Point defect approach to enhance the thermoelectric performance of Zintl-phase BaAgSb

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ABSTRACT Zintl-phase compounds have great potential in thermoelectric applications owing to their “phonon glass-electron crystal” (PGEC) structures. In this paper, a new Zintl-phase thermoelectric material BaAgSb is reported. Ba deficiency increased the carrier concentration, and then suppressed the intrinsic excitation. The peak ZT value of Ba_{0.98}AgSb reached ~0.56 at 773 K. Moreover, Eu alloying at Ba site not only lowered the lattice thermal conductivity by inducing point-defect scattering, but also improved the electrical properties by increasing the carrier mobility. Finally, a peak ZT of ~0.73 was achieved in Ba_{0.78}Eu_{0.2}AgSb.

Keywords: thermoelectric, Zintl phase, point defect, isoelectronic alloying

INTRODUCTION

Various energy conversion technologies have been suggested to reduce the consumption of non-renewable resources, and promote the sustainable development of global community. Thermoelectric materials, which can realize the mutual conversion between electricity and thermal energy, have a great prospect in waste heat recovery and solid-state refrigeration [1,2]. However, the development of devices made of thermoelectric materials is still limited by the energy conversion efficiency that requires a high figure-of-merit $ZT = S^2\sigma T/\kappa$, where S , σ , κ and T are Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature, respectively [3]. To achieve high thermoelectric performance,

excellent electrical properties and low thermal conductivity are necessary. Up to now, band engineering [4,5], point defects engineering [6,7], nanoscale engineering [8,9], entropy engineering [10,11], phase diagram engineering [12,13], etc. have proved effective in optimizing thermoelectric properties.

Zintl-phase compounds are promising thermoelectric materials with typical “phonon glass-electron crystal” (PGEC) structure [14,15]. Point defects mainly caused by dopants, vacancies, alloying, and interstitials are easily introduced in this kind of compounds, because of the complex structure and rich component elements [14,16]. The dopant or interstitial atoms can regulate the Fermi level by tuning the carrier concentration, and the alloying atoms can optimize the band structure by orbital alignment for the improvement of the electrical transport properties [17–21]. In addition, the guest atoms or vacancies can suppress the lattice thermal conductivity by strengthening phonon scattering [22–24]. Indeed, high thermoelectric efficiency has been realized in some Zintl phases, such as YbZn₂Sb₂ [25,26], Ca₉Zn_{4.5}Sb₉ [27,28], Ca₅Al₂Sb₆ [29], and Yb₁₄MnSb₁₁ [30]. Our previous studies reported the thermoelectric performance of the ZrBeSi-type Zintl-phase Eu₂ZnSb₂, and a ZT value of 1.0 was achieved at 823 K [31]. Different from Eu₂ZnSb₂, SrAgSb and EuAgSb possess more attractive electrical transport properties due to the fully occupied framework [32–34]. As a typical ZrBeSi-type Zintl compound, BaAgSb may also have promising thermoelectric perfor-

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mance after coordinate regulation of electrical and phononic properties.

In this work, Zintl-phase BaAgSb was prepared by high-energy ball milling followed by spark plasma sintering (SPS). The intrinsic excitation inhibited the thermoelectric performance of BaAgSb at high temperatures. In order to optimize the thermoelectric properties of BaAgSb, two types of point defects were introduced. Firstly, Ba deficiency introduced more hole carriers, and suppressed the intrinsic excitation. Benefiting from the improved electrical properties, a ZT value of ~ 0.56 was achieved in $\text{Ba}_{0.98}\text{AgSb}$ at 773 K. Furthermore, $\text{Ba}_{0.98-y}\text{Eu}_y\text{AgSb}$ ($y = 0.1, 0.2$, and 0.3) were designed to regulate the thermoelectric properties. The reduction in the lattice thermal conductivity was achieved through alloying Eu at the Ba site. In addition, Eu alloying brought about both the increased carrier concentration and mobility. As a result, maximum power factor and ZT reached respectively $\sim 1.2 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-2}$ and ~ 0.73 at 773 K for $\text{Ba}_{0.78}\text{Eu}_{0.2}\text{AgSb}$.

