Improved thermoelectric properties in Zn-doped Ca$_5$Ga$_2$Sb$_6$

Samantha I. Johnson, Alex Zevalkink and G. Jeffrey Snyder*

Zintl compounds with the chemical formula Ca$_5$M$_2$Sb$_6$ have attracted attention as candidates for use in thermoelectric applications due to their low thermal conductivity and promising high temperature performance (i.e., $zT = 0.6$ at 1000 K in Ca$_5$Al$_2$$_x$Na$_{1-x}$Sb$_6$). We have shown previously that, relative to Ca$_5$Al$_2$Sb$_6$, both Ca$_5$Ga$_2$Sb$_6$ and Ca$_5$In$_2$Sb$_6$ have reduced phonon velocities and improved carrier mobility, suggesting that improved $zT$ can be achieved in these materials. Here we further investigate Ca$_5$Ga$_2$Zn$_x$Sb$_6$, which is an intrinsic semiconductor with a small concentration of p-type carriers. By substituting Zn$^{2+}$ on the Ga$^{3+}$ site, we show that it is possible to increase and control the carrier concentration in Ca$_5$Ga$_2$Zn$_x$Sb$_6$ and thus optimize its thermoelectric behavior. A single parabolic band model was used to estimate an effective mass of $m^* = 1.6m_e$, which is slightly lower than Al-based compounds. Though the reduced $m^*$ leads to a lower Seebeck coefficient, it also leads to a much higher electronic mobility. The high mobility leads to increased thermoelectric figure of merit ($zT$) at low and intermediate temperatures relative to Zn-doped Ca$_5$Al$_2$Sb$_6$. However, due to the decreased band gap in Ca$_5$Ga$_2$Sb$_6$ relative to Ca$_5$Al$_2$Sb$_6$, the maximum $zT$ in optimally doped Ca$_5$Ga$_2$Zn$_x$Sb$_6$ is reduced (peak $zT \sim 0.35$ at $T = 775$ K).

Introduction

Thermoelectric devices are able to directly convert heat to electricity, making them relevant to today’s energy concerns. These devices are currently used for energy generation in deep-space missions and waste heat recovery in industry, and they have the potential to increase the overall efficiency of automobiles. However, widespread use of thermoelectric materials has been limited by their poor efficiency. The maximum efficiency of these materials is governed by the thermoelectric figure of merit, $zT = \frac{775 K}{2k_B} \alpha^2 T \rho$, where $\alpha$ is the Seebeck coefficient, $\rho$ is electrical resistivity, and $k$ is the thermal conductivity. To optimize $zT$, a careful balance between these properties must be found.

The ideally engineered thermoelectric material has the electronic properties of a crystal and the low thermal conductivity of a glass, giving rise to the term “electron-crystal, phonon-glass”.

Zintl phases, characterized by covalently bonded anionic structures surrounded by ionically bonded cations, have been recently recognized as promising thermoelectric materials. The need to satisfy valence often leads to incredibly complex structures, making many Zintl compounds natural “phonon glasses”. At the same time, the complex, often highly anisotropic, covalent structures can potentially be harnessed for electronic conduction, leading to the desired “electron crystal” behavior.

Among Zintl compounds, a diverse array of polyanions can be found, ranging from isolated (0-dimensional) MnSb$_4$ tetrahedra and linear Sb trimers found in Yb$_4$MnSb$_{11}$, to the 3-dimensional, cage-like networks that characterize clathrate and skutterudite compounds. Excellent thermoelectric properties ($zT$ greater than 1) have been demonstrated in compounds at both ends of this spectrum as well as in compounds with 2-dimensional anionic structures (i.e., AM$_2$Sb$_3$ compounds, where A = alkaline or rare earth metal and M = transition metal).

