Planar Zintl-phase high-temperature thermoelectric materials XCuSb (X = Ca, Sr, Ba) with low lattice thermal conductivity

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Abstract: A recent discovery of high-performance Mg₃Sb₂ has ignited tremendous research activities in searching for novel Zintl-phase compounds as promising thermoelectric materials. Herein, a series of planar Zintl-phase XCuSb (X = Ca, Sr, Ba) thermoelectric materials are developed by vacuum induction melting. All these compounds exhibit high carrier mobilities and intrinsic low lattice thermal conductivities (below 1 W·m⁻¹·K⁻¹ at 1010 K), resulting in peak p-type zT values of 0.14, 0.30, and 0.48 for CaCuSb, SrCuSb, and BaCuSb, respectively. By using BaCuSb as a prototypical example, the origins of low lattice thermal conductivity are attributed to the strong interlayer vibrational anharmonicity of Cu–Sb honeycomb sublattice. Moreover, the first-principles calculations reveal that n-type BaCuSb can achieve superior thermoelectric performance with the peak zT beyond 1.1 because of larger conducting band degeneracy. This work sheds light on the high-temperature thermoelectric potential of planar Zintl compounds, thereby stimulating intense interest in the investigation of this unexplored material family for higher zT values.

Keywords: Zintl-phase; thermoelectric materials; honeycomb lattice; intrinsic low κL

1 Introduction

Effectively harnessing waste heat dissipated during burning fossil fuels to generate electricity is of vital significance for decreasing the emission of greenhouse gases and lightening the burden on energy supply, which requires advanced energy conversion technologies. Thermoelectric technology, which can directly convert heat into electricity, stands out due to the advantages of ultra-long operational lifetime, no noise, and solid-state nature [1]. The conversion efficiency can be evaluated by the dimensionless figure of merit zT = S²σT/κtot, where S, σ, and T represent the Seebeck coefficient, electrical conductivity, and absolute temperature, respectively. The total thermal conductivity (κtot) consists
of the lattice ($\kappa_L$) and electronic ($\kappa_e$) counterparts. Since these parameters are closely coupled with each other via carrier concentration, it is difficult to largely improve the $zT$ values. Presently, the optimization of the thermoelectric performance is mainly focused on two aspects: (i) enhancing the power factor (PF = $S^2\sigma$) via tuning carrier concentration [2–5] and modifying band structures [6–8]; and (ii) lowering the thermal conductivity by refining grains [9,10], introducing the second phases or defects [11–13], and increasing the configuration entropy [14–17]. On the other hand, seeking new materials with intrinsic promising performance will also promote the development of thermoelectrics. Up to now, dozens of novel thermoelectric compounds with high $zT$ above 1.0 have been found to be appreciable for practical applications [18,19].

Zintl-phase thermoelectric materials, represented by Mg$_3$Sb$_2$ [20,21], have attracted extensive interest owing to their promising performance in room-to-moderate temperature, good mechanical properties, and low-cost constituent elements. This material family can be roughly classified according to the structure of covalently bonded lattice, including 1–2–2 type [22,23], 9–(4+π)x–9 type [24,25], 3–1–3 type [26,27], 14–1–11 type [28,29], etc. [30,31]. Most recently, a new kind of ZrBeSi-type (1–1–1 type) Zintl-phase with the space group of P63/mmc was explored for potential thermoelectric applications. Compared to the well-known Mg$_3$Sb$_2$, the anionic groups of ZrBeSi-type compounds can provide graphene-like honeycomb conductive channels, which boost the electron transport and induce favorable device output power. Indeed, extraordinary $zT$ values above 1.0 have been obtained in p-type Eu$_2$ZnSb$_2$ [32] and BaAgAs [33], which are superior to the thermoelectric performance of p-type Mg$_3$Sb$_2$-based materials. Moreover, in ZrBeSi-type lattice, three different atomic coordinates can be occupied by various elements, implying a large room for developing analogs in this material family. To date, new ZrBeSi-type compounds, e.g., BaAgSb [34,35], BaAgBi [36], SrAgSb [37], EuAgSb [37], and EuCuSb [37], have been reported to exhibit promising $zT$ values, which shows great potentials for searching high-performance thermoelectric materials.