EXPERIMENTAL SECTION

Synthesis

Barium (Ba, 99.9%, pieces), silver (Ag, 99.9%, powder), antimony (Sb, 99.999%, shots), and europium (Eu, 99.9%, chunk) were weighed according to the nominal compositions of $\text{Ba}_{1-x}\text{AgSb}$ ($x = 0, 0.01, 0.02$, and 0.03) and $\text{Ba}_{0.98-y}\text{Eu}_y\text{AgSb}$ ($y = 0.1, 0.2$, and 0.3), and loaded into a stainless-steel jar with stainless-steel balls in a glove box. The mixtures were ball-milled continuously for 10 h using a high energy ball mill (SPEX 8000 M). The obtained powder was sintered into a dense disk at 923 K for 2 min by SPS under a pressure of 60 MPa.

Characterization

The crystal structures were studied by X-ray diffraction (XRD, Rigaku D/max 2500 PC). The microstructures were investigated by a spherical aberration-corrected (Cs-corrected) electron microscope (JEM-ARM200F). The electrical conductivity and Seebeck coefficient were measured on a commercial apparatus (CTA-3, Cryoall). The uncertainty for the electrical conductivity and the Seebeck coefficient are 3% and 5%, respectively. The thermal conductivity (κ) was calculated using $\kappa = DC_p\alpha$, where D is the volume density determined by the Archimedes method (shown in Table S1), C_p is the specific heat estimated by a differential scanning calorimetry thermal analyzer (Netzsch DSC 404F3), and α is the thermal diffusivity measured on a laser flash apparatus

(Netzsch LFA 457). The uncertainty for the thermal conductivity is 6% (comprising uncertainties of 4% for the thermal diffusivity, 3.5% for the specific heat, and 3% for the density). The temperature-dependent Hall coefficient (R_H) was measured based on the van-der-Pauw technique under a reversible magnetic field of 1.5 T. The Hall carrier concentration (n_H) and Hall mobility (μ_H) were calculated using $n_H = 1/(eR_H)$ and $\mu_H = \sigma R_H$, respectively. The relation of Kubelka-Munk function ($F(R)$) versus wavelength (λ) was obtained by a Nicolet IS50 FT-IR spectrophotometer. For the indirect transition, the optical band gap (E_g) was determined based on the relational expression $(F(R) \cdot h\nu)^{0.5} = B(h\nu - E_g)$, where h is the Planck constant, and ν is the frequency of light.

Calculation

The density functional theory (DFT) calculations were performed using the Vienna *Ab-initio* Simulation Package (VASP). The generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) functional with the projector-augmented wave (PAW) method was used during the calculations of the total energies, band structure, and the geometry relaxations [35,36]. The total energy and Hellmann-Feynman force convergence criteria were $0.1 \text{ meV atom}^{-1}$ and $0.01 \text{ eV } \text{\AA}^{-1}$, respectively. A plane wave cutoff energy of 400 eV and a Gamma centered k -mesh $6 \times 6 \times 4$ were chosen for the crystal structure relaxation.

RESULTS AND DISCUSSION

ZrBeSi-type Zintl compounds with hexagonal structure (space group: $P6_3/mmc$) have been considered as promising mid-temperature thermoelectric materials [16,31,33]. Different from ZrBeSi-type Eu_2ZnSb_2 [31] and Eu_2ZnBi_2 [37], which have 50% vacancies at the Zn sites, the Ag sites are 100% occupied in BaAgSb, as shown in Fig. 1a, b. This fully occupied anionic framework benefits the carrier transport. Fig. 1c shows the electron localization function (ELF) of BaAgSb with the slice parallel to the (110) plane. ELF provides a good description of electron delocalization, which can be used to well understand the Zintl structure. The values of 1 and 0 correspond to fully localized and very low charge density, respectively [38]. The overlap of ELF between Ag and Sb suggests that they are connected by strong chemical bonds. The low charge density between Ba^{2+} and $[\text{AgSb}]^{2-}$ framework indicates that ionic bond exists in the BaAgSb Zintl phase. We also calculated the band structure of BaAgSb using density functional method and presented the results in Fig. 1d. The calculated band gap of BaAgSb

Figure 1 Crystal structure of Zintl-phase BaAgSb viewed from (a) [110] and (b) [001] direction. The cyan, gray, and golden spheres represent the barium, silver, and antimony, respectively. (c) Electron localization function (ELF) of BaAgSb. (d) Calculated band structure of BaAgSb. (e) XRD patterns of $\text{Ba}_{1-x}\text{AgSb}$ ($x = 0, 0.01, 0.02$, and 0.03). The patterns from 30° to 31° are enlarged.