Zintl compounds based on 1-dimensional anionic chains have only recently become of interest for thermoelectric applications. Ca$_5$Al$_2$Sb$_6$, Sr$_5$GaSb$_3$, and Ca$_5$Al$_2$Sb$_6$ are a few examples, each forming a different crystal structure based on chains of corner-linked M$_2$Sb$_4$ tetrahedra. All are intrinsic semiconductors with low lattice thermal conductivity (~0.6 W m$^{-1}$ K$^{-1}$) and promising high temperature thermoelectric properties ($zT > 0.6$) when optimally doped. Of these chain-forming crystal structures, that of Ca$_5$Al$_2$Sb$_6$ (Ca$_5$Ga$_2$As$_6$ structure type) is the most tolerant of chemical substitutions; Ga or In can substitute for Al, and Sr, Ba, or Eu, can substitute for Ca (in the In analogue). The Ca$_5$Ga$_2$As$_6$ structure type, shown in Fig. 1 for Ca$_5$Ga$_2$Sb$_6$, is comprised of chains of corner-linked GaSb$_4$ tetrahedra. Neighboring chains are joined by Sb-Sb bonds to form infinite ladder-like structures. Valence counting in these anionic chains finds two Sb$^{4-}$ bridging across the chains, two corner sharing Sb$^{5-}$ linking tetrahedra along the...
chain, and two Sb$^{2-}$ that are covalently bonded only to the Ga. The two Ga atoms are each bonded to four antimony atoms, yielding a formal valence of $-1$. Surrounding the “ladders” are five Ca$^{2+}$ cations, which provide overall charge balance.$^{22,23}$

Our recent study comparing undoped Ca$_5$M$_2$Sb$_6$ compounds (M = Al, Ga, In) showed decreased phonon velocities and improved electronic mobility in the undoped Ga and In analogues relative to undoped Ca$_5$Al$_2$Sb$_6$. This motivates us to study Ca$_5$Ga$_2$Sb$_6$, despite the disadvantage of the increased cost of Ga relative to Al. Ca$_5$Ga$_2$Sb$_6$ like the Al analogue, requires doping to optimize its electronic properties and realize its maximum possible $zT$. We have previously shown that Ca$_5$Al$_2$Sb$_6$ can be doped with Na on the Ca site, or with Zn or Mn on the Al site to increase the p-type carrier concentration, thereby drastically improving the $zT$.$^{24,25}$ Zn doping yielded the best control of the carrier concentration, and is therefore used here. This study explores the properties of Ca$_5$Ga$_2$$_{1-x}$Zn$_x$Sb$_6$ with $x$ ranging from 0 to 0.3. We use a combination of high temperature electronic and thermal transport measurements and simple modeling assuming a single parabolic band to characterize and optimize the thermoelectric properties of this system.

**Results and discussion**

The phase purity of the Ca$_5$Ga$_2$$_{1-x}$Zn$_x$Sb$_6$ ($x = 0, 0.05, 0.1, 0.2, 0.3$) samples and the reference sample was determined by XRD and SEM. Representative patterns of the $x = 0$ and $x = 0.3$ samples can be seen in Fig. 2. A simulated Rietveld fit using the reported crystal structure is also shown underneath.$^{22}$ The reflection denoted by an asterisk in the undoped sample is a secondary phase, identified as CaSb$_2$ using EDS. In all of the Ca$_5$Ga$_2$$_{1-x}$Zn$_x$Sb$_6$ ($x = 0, 0.05, 0.1, 0.2, 0.3$) samples, a small fraction (~1 volume%) of this secondary phase was observed for comparison, an Al-based sample (Ca$_5$Al$_{1-x}$Zn$_x$Sb$_6$) was also synthesized for this study. The Al-based reference sample was synthesized using the method described in,$^{25}$ with one exception: the hot pressing temperature was increased from 873 K to 1073 K. This change was made to correct for the extremely low mobility in our initial study of Zn-doped Ca$_5$Al$_2$Sb$_6$. For Al-based samples of the Ca$_5$M$_2$Sb$_6$ system, large decreases in mobility were observed for $x > 0$. As shown in Fig. 2, the Al-based reference sample shows a similar decrease in mobility for $x > 0$, hence we focus only on the Ga-doped samples in this study.