In this work, p-type Zintl-phase compounds XCuSb (X = Ca, Sr, Ba) were rapidly prepared by vacuum induction melting, and their thermoelectric properties were systematically studied. It is found that BaCuSb and SrCuSb exhibit excellent carrier mobilities above 120 cm$^2$·V$^{-1}$·s$^{-1}$ profited by the honeycomb Cu–Sb conductive channels, giving rise to excellent power factors of $\sim$1 mW·m$^{-1}$·K$^{-2}$. Additionally, all these three compounds hold intrinsic low lattice thermal conductivity below 1 W·m$^{-1}$·K$^{-1}$ at high temperatures. The underlying mechanism of the ultralow lattice thermal conductivity was revealed by the first-principles calculations, using BaCuSb as an example, which should be attributed to the intense interlayer vibrational anharmonicity of the Cu–Sb honeycomb sublattice. Finally, BaCuSb was found to hold the highest p-type $zT$ of $\sim$0.48 at 1010 K.

2 Experimental

2.1 Sample synthesis

The raw materials for the syntheses of XCuSb (X = Ca, Sr, Ba) were Ca (chunks, 99%), Sr (chunks, 99%), Ba (chunks, 98%), Cu (granules, 99.999%), and Sb (pellets, 99.999%), which were weighed according to the stoichiometric ratio and loaded into carbon tubes. 2% excess Ba was added because it is oxidized easily even in the glove box. The carbon tube was heated to 1573 K and held for 5 min by vacuum induction melting. The obtained granules were ground into powders, which was sintered into dense ingots by hot-pressing at 1173 K over 30 min under a pressure of 60 MPa. The relative density of all the obtained ingots is larger than 93%. All the preparation processes were handled inside an argon-filled glovebox.

2.2 Material characterization

All X-ray diffraction (XRD) patterns were collected on the powder samples by a PANalytical X’pert diffractometer (Cu Kα radiation, $\lambda = 1.5418 \text{ Å}$). Microstructure and elemental distribution were characterized by a scanning electron microscope (SEM; Thermo Scientific, Quattro S). The electrical properties of XCuSb were measured by the Linseis LSR-3 instrument from 320 to 1010 K. The thermal conductivity was calculated by $\kappa_{tot} = \rho c_p D$. The thermal diffusivity coefficient ($D$) was measured by the Netzsch LFA-467 instrument from 320 to 1010 K. The densities ($\rho$) of the samples were obtained by measuring the mass/volume ratio. The heat capacities ($c_p$) were determined from the theoretical values of the Dulong–Petit formula. The lattice thermal conductivity ($\kappa_L$) was obtained by the relationship of $\kappa_L = \kappa_{tot} - \kappa_e$. 

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The electronic thermal conductivity ($\kappa_e$) was calculated by the Wiedemann–Franz law, $\kappa_e = \sigma LT$, where $L$ is the Lorenz constant given by the single parabolic band (SPB) model, as described in the Electronic Supplementary Material (ESM). The room-temperature sound velocities were obtained by the ultrasonic pulse-echo method. The carrier concentration and mobility at 320 K were obtained via Hall measurements performed under a magnetic field of $\pm 1$ T.

### 2.3 Density functional theory (DFT) calculations

The electronic band structures were calculated within the DFT [38,39], as implemented in the Quantum Espresso packet [40]. The exchange-correlation functional was in the form of Perdew–Burke–Ernzerhof [41] with the norm-conserving pseudopotentials and spin–orbit coupling considered. A $17 \times 17 \times 9$ Monkhorst–Pack $k$-points and a plane–wave cutoff of 120 Ry were used for converged results. In addition, the advanced method by considering the quasiparticle properties with the GW$_0$ approximation was adopted for accurate band structures [42]. The spin–orbit coupling effect was included in the band structure calculations [43]. Based on the GW$_0$ calculated results, we employed the Boltzmann theory [44] and the maximally localized Wannier function [45] with a very dense $96 \times 96 \times 96$ mesh in the whole Brillouin zone to compute the electronic transport coefficients. The $p$-type relaxation time could be obtained by fitting the experimental results, and the $n$-type value was given based on the deformation potential theory, as described in the ESM.