is near 0 eV. Considering that PBE usually underestimates experimental band gap, the BaAgSb might be a semiconductor with a narrow band gap, which is similar with SrAgSb and EuAgSb [33]. The conduction band minimum (CBM) locates around the M point, while the valence band maximum (VBM) locates around the Γ point. Two hybrid bands are observed near the band edge of the valence band without obvious energy difference, which is good for the electrical properties [39]. By directly ball milling and hot pressing, a series of samples with different contents of Ba in $\text{Ba}_{1-x}\text{AgSb}$ ($x = 0, 0.01, 0.02$, and 0.03) were prepared. As shown in Fig. 1e, the main peaks of BaAgSb match well with the standard diffraction pattern; however, a little amount of impurity Ba is also observed. The peak of this secondary phase is weakened with the decrease of the Ba content.

Temperature-dependent electrical conductivity and Seebeck coefficient of $\text{Ba}_{1-x}\text{AgSb}$ ($x = 0, 0.01, 0.02$, and 0.03) are shown in Fig. 2a, b, respectively. The electrical conductivity increases and the Seebeck coefficient decreases with the reduced Ba content because of the increased carrier concentration caused by Ba deficiency at temperatures below 550 K. Due to the onset of the intrinsic excitation at temperatures higher than 550 K, the Seebeck coefficient decreases significantly, causing a reduced power factor of BaAgSb, as shown in Fig. 2c. With

decreasing content of Ba and then increasing carrier concentration, the intrinsic excitation is suppressed, contributing to an enhanced power factor at high temperatures. The maximum power factor of $\text{Ba}_{0.98}\text{AgSb}$ reaches $\sim 1.0 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-2}$ at 773 K, which is higher than those of Eu_2ZnSb_2 -based Zintl compounds [34,37]. The temperature-dependent carrier concentration and mobility are plotted in Fig. 2d. With the introduction of Ba deficiency, the intrinsic excitation moves to higher temperatures. Meanwhile, the increased carrier concentration strengthens the carrier scattering and leads to decreased carrier mobility.

The thermal conductivity and ZT values of $\text{Ba}_{1-x}\text{AgSb}$ ($x = 0, 0.01, 0.02$, and 0.03) are presented in Fig. 3. The thermal conductivity of $\text{Ba}_{1-x}\text{AgSb}$ displays a decreasing trend with increasing temperature. Compared with the electrical properties, Ba deficiency brings about a small impact on the thermal conductivity. The slightly increased thermal conductivities of $\text{Ba}_{0.98}\text{AgSb}$ and $\text{Ba}_{0.97}\text{AgSb}$ are mainly related to the increased carrier contribution. The lattice thermal conductivity κ_L was obtained by subtracting the carrier contribution κ_c from the total thermal conductivity κ . The κ_c was estimated using the Wiedemann-Franz relationship ($\kappa_c = L\sigma T$), where L is the Lorenz number and calculated using a single parabolic band (SPB) model [19,22,33]. To be

Figure 2 Temperature-dependent (a) electrical conductivity, (b) Seebeck coefficient, and (c) power factor of $\text{Ba}_{1-x}\text{AgSb}$ ($x = 0, 0.01, 0.02$, and 0.03). (d) n_{H} and mobility of $\text{Ba}_{1-x}\text{AgSb}$ ($x = 0, 0.01, 0.02$, and 0.03) as a function of temperature.

Figure 3 (a) Temperature-dependent thermal conductivity of $\text{Ba}_{1-x}\text{AgSb}$ ($x = 0, 0.01, 0.02$, and 0.03). The inset shows the lattice thermal conductivity. (b) Temperature-dependent ZT of $\text{Ba}_{1-x}\text{AgSb}$ ($x = 0, 0.01, 0.02$, and 0.03).

noted, the difference of lattice thermal conductivity at high temperatures is probably due to the intrinsic excitation, which makes the SPB model not suitable [40]. Benefiting from the suppressed intrinsic excitation, the maximum ZT value of $\text{Ba}_{0.98}\text{AgSb}$ reaches ~ 0.56 at 773 K, which is higher than that of BaAgSb .

