Optimizing the Dopant and Carrier Concentration of Ca$_5$Al$_2$Sb$_6$ for High Thermoelectric Efficiency

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The effects of doping on the transport properties of Ca$_5$Al$_2$Sb$_6$ are investigated using first-principles electronic structure methods and Boltzmann transport theory. The calculated results show that a maximum $ZT$ value of 1.45 is achieved with an optimum carrier concentration at 1000 K. However, experimental studies have shown that the maximum $ZT$ value is no more than 1 at 1000 K. By comparing the calculated Seebeck coefficient with experimental values, we find that the low dopant solubility in this material is not conductive to achieve the optimum carrier concentration, leading to a fairly complex crystal structure as shown in Fig. 1. A 2 × 2 × 1 supercell is shown in the figure for a better illustration of the bonding structure. This complex structure provides ample space for materials optimization.

$\begin{align*}
\text{ZT} &= \frac{S^2\sigma T}{\kappa_e + \kappa_l + \kappa_G} \\
S &= \text{Seebeck coefficient} \\
\sigma &= \text{electrical conductivity} \\
T &= \text{temperature} \\
\kappa_e &= \text{electric thermal conductivity} \\
\kappa_l &= \text{lattice thermal conductivity} \\
\kappa_G &= \text{Gruneisen term for heat capacity}
\end{align*}$

The global trend of energy use is moving towards sustainable development and the waste-to-energy concept is being highly promoted as a part of this effort. Thermoelectric devices can convert some of waste heat into useful electricity. In essence, thermoelectric coolers and generators are heat engines thermodynamically similar to conventional vapor power generation or heat pumping cycles, but they use electrons as the working fluid instead of gases or liquids. Thus, thermoelectric devices have the advantages of being solid-state devices, low maintenance costs and long lifetime. Currently, the two main focuses in thermoelectrics research are the discovery of new materials with high thermoelectric efficiency and the design and optimization of thermoelectric generators. Our work focuses on materials optimization for thermoelectric applications.

$\text{Ca}_5\text{Al}_2\text{Sb}_6$ is a promising thermoelectric material, not only because Ca, Al, and Sb are inexpensive and non-toxic but also because Ca$_5$Al$_2$Sb$_6$ possesses an extremely low lattice thermal conductivity. In addition, the total $\kappa$ is not significantly affected by doping. More importantly, Ca$_5$Al$_2$Sb$_6$ contains both covalent and ionic bondings, leading to a fairly complex crystal structure as shown in Fig. 1. A 2 × 2 × 1 supercell is shown in the figure for a better illustration of the bonding structure. This complex structure provides ample space for materials optimization, and controlling the carrier concentration has been a primary means to improve the thermoelectric conversion efficiency ($ZT$) of Ca$_5$Al$_2$Sb$_6$. Several experiments have been done to improve the thermoelectric properties of Ca$_5$Al$_2$Sb$_6$ by tuning the carrier concentration. For example, Na$^{+}$ doping on the Ca$^{2+}$ sites results in the highest figure of merit (a peak $ZT$ of 0.6 at 1000 K). It is known that Na has disadvantage of having a low solubility and low doping effectiveness, and Zn$^{2+}$ (substituting Al$^{3+}$) is a more effective dopant. Surprisingly, the $ZT$ value is no more than 1 at 1000 K.

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values of Zn doped samples are lower than those of Na doped samples\(^14\). Incomplete dopant activations yielding low hole concentrations have been observed in Mn\(^{2+}\) doped sample (substituting the Al\(^{3+}\) sites) and higher ZT values have not been achieved via Mn doping\(^15\).