### 3 Results and discussion

XCuSb compounds possess hexagonal layered structures and belong to the space group of $P6\overline{3}mmc$ [46]. As shown in Fig. 1(a), XCuSb is composed of two planar units, i.e., the loose mono-hexagonal layer with ionically bonded $X$ atoms and the honeycomb covalently bonded $CuSb$ layer, stacked alternatively along the $c$-direction with weak interlayer interactions. This unique crystal structure may simultaneously achieve strong lattice vibrational anharmonicity and large carrier mobility, which is highly desirable for thermoelectric materials. XCuSb can be successfully prepared by the vacuum induction melting technology with the advantages of high efficiency and energy saving, as schematically shown in Fig. 1(b). The XRD patterns of XCuSb are presented in Fig. 1(c), where their diffraction peaks match well with their standard diffraction patterns except for few Sr$_2$Sb impurities in SrCuSb. The content of the impurity phase in SrCuSb is as low as $\sim$1%, as determined by the Rietveld refinement method in the GSAS software (Fig. S1 in the ESM). With the ionic radius of $X$ ($Ca < Sr < Ba$) increasing, the low-angle shift of the diffraction peak can be observed, which indicates that the lattices are expanded by larger atomic radiiuses accordingly.

To observe the micro-morphologies of the XCuSb samples, the fractured surface was characterized by the SEM. The low-magnification image (Fig. S2 in the ESM) shows that the samples have fewer pores, which suggests that they are densely sintered. Figures 2(a)–2(c)

![Figure 1](image_url)

**Fig. 1** XCuSb ($X = Ca, Sr, Ba$): (a) crystal structures from side and top views, (b) schematic diagram of vacuum induction melting, and (c) XRD patterns.
Fig. 2  SEM images and the corresponding EDS elemental mappings on the sectional surface: (a) CaCuSb, (b) SrCuSb, and (c) BaCuSb.

display the SEM images and the corresponding EDS elemental mappings of XCuSb, indicating that the elements (Ca, Sr, Ba, Cu, and Sb) in these samples are homogenously distributed.

The band structures of XCuSb were calculated based on the DFT, as plotted in Fig. 3(a). All three compounds hold indirect band gaps with similar band structures. The band gaps of CaCuSb, SrCuSb, and BaCuSb are estimated to be 0.217, 0.218, and 0.204 eV, respectively. Due to the similar dispersions around valence band maximum (VBM) located at the Γ point, the p-type density of state (DOS) effective mass ($m^*_d$) of

Fig. 3  (a) Band structures of XCuSb. Temperature-dependent (b) electrical conductivity and (c) Seebeck coefficient. (d) Pisarenko curves plotted at 320 K and the fitted DOS effective mass in the illustration. (e) Hall carrier concentration ($n_H$) and Hall mobility ($\mu_H$) at 320 K. (f) Temperature-dependent power factor.

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we see from Fig. 3(f) that the maximum PF of BaCuSb polycrystalline thermoelectric materials. As a consequence, mXCuSb are all estimated to be 0.47

\[ 120 \text{ cm}^2\cdot\text{V}^{-1} \cdot\text{s}^{-1} \] and SrCuSb show extraordinary carrier mobility above relatively small amounts of vacancies, both BaCuSb and mXCuSb are found to be 0.90, 0.70, and 0.54 W·m⁻¹·K⁻¹ at 1010 K. Instead, the highest zT of 0.48 is realized in BaCuSb, which indicates the promising thermoelectric potential operated at high temperatures.