Compared with Eu_2ZnSb_2 , BaAgSb has better electrical properties and relatively higher thermal conductivity. To further enhance the thermoelectric properties, a series of

samples $\text{Ba}_{0.98-y}\text{Eu}_y\text{AgSb}$ ($y = 0.1, 0.2$, and 0.3) were prepared by isoelectronic alloying Eu at the Ba site. As shown in Fig. 4a, all the Eu-alloyed samples are single phase with ZrBeSi structure. The secondary phase Ba disappears after Eu alloying. The XRD peak positions move slightly to a larger angle with increasing Eu content because of the smaller atomic radius of Eu. The whole-pattern refined lattice parameters (displayed in Fig. 4b) decrease from $a = b = 4.847 \text{ \AA}$ and $c = 9.186 \text{ \AA}$ for $\text{Ba}_{0.98}\text{AgSb}$ to $a = b =$

Figure 4 (a) XRD patterns and (b) refined lattice parameters of $\text{Ba}_{0.98-y}\text{Eu}_y\text{AgSb}$ ($y = 0, 0.1, 0.2$, and 0.3). (c) Low-magnification TEM image of $\text{Ba}_{0.78}\text{Eu}_{0.2}\text{AgSb}$. (d) STEM image of two contiguous grains. The insets in (d) are the SAED patterns taken along the $[001]$ direction. (e) HAADF-STEM image along the $[100]$ direction of $\text{Ba}_{0.78}\text{Eu}_{0.2}\text{AgSb}$. (f) The intensity profile of different atoms along the aquamarine line in (e).

4.821 Å and $c = 8.899$ Å for $\text{Ba}_{0.68}\text{Eu}_{0.3}\text{AgSb}$. Fig. 4c shows the low-magnification transmission electron microscopy (TEM) image of the $\text{Ba}_{0.78}\text{Eu}_{0.2}\text{AgSb}$ sample, which displays that the grain size is ~ 200 nm. Small grain size usually indicates that a lot of grain boundaries exist in the sample. The scanning TEM (STEM) image of two contiguous grains with clear grain boundary is presented in Fig. 4d. The corresponding selected area electron diffraction (SAED) pattern (insets of Fig. 4d) can be indexed along the $[001]$ direction. We also estimated the angle between the two grains, which is about 28.3° . The Cs-corrected high-angle annular dark-field STEM (HAADF-STEM) image of BaAgSb is shown in Fig. 4e. As is well known, the HAADF-STEM offers a unique technique to characterize the crystal structure. The atomic sites match well with the projection structure of BaAgSb along the $[100]$ direction. Ba vacancies are difficult to be observed in the HAADF-STEM image, because the content of Ba deficiency is too small. The intensity of the atoms along the aquamarine line in Fig. 4e is plotted in Fig. 4f. Different from the conventional TEM images, the contrast of HAADF-STEM images is roughly proportional to $Z^{1.7}$ (Z is the atomic number). Six atoms at the Ba sites stand in the aquamarine line. Parts of atomic intensities at the Ba sites are higher than others. We believe that the Eu atoms

partially occupy the Ba sites due to the larger atomic number of Eu(63) than that of Ba(56). The signals of Ag and Sb (purple peaks) are weak, because the aquamarine line does not cross directly above Ag and Sb atoms.

The temperature-dependent electrical conductivity and Seebeck coefficient of $\text{Ba}_{0.98-y}\text{Eu}_y\text{AgSb}$ ($y = 0, 0.1, 0.2$, and 0.3) are shown in Fig. 5a, b, respectively. With increasing content of Eu, the electrical conductivity improves over the whole temperature range, while the Seebeck coefficient decreases after Eu alloying. The obviously improved electrical conductivity contributes to the enhanced power factor, presented in Fig. 5c. The maximum power factor reaches $\sim 1.2 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-2}$ at ~ 773 K for $\text{Ba}_{0.78}\text{Eu}_{0.2}\text{AgSb}$ and $\text{Ba}_{0.68}\text{Eu}_{0.3}\text{AgSb}$. Fig. 5d shows the room-temperature Hall carrier concentration and mobility of $\text{Ba}_{0.98-y}\text{Eu}_y\text{AgSb}$ ($y = 0.1, 0.2$, and 0.3). The increased electrical conductivity of Eu-alloyed samples is not only due to the increased carrier concentration but also the increased mobility.