There have also been a few theoretical studies reported for the thermoelectric properties of Ca\(_5\)Al\(_2\)Sb\(_6\)\(^17–19\). For example, in an earlier paper\(^17\), we have employed first-principles calculations and Boltzmann transport theory to investigate the thermoelectric performance of Ca\(_5\)Al\(_2\)Sb\(_6\) and have obtained results in terms of the thermoelectric powerfactor to the relaxation time ratio \((S/\sigma/\tau)\)\(^17\). In order to better compare with experiments and provide a theoretical guidance for future experiments, in this work, we use the method of Ong and coworkers\(^20\) to eliminate the uncertainly in the relaxation time \(\tau\) and estimate the values of ZT using the experimental lattice thermal conductivity. The calculated results show that the maximum ZT value at optimum carrier concentration is 1.45 at 1000 K. However, experimental studies have indicated that the maximum ZT value was no more than 1.15–15. In this paper, we would like to address the discrepancy between theory and experiment and provide some general guidance for future materials optimization towards achieving a maximum ZT value.

**Result and Discussion**

**Band Structure.** Our calculations using the TB-mBJ\(^21\) potential result a nearly direct band gap of about 0.52 eV (shown in Fig. 2), which agrees well with the experimental value of 0.5 eV\(^13\). This suggests that the TB-mBJ method may give more reliable results compared with a previous study using the Perdew-Burke-Ernzerhof (PBE) functional\(^17\). High thermoelectric performance is generally found in heavily-doped semiconductor with carrier concentrations on the order of 10\(^{19}\) to 10\(^{21}\) cm\(^{-3}\). Therefore, at high temperatures, the most important effects of the polycrystalline samples are the random orientation of the grains. In temperatures, the most important effects of the polycrystalline samples are the random orientation of the grains. In this case, the boundary effects become less important with increasing temperature. For example, Atakulov et al.\(^13–15,23\) also reported that the polycrystalline samples have larger than that of the n-type. So for the same carrier concentration and temperature, the inertial mass \(N\) is the degeneracy of the valence states near the Fermi level.

\[ S = \frac{8\pi^2 k_B^2 m^*_{\text{DOS}} T}{3e^4 h^2} \left( \frac{\pi^2}{3n} \right)^{\frac{1}{2}} \]  

where \(k_B\) is Boltzmann’s constant, \(e\) the electron charge, \(n\) the carrier concentration, and \(m^*_{\text{DOS}}\) the density-of-state effective mass. \(m^*_{\text{DOS}} = N \left( m_{\text{h}}(x) m_{\text{h}}(y) m_{\text{h}}(z) \right)^{\frac{1}{3}}\) for an anisotropic material having band masses of \(m_{\text{h}}(x), m_{\text{h}}(y),\) and \(m_{\text{h}}(z)\) along the three principle directions. \(N\) is the degeneracy of the valence states near the Fermi level. Equation (1) shows \(S\) is proportional to \(m^*_{\text{DOS}}\) temperature \(T\), and \(n^{-\frac{1}{2}}\). On the other hand, from Table 1, we can see that \(m^*_{\text{DOS}}\) of p-type doping is greater than that of n-type doping. Therefore, given the same temperature and carrier concentration, p-type materials should have higher Seebeck coefficients than those of n-type materials. The electrical conductivity is given by

\[ \sigma = n e \eta, \]  

where \(\eta\) is the carrier mobility. It is well known that the mobility \(\eta\) is inversely proportional to inertial mass \(m\)

\[ m = 3/(1/m_{\text{h}}(x) + 1/m_{\text{h}}(y) + 1/m_{\text{h}}(z)) \]

Table 1 also shows that the inertial mass \(m\) of p-type doping is smaller than that of n-type doping. So for the same carrier concentration and temperature, \(\sigma\) of the p-type material should be larger than that of the n-type.

**Transport properties of Ca\(_5\)Al\(_2\)Sb\(_6\)**. The synthesized Ca\(_5\)Al\(_2\)Sb\(_6\) samples are polycrystalline\(^13–15,23\). The scattering from grain boundaries will affect the transport properties. There is experimental evidence, however, that the boundary effects become less important with increasing temperature. For example, Atakulov et al.\(^13–15,23\) also reported that the polycrystalline samples have minor effect on the carrier mobility of Ca\(_5\)Al\(_2\)Sb\(_6\) doped with Na, Zn, and Mn above 300 K. Therefore, at high temperatures, the most important effects of the polycrystalline samples are the random orientation of the grains. In
this work, the transport properties of Ca₅Al₂Sb₆ are calculated by averaging over three principal crystal axes. The anisotropic transport properties are shown in supplemental Fig. 1. Taking into account the solubilities of dopants in Ca₅Al₂Sb₆, we only report the calculated transport coefficient for carrier concentration ranging from −0.4 e/uc to −0.01 e/uc and 0.01 h/uc to 0.4 h/uc. These parameters are more realistic than those used in our previous work (from −6.5 e/uc to 6.5 h/uc)¹⁷.