Figures 3(b) and 3(c) illustrate the temperature dependence of the electrical conductivity and the Seebeck coefficient for XCuSb, respectively. The electrical conductivity of all samples decreases with the elevated temperatures, which indicates the typical degenerate semiconductor behavior. The positive Seebeck coefficient within the test temperature range implies p-type characteristics. The electrical conductivity of CaCuSb is found to increase at high temperatures, which should be attributed to the bipolar effect, as evidenced by the elevated carrier concentration beyond 600 K (Fig. S3 in the ESM). Compared with SrCuSb and CaCuSb, BaCuSb is found to possess lower electrical conductivity and larger Seebeck coefficient. According to the first-principles calculations, three XCuSb systems exhibit similar valence band structure and almost identical hole DOS effective mass, which is also verified by the Pisarenko relationship, as shown in Fig. 3(d). Therefore, different values of the Seebeck coefficients should be attributed to distinct carrier concentrations based on the relation of \( S \propto m_e^* T (3 n_H)^{-2/3} \). As plotted in Fig. 3(e), the measured carrier concentrations are gradually decreased with X varying from Ca to Sr and Ba, because the gradually intensified bonding strengths between X and Cu–Sb ring diminish the cationic vacancies, giving rise to the highest carrier mobility in BaCuSb [47]. To further confirm this point, we have done additional first-principles calculations to compare the formation energy of the cationic vacancies in XCuSb based on a modal of one X vacancy in a \( 3 \times 3 \times 3 \) supercell. The results for CaCuSb, SrCuSb, and BaCuSb are 103, 121, and 153 meV, respectively, which also imply fewer vacancies in BaCuSb. Benefiting from the honeycomb Cu–Sb lattice and relatively small amounts of vacancies, both BaCuSb and SrCuSb show extraordinary carrier mobility above 120 cm²·V⁻¹·s⁻¹, which are competitive among polycrystalline thermoelectric materials. As a consequence, we see from Fig. 3(f) that, the maximum PF of BaCuSb can reach 0.9 mW·m⁻¹·K⁻², and the value of SrCuSb exceeds 1 mW·m⁻¹·K⁻² at 1010 K, which are comparable with those of typical thermoelectric materials such as Cu₃Se [48], Mg₃Sb₂ [49], and half-Heuslers [50].

Figure 4(a) plots the temperature-dependent total thermal conductivities of XCuSb. The \( \kappa_{\text{tot}} \) values of the three compounds are relatively high, especially at room temperature, due to the large electronic counterpart arising from high carrier concentrations. By comparison, the \( \kappa_{\text{tot}} \) of BaCuSb is lower than those of the others within the whole temperature range, which decreases from 3.9 W·m⁻¹·K⁻¹ at room temperature to 1.89 W·m⁻¹·K⁻¹ at 1010 K. Figure 4(b) shows the lattice thermal conductivity (\( \kappa_l \)) of XCuSb as a function of temperature, which is obtained by subtracting the electronic thermal conductivity (\( \kappa_e \)) from \( \kappa_{\text{tot}} \), based on the SPB model in the ESM. At the high temperature of 1010 K, the lattice thermal conductivities of CaCuSb, SrCuSb, and BaCuSb are 0.90, 0.70, and 0.54 W·m⁻¹·K⁻¹, respectively. Such low thermal conductivities are favorable for the development of high-temperature thermoelectric devices. Due to the simultaneously lower thermal conductivity and larger power factor, BaCuSb exhibits the best thermoelectric performance among the three compounds. Figure 4(c) depicts the \( zT \) values of XCuSb as a function of temperature. Suffering from the much high carrier concentrations, the peak \( zT \) values of CaCuSb and SrCuSb can only reach 0.14 and 0.30 at 1010 K, respectively. Instead, the highest \( zT \) of 0.48 is realized in BaCuSb, which indicates the promising thermoelectric potential operated at high temperatures.

To elucidate the origins of the intrinsic low lattice thermal conductivity, the phonon dispersions, scattering rates, and atomic displacement parameters (ADPs) of BaCuSb were calculated. The phonon dispersions (Fig. 4(d)) of BaCuSb along high symmetry lines show that the highest occupied frequency is close to 5 THz, which is comparable to those of the advanced thermoelectric materials, such as SnSe [51,52] and SnS [53,54]. Meanwhile, the highest frequency of the acoustic branch is as low as 2.0 THz. These phenomena suggest that BaCuSb has a low phonon group velocity (\( v_{ph} \)). The experimental results of longitudinal (\( v_l \)), transverse (\( v_t \)), and mean (\( v_s \)) sound velocities of BaCuSb are 3808, 2278, and 2521 m/s, respectively, which are in good agreement with the theoretical values fitted from the calculated phonon dispersions (\( v_l = 3812 \) m/s and \( v_s = 2177 \) m/s) and verify the low phonon group velocity. Another key factor that determines the lattice heat...
transport is the phonon scattering rate. As shown in Fig. 4(e), BaCuSb has a large phonon scattering rate with an averaged value of \(-0.28\) ps\(^{-1}\), which means a short phonon lifetime (\(\tau\)). Low \(v_{\text{ph}}\) and short \(\tau\) effectively reduce the mean free path (MFP) of phonons \((l = v_{\text{ph}} \tau)\), and thus lead to intrinsic low lattice thermal conductivity. To deeply understand the strong phonon scattering, the ADPs are simulated, as indicated in Fig. 4(f), which reflects the strength of the vibrational anharmonicity. The ADPs of Ba are isotropic and relatively high, indicating the weak bonding feature along both intralayer and interlayer directions. In comparison, the ADPs of Cu and Sb are highly anisotropic. Both atoms exhibit much stronger vibrational anharmonicity along the \(z\)-axis, which should be responsible for the larger phonon scattering rate. This indicates that the weak bonds between Cu–Sb rings and Ba atoms can result in strong interlayer lattice vibration, thereby effectively scattering phonons. According to the gas-dynamic thermal conductivity model \((\kappa_L = \frac{1}{3} c_v v_{\text{ph}}^2 \tau, \kappa_T = \frac{1}{3} c_p v_{\text{ph}} \tau)\), where \(c_v\) is the heat capacity at constant volume), the intrinsic low \(\kappa_L\) of BaCuSb should be attributed to the synergistic effects of both small group velocity and strong phonon scattering.