Normally, the increased carrier concentration will aggravate the carrier scattering, and bring about the decreased mobility. To further clarify the electrical transport mechanism, high-temperature Hall measurement was conducted, and the results are presented in Fig. 6a, b. With the increase of Eu substitution, the carrier con-

Figure 5 Temperature-dependent (a) electrical conductivity, (b) Seebeck coefficient, and (c) power factor of $\text{Ba}_{0.98-y}\text{Eu}_y\text{AgSb}$ ($y = 0, 0.1, 0.2$, and 0.3). (d) Room-temperature Hall carrier concentration and mobility of $\text{Ba}_{0.98-y}\text{Eu}_y\text{AgSb}$ ($y = 0, 0.1, 0.2$, and 0.3).

Figure 6 (a) Hall carrier concentration and (b) mobility of $\text{Ba}_{0.98-y}\text{Eu}_y\text{AgSb}$ ($y = 0, 0.1, 0.2$, and 0.3) as a function of temperature. (c) Normalized optical absorption versus photon energy for $\text{Ba}_{0.98-y}\text{Eu}_y\text{AgSb}$ ($y = 0.1, 0.2$, and 0.3). (d) Room-temperature Pisarenko relations of $\text{Ba}_{1-x}\text{AgSb}$ ($x = 0, 0.01, 0.02$, and 0.03) and $\text{Ba}_{0.98-y}\text{Eu}_y\text{AgSb}$ ($y = 0.1, 0.2$, and 0.3).

centration increases below the intrinsic excitation temperature because of the high carrier concentration of EuAgSb [33]. The carrier mobility tends to show a $\mu_H \propto T^{-1.5}$ relationship, implying that the transport scattering mechanism is dominated by phonon scattering. As shown in Fig. 6c, the measured E_g of $\text{Ba}_{0.98}\text{AgSb}$ is ~ 0.13 eV, and then the value decreases after Eu alloying. The room-temperature Pisarenko relation of $\text{Ba}_{1-x}\text{AgSb}$ ($x = 0, 0.01, 0.02$, and 0.03) and $\text{Ba}_{0.98-y}\text{Eu}_y\text{AgSb}$ ($y = 0.1, 0.2$, and 0.3) is shown in Fig. 6d. The relationship of Seebeck coefficient and carrier concentration for $\text{Ba}_{1-x}\text{AgSb}$ matches well with the Pisarenko relation estimated by the SPB model. With the increase of Eu content, the effective mass decreases gradually from $\sim 0.38 m_0$ (m_0 is electron mass) to $\sim 0.35 m_0$, which is believed to contribute to the enhanced μ_H . In addition, the disappearance of secondary phase also leads to the improvement of μ_H .

The temperature-dependent total thermal conductivity and lattice thermal conductivity are plotted in Fig. 7a, b, respectively. The room-temperature thermal conductivity of $\text{Ba}_{0.98-y}\text{Eu}_y\text{AgSb}$ decreases from ~ 2.5 to $\sim 1.5 \text{ W m}^{-1} \text{ K}^{-1}$. In Fig. 7b, the lattice thermal conductivity is obviously reduced by Eu alloying. With the

increasing Eu content, an approximate $\kappa_L \propto T^{-0.5}$ relationship between the lattice thermal conductivity and temperature indicates that strong alloy scattering dominates [41]. In order to further describe the scattering mechanisms, we used the Callaway model to analyze the lattice thermal conductivity with phonon relaxation time under different scattering mechanisms [42]:

$$\kappa_L = \int_0^{\omega_D/k_B T} \kappa_s(\omega) d\omega = \frac{k_B}{2\pi^2 v} \left(\frac{k_B}{\hbar} \right)^3 T^3 \int_0^{\theta_D/T} \tau(x) \frac{x^4 e^x}{(e^x - 1)^2} dx, \quad (1)$$

where k_B , v , $\hbar$, T , θ_D , and τ are the Boltzmann constant, phonon velocity, reduced Planck constant, absolute temperature, Debye temperature, and phonon relaxation time, respectively, and x is the reduced phonon frequency $x = \hbar\omega/k_B T$ (ω is the phonon frequency). The phonon relaxation time τ can be obtained by the addition of the inverse relaxation times for different scattering processes:

$$\tau^{-1} = \tau_U^{-1} + \tau_N^{-1} + \tau_B^{-1} + \tau_{PD}^{-1}, \quad (2)$$

where τ_U , τ_N , τ_B , and τ_{PD} refer to the phonon relaxation time for Umklapp scattering, normal scattering, boundary