Figure 3(a,b) show the calculated Seebeck coefficient as a function of the carrier concentration for n-type and p-type Ca₅Al₂Sb₆ for $T = 300, 500, 800, 1000, \text{ and } 1200 \text{K}$. Comparing the two figures, we can see that, regardless of n-type or p-type doping, the absolute values of $S$ increase with increasing temperature and decreasing carrier concentration between 300 K and 800 K. At the same temperature and carrier concentration, the absolute values of $S$ for the p-type systems are larger than those of n-type ones. These results are consistent with the understanding that $m^\text{DOS}_{(\text{hole})} > m^\text{DOS}_{(\text{electron})}$. However, between 1000 K and 1200 K, the absolute value of $S$ first increases with increasing carrier concentration and decreasing temperature, then decreases with increasing carrier concentration. This is likely due to the enhanced bipolar transport effects at high temperature.

We have also carried out calculations beyond the rigid-band approximation by introducing dopants to the system explicitly as shown in Supplemental Fig. 3. In this calculation, one Sb is substituted by one Ga, which naturally introduces hole carriers in the system. Additional carriers can be further introduced to the system starting from the band structure calculated with dopants included. We find that the overall trend of the calculated transport properties remains unchanged. The calculated optimal $ZT$ values, however, are slightly lower than those obtained using the rigid-band approximation due to presence of defect states and distortions to the band structure near the Fermi level. Unfortunately, realistic modeling of effects of impurities is still challenging due to the enormous computational cost.

As will be discussed later, the hole carrier concentration for the Ca₄.₇₅Na₀.₂₅Al₂Sb₆ system is about 0.07 h/uc at 800 K¹³. At this temperature, the reported experimental resistivity is approximately $8.0 \times 10^{-5} \Omega \cdot \text{m}$, which can be combined with the calculated $\sigma/\tau$ to give a relaxation time $\tau = 1.7 \times 10^{-15} \text{s}$ for Ca₄.₇₅Na₀.₂₅Al₂Sb₆ at 800 K. Near

|           | $m_{\text{b1}}$ | $m_{\text{b2}}$ | $m_{\text{b3}}$ | $m^\text{DOS}_{(\text{electron})}$ | $m^\text{DOS}_{(\text{hole})}$ |
|-----------|----------------|----------------|----------------|-----------------------------------|-------------------------------|
| Electrons | 3.23           | 0.59           | 1.62           | 4.810                             | 2.6218                        |
| Holes     | 6.61           | 2.15           | 0.54           | 6.513                             | 1.1564                        |

Table 1. Calculated band effective masses along three principle axes, density of states effective mass, and inertial effective mass.
this temperature, the experimental data for this sample and others follow an approximate electron–phonon $T$ dependence, i.e., $\sigma \propto \frac{1}{T}$. Taking into account the doping effects, we have $\tau = 8.68 \times 10^{-6} T^{-1} n^{-1/3}$. Figure 3(c,d) show $\sigma$ as a function of carrier concentration for n-type and p-type Ca$_5$Al$_2$Sb$_6$ for $T = 300, 500, 800, 1000,$ and 1200 K. Regardless of n-type or p-type doping, the electrical conductivities increase with increasing carrier concentration. These figures also show that for the same carrier concentration, the conductivity decreases with increasing temperature as a result of decreased carrier mobilities. At the same temperature and carrier concentration, the absolute values of $\sigma$ of p-type doping are larger than those of n-type doping, which can be explained by the fact that $m_I$ (hole) $< m_I$ (electron).