To further evaluate the thermoelectric potential of BaCuSb, we calculate its \(zT\) values at different temperatures as a function of carrier concentration based on the DFT and Boltzmann transport equations. Figure 5(a) shows the chemical potential (\(\mu\)) dependent power factors at different temperatures. There is little room for the improvement of the PF for p-type BaCuSb, and its maximum value is about 1 mW·m\(^{-1}\)·K\(^{-2}\). However, the PF\(_{\text{max}}\) of n-type is 3 times that of p-type, which can reach 3 mW·m\(^{-1}\)·K\(^{-2}\). This is attributed to the higher band degeneracy of conduction pockets, as compared in Fig. 5(b). Figures 5(c) and 5(d) plot the \(zT\) values as a function of carrier concentration under different temperatures. At present, the carrier concentration of p-type BaCuSb is relatively high. If the carrier concentration can be appropriately reduced, the maximum \(zT\) value will be increased by 20%, which can reach 0.58 at 1010 K with the optimized carrier concentration of \(9.7 \times 10^{19}\) cm\(^{-3}\). Benefiting from the high band degeneracy, n-type BaCuSb exhibits better thermoelectric performance, and the maximum \(zT\) value can reach 1.12 at 1010 K with the carrier concentration of \(2.7 \times 10^{20}\) cm\(^{-3}\). Such high \(zT\) is comparable with those of state-of-the-art high-temperature thermoelectric materials, implying the promising potential of BaCuSb. Note that it is hard to dope the XCuSb and other ZrBeSi-type materials to n-type regimes due to the unique crystal structure. Despite the poor doping efficiency, it is believed that these compounds can be doped to n-type regimes by seeking appropriate dopants and preparation methods, which requires more experimental efforts.
Fig. 5 BaCuSb: (a) chemical potential and temperature dependence of the power factor, and (b) isoenergetic surface for the VBM and CBM. Carrier concentration dependence of (c) p-type and (d) n-type $zT$ values. The spherical symbols are the experimental results.

4 Conclusions

In summary, the thermoelectric properties of planar Zintl compounds $X$CuSb ($X = \text{Ca, Sr, Ba}$) have been investigated through comprehensive experimental measurements and theoretical calculations. Both SrCuSb and BaCuSb exhibit high carrier mobility exceeding 120 cm$^2$·V$^{-1}$·s$^{-1}$, owing to the honeycomb Cu–Sb conductive channels and moderate carrier concentrations, which result in excellent p-type power factors of $\approx$1 mW·m$^{-1}$·K$^{-2}$. Besides, all the $X$CuSb compounds hold low lattice thermal conductivity at high temperatures, especially for BaCuSb (0.54 W·m$^{-1}$·K$^{-1}$ at 1010 K). The first-principles calculations uncover the physical origins underlying low $\kappa_L$: Weak chemical bonds between $X$ atoms and Cu–Sb sublattices give rise to small sound velocity and strong vibrational anharmonicity. Finally, the p-type $zT$ of BaCuSb can reach 0.48 at 1010 K, and theoretical predictions suggest a much higher n-type $zT$ beyond 1.1 due to larger conducting band degeneracy. Our study reveals important implications for understanding the thermal and electrical transport properties of planar Zintl-phase compounds and broadens the research areas for the development of high-temperature thermoelectric materials.

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Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

Electronic Supplementary Material

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