Figure 7 (a) Thermal conductivity and (b) lattice thermal conductivity of $\text{Ba}_{0.98-y}\text{Eu}_y\text{AgSb}$ ($y = 0, 0.1, 0.2$, and 0.3) as a function of temperature. (c) Frequency-dependent lattice thermal conductivity of $\text{Ba}_{0.78}\text{Eu}_{0.2}\text{AgSb}$. (d) Room-temperature lattice thermal conductivity of $\text{Ba}_{0.98-y}\text{Eu}_y\text{AgSb}$ as a function of y .

scattering, and point defect scattering, respectively. Their detailed formulas can be found in the Supplementary information and the related publications [42–44]. Here the electron-phonon scattering was not considered because $\text{Ba}_{0.98-y}\text{Eu}_y\text{AgSb}$ has much lower carrier concentrations than those of half-Heusler alloys [42]. Fig. 7c shows the frequency-dependent lattice thermal conductivity of $\text{Ba}_{0.78}\text{Eu}_{0.2}\text{AgSb}$. The thermal conductivity decreased by grain boundary scattering is concentrated in the range of frequency <5 THz (blue region), while the thermal conductivity decreased by point defects is in the range of medium-to-high frequency (red region). The decreased lattice thermal conductivity in $\text{Ba}_{0.98-y}\text{Eu}_y\text{AgSb}$ is mainly related to the point defects, as demonstrated in Fig. 7d.

The ZT values of BaAgSb and $\text{Ba}_{0.98-y}\text{Eu}_y\text{AgSb}$ ($y = 0, 0.1, 0.2, \text{ and } 0.3$) are presented in Fig. 8. The point defects introduced by both Ba deficiency and Eu alloying are of great benefit to the thermoelectric properties of BaAgSb . The peak ZT of $\text{Ba}_{0.78}\text{Eu}_{0.2}\text{AgSb}$ reaches ~ 0.73 at 773 K, which is comparable to some typical Zintl-phase thermoelectric materials. This work enriches the family of Zintl-phase thermoelectric materials for the mid-temperature thermoelectric applications.

CONCLUSION

In summary, the intrinsic excitation in BaAgSb prevents the increase of ZT at high temperatures. Ba deficiency can increase the carrier concentration, and lead to enhanced thermoelectric properties at high temperatures. A peak ZT of ~ 0.56 was obtained in $\text{Ba}_{0.98}\text{AgSb}$ at 773 K. Furthermore, Eu alloying at Ba site can not only lower the lattice thermal conductivity by inducing point-defect

scattering, but also improve the electrical properties by increasing the carrier mobility. Benefitting from the enhancement by two types of point defects, the ZT value was improved from ~ 0.34 for BaAgSb to ~ 0.73 for $\text{Ba}_{0.78}\text{Eu}_{0.2}\text{AgSb}$ at 773 K. These results thus demonstrate that point defect engineering is promising for further optimizing Zintl-phase thermoelectric materials.

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Figure 8 Temperature-dependent ZT values of BaAgSb and $\text{Ba}_{0.98-y}\text{Eu}_y\text{AgSb}$ ($y = 0, 0.1, 0.2, \text{ and } 0.3$).

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Author contributions Chen Y, Cao F, and Zhang Q conceived the project; Huang Y, Chen C, Zhang W, and Li X prepared the samples; Huang Y, Liu Y, Wang X, and Zhang Z performed the property measurements; Xue W performed the TEM measurement; Yao H conducted the DFT calculation; Wang Y, Liu X, Cao F, and Zhang Q contributed new reagents/analytic tools; Chen C, Huang Y, Wang Y, Chen Y, Cao F, and Zhang Q analyzed the data and wrote the paper.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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利用点缺陷策略提高Zintl相BaAgSb的热电性能

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摘要 Zintl相化合物由于其独特的“声子玻璃-电子晶体”(PGEC)结构在热电领域具有广泛的应用前景. 本文报道了Zintl相热电材料BaAgSb的热电性质. 通过引入Ba空位, 可以提高p型BaAgSb的载流子浓度, 抑制其本征激发, Ba_{0.98}AgSb的ZT值在773 K达到了~0.56. 此外, 在Ba位进一步合金化Eu, 不仅能够引入点缺陷散射降低晶格热导率, 而且由于载流子迁移率的提高使其电输运性质也得到了改善. 最终, Ba_{0.78}Eu_{0.2}AgSb的ZT值在773 K达到~0.73.