Previous experimental studies have shown that Ca$_5$Al$_2$Sb$_6$ possesses an extremely low lattice thermal conductivity (0.6 WmK$^{-1}$ at 850 K), and the total thermal conductivity is not significantly affected by doping$^{13-15}$ (also see supplemental Fig. 2 for more details). Here we use the experimental thermal conductivity of Ca$_4.75$Na$_{0.25}$Al$_2$Sb$_6$ from the work of Toberer et al.$^{13}$, which falls within the range of the measured values for similar systems. The calculated $ZT$ as a function of $T$ and carrier concentration are shown in Fig. 3(e,f). Comparing the two figures, we find that, at the same temperature, the values of $ZT$ for the p-type systems are much higher than those for the n-type ones. Interestingly, Ca$_5$Al$_2$Sb$_6$ almost always has excess holes$^{13-15,23}$. As depicted in the figure, the optimum carrier concentration changes from $-0.01 \text{ e/uc}$ at 300 K to $0.18 \text{ e/uc}$ at 1200 K for electron-doped systems and changes from $0.01 \text{ h/uc}$ at 300 K to $0.17 \text{ h/uc}$ at 1200 K for hole-doped ones. The maximum figure of merit at the optimum carrier concentration increases from 0.21 at 300 K to 0.95 at 1200 K for n-type materials and from 0.24 at 300 K to 1.65 at 1200 K for p-type ones. Our results suggest that the maximum $ZT$ value at 1000 K is 1.45.

Choosing suitable dopants. In order to understand the remarkable difference in the maximum $ZT$ value between theory and experiment, a comparison between the calculated and experimental values$^{13-15}$ of the Seebeck coefficient is shown in Fig. 4, where $p$ represents the theoretical hole carrier per unit cell. Comparing

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**Figure 3.** Thermoelectric coefficients as functions of the carrier concentration for n-type (left) and p-type (right) Ca$_5$Al$_2$Sb$_6$ for $T = 300, 500, 800, 1000,$ and 1200 K.
the calculated and experimental values of $S$, we find that results for the supposedly intrinsic samples$^{13,14}$ are to be compared with the theoretical, carrier concentration of about 0.03–0.055 $h/uc$. This suggests that unintentional doping cannot be overlooked. In addition, the results for the Ca$_{5-x}$Na$_x$Al$_2$Sb$_6$ sample$^{13}$ are better compared with theoretical results calculated with 0.05–0.06 $h/uc$, which is only half of the nominal doping. Note that each unit cell contains two Ca$_7$Al$_2$Sb$_6$ formula units. For Ca$_{5-x}$Mn$_x$Sb$_6$ and Ca$_{5-x}$Zn$_x$Sb$_6$,$^{14}$ the corresponding hole densities are approximately 0.065–0.07 $h/uc$. Therefore, there is a significant difference between the nominal doping and the carrier concentration, and the solubility limit may play an important role. These results suggest that in the high doping region, the solid solubility limits of Na, Mn, and Zn in Ca$_7$Al$_2$Sb$_6$ may be a determining factor that controls the carrier concentration in experiment. As we have mentioned in the previous section, the optimum carrier concentration changes from 0.01 $h/uc$ at 300 K to 0.17 $h/uc$ at 1200 K.

Therefore, while comparing with the experimental results, one must consider the solubility limit of the dopant. In order to achieve the optimal carrier concentration, it is important to find suitable dopants. To this end, we have calculated the formation energy $\Delta E$ for Ca$_{5-x}$M$_x$Al$_2$Sb$_6$ ($M=\text{Na}, \text{Mg}, \text{Ga}, \text{Zn}$), Ca$_{5-x}$M$_x$Al$_2$Sb$_6$ ($M=\text{Ga}, \text{Mn}, \text{Zn}$), and Ca$_{5-x}$Al$_{2-x}$M$_x$Sb$_6$ ($M=\text{Ga}, \text{Mn}, \text{Zn}$). As an example, the formation energy of Ca$_{5-x}$Na$_x$Al$_2$Sb$_6$ is defined as

$$\Delta E = E_{(5-x)\text{Na}_x\text{Al}_2\text{Sb}_6} + xE_{(\text{Ca})} - E_{(\text{Ca}_7\text{Al}_2\text{Sb}_6)} - xE_{(\text{Na})}$$

