0.05) e.u.c.$^{-1}$, remaining at reasonable doping levels. Here, e.u.c.$^{-1}$ is given in electrons per unit cell. The calculated ZT values are much larger than the experimental results[7] at the same temperature. So, our present theoretical investigations suggest that the appropriate doping can be an effective way of improving the thermoelectric performance of $BaSi_2$.

Table 1. The calculated maximum of figure of merit $ZT_{\rm max}$ and its corresponding carrier concentration N and optimal doping level n of $BaSi_2$ at 300 K. Carrier concentrations are in units of 10^{18} cm^{-3}. The p(−) and n(+) doping concentrations are in units of e.u.c.$^{-1}$.

	direction	$ZT_{\rm max}$	N	n
p	$\boldsymbol{x}$	0.71	3.2	+0.016
	$\boldsymbol{y}$	0.25	5.1	+0.024
	$\boldsymbol{z}$	0.23	5.1	+0.024
n	$\boldsymbol{x}$	0.50	6.2	–0.028
	$\boldsymbol{y}$	0.73	10.4	–0.048
	$\boldsymbol{z}$	0.41	5.0	–0.023

Note that in our calculation, the thermoelectric transport property is investigated for single crystal $BaSi_2$. However, polycrystalline materials are mainly used in practical applications. Since the transport properties of $BaSi_2$ crystals are anisotropic, in experiment the texture control during material processing can be used to improve the thermoelectric properties. According to our calculation result, textures along [100] and [010] crystallographic axes are preferred for p- and n-doped $BaSi_2$, respectively. For polycrystalline $BaSi_2$ with a random texture, the thermoelectric transport coefficient can be approximated as an average value of each direction.

4. Conclusions

We have performed the first principle electronic structure calculations with the Boltzmann transport theory to study the transport properties of $BaSi_2$. The calculated electronic band structure shows that the indirect band gap of $BaSi_2$ is 0.78 eV. Transport properties are more sensitive to the 3p states of Si and 5d states of Ba. Moreover, thermoelectric transport coefficient analysis shows that the Seebeck coefficient is more anisotropic than the electrical conductivity. The estimated maximum ZT value can reach 0.7 at room temperature by effective doping.

References

[1] Rowe D M 1995 *CRC Handbook of Thermoelectrics* (Boca Raton: CRC Press) p. 211

[2] Zhang Q, Zhao X B, Yin H and Zhu T J 2008 *J. Alloys Compd.* **464** 9

[3] Nolas G S, Wang D and Beekman M 2007 *Phys. Rev.* B **76** 235204

[4] Peng H, Wang C L, Li J C, Wang H C and Wang M X 2010 *Acta Phys. Sin.* **59** 4123 (in Chinese)

[5] Li H, Tang X F, Chao W Q and Zhang Q J 2009 *Chin. Phys.* B **18** 287

[6] Chen Y Q, Luo J, Liang J K, Li J B and Rao G H 2009 *Chin. Phys.* B **18** 4944

[7] Hashimoto K, Kurosaki K, Imamura Y, Muta H and Yamanaka S 2007 *J. Appl. Phys.* **102** 063703

[8] Hashimoto K, Kurosaki K, Muta H and Yamanaka S 2008 *Mater. Trans.* **49** 1737

[9] Zaitsev V K, Fedorov M I, Gurieva E A, Eremin I S, Konstantinov P P, Samunin A Y and Vedernikov M V 2006 *Phys. Rev.* B **74** 045207

[10] Imai Y, Watanabe A and Mukaida M 2003 *J. Alloys Compd.* **358** 257

[11] Kishino S, Imai T, Iida T, Nakaishi Y, Shinada M, Takanashi Y and Hamada N 2007 *J. Alloys Compd.* **428** 22

[12] Nakamura T, Suemasu T, Takakura K, Hasegawa F, Wakahara A and Imai M 2002 *Appl. Phys. Lett.* **81** 1032

[13] Imai M and Hirano T 1995 *J. Alloys Compd.* **224** 111

[14] Schwarz K, Blaha P and Madsen G K H 2002 *Comput. Phys. Commun.* **147** 71

[15] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865

[16] Madsen G K H and Singh D J 2006 *Comput. Phys. Commun.* **175** 67

[17] Wang D, Tang L, Long M Q and Shuai Z G 2009 *J. Chem. Phys.* **131** 224704

[18] Evers J 1980 *J. Solid State Chem.* **32** 77

[19] Morita K, Inomata Y and Suemasu T 2006 *Thin Solid Films* **508** 363