(3)

where $E_{(5-x)\text{Na}_x\text{Al}_2\text{Sb}_6}$ and $E_{(\text{Ca}_7\text{Al}_2\text{Sb}_6)}$ are the total energies of the Ca$_7$Al$_2$Sb$_6$ with and without doping, respectively. $E_{(\text{Ca})}$ and $E_{(\text{Na})}$ are the total energies per atom of Ca and Na solids, respectively, and $x$ is the dopant concentration. We used a $2 \times 1 \times 2$ supercell containing 104 atoms for all formation energy calculations. A comparison of the formation energy for different dopants is given in Table 2. It is important to point out to the calculated formation energies are negative for Ca$_{5-x}$Ga$_x$Sb$_6$ and Ca$_{5-x}$Ga$_x$Sb$_6$, $\text{Ge}$ ($x=0.125, 0.25$, and 0.375), which suggests that these doping positions and dopants are energetically favorable. The formation energies are positive for Ca$_{5-x}$Na$_x$Al$_2$Sb$_6$, Ca$_{5-x}$Mg$_x$Al$_2$Sb$_6$, Ca$_{5-x}$Mg$_x$Al$_2$Sb$_6$, Ca$_{5-x}$Al$_x$Sb$_6$, Ca$_{5-x}$Mn$_x$Sb$_6$, and Ca$_{5-x}$Zn$_x$Sb$_6$ ($x=0.125, 0.25$, and 0.375), indicating that they are thermodynamically unstable. Interestingly, the formation energies of Ca$_{5-x}$Ga$_x$, Ca$_{5-x}$Mg$_x$, Ga$_x$, Ca$_{5-x}$Mn$_x$, and Ca$_{5-x}$Zn$_x$ change from negative to positive, which suggests a decreasing thermodynamic stability with increasing carrier concentration. From Table 2, we can conclude that Sb is the most favorable site for substitution, which is followed by Al, and Ca is least favorable site.

It would be interesting to understand why Al and Sb positions are suitable doping positions and how one can select appropriate dopants to achieve optimal carrier concentrations. In Ca$_7$Al$_2$Sb$_6$, the anionic building block is [Al$_2$Sb$_6$]$^{10-}$ and Ca atoms donate all of their valence electrons to the Al$_2$Sb$_6$ structure. The Sb(3)-Sb(3) and the Al-Sb bonds are weak to moderate covalent bonds, as shown Fig. 1(a). There is a strong Coulomb interaction between Ca cations and the [Al$_2$Sb$_6$]$^{10-}$ anion. Therefore, in Ca$_7$Al$_2$Sb$_6$, substituting Ca is the most difficult and substitution of Sb(3) is the easiest. This is consistent with the conclusion from our formation energy calculations. We also find that, for a given doping position, the formation energy is closely related to the electronic

![Figure 4. Calculated $S$ versus temperature compared with experimental data for Ca$_{5-x}$Na$_x$Al$_2$Sb$_6$ (Toberer et al.$^{13}$), Ca$_{5-x}$Mn$_x$Sb$_6$ (Zevalkink et al.$^{14}$), and Ca$_{5-x}$Zn$_x$Sb$_6$ (Snyder et al.$^{15}$), where $p$ presents the theoretical hole carrier concentration.](image-url)

| $x$ | Ca$_{5-x}$M$_x$Al$_2$Sb$_6$ | Ca$_{5-x}$M$_x$Al$_2$Sb$_6$ | Ca$_{5-x}$M$_x$Sb$_6$ |
|----|-----------------|-----------------|-----------------|
| Na | 2.943 | 2.952 | 3.606 |
| Mg | 3.911 | 2.524 | 4.542 |
| Mn | 0.125 | 1.459 | 4.456 |
| Zn | 0.25 | 1.569 | 2.414 |
| Ge | 0.375 | 1.677 | 0.289 |
| Ga | 1.125 | 1.321 | 1.290 |
| Zn | 0.674 | 0.710 | 0.994 |

Table 2. Formation Energy (eV) of Ca$_{5-x}$M$_x$Al$_2$Sb$_6$, Ca$_{5-x}$M$_x$Al$_2$Sb$_6$, and Ca$_{5-x}$Al$_{2-x}$M$_x$Sb$_6$.
configuration of the dopant. It appears that dopants with an electronic configuration that is similar to the atom being substituted usually have low formation energies. For example, the valence electronic configuration of Sb is 5s25p6. Therefore, according to the electronic configuration of the dopant, there are two classes of suitable dopants. The first class have partially occupied 4p state (e.g., Ge: 4s24p2 and Ga: 4s24p1), which is very similar to that of Sb. The second class have unoccupied 4p orbital (e.g., Zn: 4s24p0). Therefore, we conclude that it is easier to dope the system when by substituting Sb atoms with electronically compatible dopants.

Conclusion

In conclusion, we have investigated the doping effects on the thermoelectric performance of Ca₅Al₂Sb₆ using first-principles electronic structure methods coupled with Boltzmann transport theory. We find that a maximum ZT value of 1.45 can be achieved with an optimum carrier concentration at 1000 K. This value is significantly higher than experimental measurement. We point out that the discrepancy between theory and experiment is likely a result of limited solubility of dopants. Our calculations suggest that substituting Sb with electronically compatible dopants may help to reach optimal carrier concentrations, thus achieving the predicted ZT limit.

Computational Detail

The projector augmented wave method of Blöchl 25 as implemented within the Vienna Ab-initio Simulation Package (VASP) 26,27 is used for structural optimization for the ideal and doped crystal structures. The Perdew-Burke-Ernzerhof-(PBE) generalized gradient approximation 28 within the density functional theory is used. A plane wave kinetic energy cut-off of 500 eV is used for all calculations. For the Brillouin zone integration, a 5 × 5 × 5 Monkhorst-Pack 29 k point grid is used for the 26-atom primitive cell. We optimize both the lattice constants and atomic positions for all systems studied. Impurity formation energies are calculated with 2 × 1 × 2 supercells containing 104 atoms. Atoms are relaxed until the residual forces are smaller than 0.02 eV/Å. The effects of similar ionic radius substitutions (e.g., Na, Mg, and Ga for Ca; Ga, Zn, and Mn for Al; and Ge, Zn, and Ga for Sb) are studied. We find that the Sb(3) sites are the most energetically favorable.

Since the electronic transport properties are strongly affected by the band-edge states, highly accurate density functional theory calculations are performed with the WIEN2k code 30 based on the full-potential linearized augmented plane-wave (FLAPW) method. Through a systematic comparison of results calculated using different exchange-correlation potentials 31-33, we find that the band gap calculated with a modified Beck–Johnson (TB-mBJ) potential provides the best agreement with experiments 34,35. Therefore, we use the TB-mBJ potential for electronic structure calculations in this work. In FLAPW calculations, we use RMT*Kₘₐₙ = 9, which determines the matrix size, where Kₘₐₙ is the plane wave cut-off and Rₘₐₙ is the smallest atomic radius. The muffin-tin radii are chosen to be 2.5 a.u. for Ca, Al, and Sb. Self-consistent calculations are carried out with 1500 k points in the irreducible Brillouin zone and the total energy is converged to within 0.0001 Ry. We include the scalar-relativistic effects for Sb. The results from the electronic structure calculations provide the necessary inputs for calculating the transport using the BoltZTrap code 34,35 under the assumption that the relaxation time τ is direction independent.

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Author Contributions
Y.Y. carried out the calculations and drafted the manuscript; G.Z., C.W. and C.P. participated in the discussion; P.Z., W.R. and Y.W. participated in design of the study, supervised the project and provided overall guidance.

Additional Information
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