**Experimental**

Ca$_5$Ga$_2$$_{1-x}$Zn$_x$Sb$_6$ samples with $x = 0.05, 0.1, 0.2, 0.3$ were prepared for this study. For undoped Ca$_5$Ga$_2$Sb$_6$ ($x = 0$), we present data from our prior work.$^{24}$ The initial GaSb precursor was formed from 99.99% Ga shot and 99.9999% Sb shot, which was mixed in equimolar amounts and vacuum sealed in a quartz tube. The mixture was held at 973 K for 12 hours and then quenched in water. The GaSb was subsequently crushed and mixed with stoichiometric amounts of 99.99% Ca dendrites, 99.99% Zn shot, and 99.9999% Sb shot from Sigma Aldrich and loaded into stainless steel vials with stainless steel balls in an argon-filled glove box. The mixture was milled for 1 h in a SPEX Sample Prep 8000 Series Mixer/Mill. The resulting powder was pressed in graphite dies (from POCO) in argon. Before pressing, the powder was held at the minimum load at 873 K for 2 h to ensure complete reaction of the GaSb. The powder was then consolidated at 973 K under 110 MPa of pressure for 3 h followed by a 2 h stress-free cool down.

For Al-based samples of the Ca$_5$M$_2$Sb$_6$ system, large decreases in mobility were observed for $x > 0$. As shown in Fig. 2, the Al-based reference sample shows a similar decrease in mobility for $x > 0$, hence we focus only on the Ga-doped samples in this study. For comparison, an Al-based sample (Ca$_5$Al$_{1-x}$Zn$_x$Sb$_6$) was also synthesized for this study. The Al-based reference sample was synthesized using the method described in,$^{25}$ with one exception: the hot pressing temperature was increased from 873 K to 1073 K. This change was made to correct for the extremely low mobility in our initial study of Zn-doped Ca$_5$Al$_2$Sb$_6$. For Al-based samples of the Ca$_5$M$_2$Sb$_6$ system, large decreases in mobility were observed for $x > 0$. As shown in Fig. 2, the Al-based reference sample shows a similar decrease in mobility for $x > 0$, hence we focus only on the Ga-doped samples in this study.
during SEM analysis (visually determined from the estimated ratio of the CaSb₂ area to that of the matrix phase). The CaSb₂ content does not appear to increase with Zn concentration. The geometric density of the samples ranges from 97–98% of the theoretical density, and grain sizes for the samples, estimated from SEM analysis of fracture surfaces, range from 1–5 μm.

Electronic transport properties

Our initial investigation of the Ca₅M₂Sb₆ compounds (M = Al, Ga, In) revealed non-degenerate semiconducting behavior and low p-type carrier concentration (~10¹⁸ h⁺ per cm³) in all three compounds. Relative to the Al- and In-based compounds, Ca₅Ga₂Sb₆ samples exhibited both a reduced band gap (E_g), determined from high temperature resistivity and Seebeck measurements, and improved hole mobility. These experimental results were consistent with density functional theory (DFT) calculations, which predicted a lighter valence band effective mass (m*) and a smaller E_g (~0.4 eV) arising from the low energy (relative to Al-Sb or In-Sb) Ga-Sb anti-bonding states at the conduction band edge. In thermoelectric materials, light m* and the corresponding high mobility are desirable, while a small band gap can be detrimental, particularly at high temperature materials.

To optimize the electronic properties of Ca₅Ga₂Sb₆, electronic doping is necessary. Motivated by the successful use of Zn²⁺ as a dopant to replace Al³⁺ in Ca₅Al₂Sb₆ here we substitute Zn²⁺ on the Ga³⁺ site. Simple valence counting predicts that each Zn substitution will yield one free hole. This simple assumption is accurate at low Zn concentrations, as illustrated by the inset in Fig. 3a. The room temperature Hall carrier concentration, n_H, is similar to the theoretical carrier concentration, n (dashed line) for x < 0.2, but diverges when x > 0.3. This divergence might be explained by a low solubility of Zn in this system or by the formation of compensating n-type defects. The highest achieved n_H is ~6 × 10²⁰ h⁺ per cm³, which is significantly higher than the maximum n_H obtained in Zn-doped Ca₅Al₂Sb₆. The ability to dope Ca₅Ga₂Sb₆ to a greater extent than Ca₅Al₂Sb₆ may result from Ga compound’s smaller band gap; this may permit a Fermi level further from the valence band edge before the system forms compensating defects.

Additionally, the more closely matched ionic radii of the Ga and Zn atoms may allow for a larger solubility of Zn, and thus higher maximum doping levels compared to the Al compound.

As the Hall carrier concentration increases in magnitude, the temperature dependence exhibits a transition from intrinsic to extrinsic semiconducting behavior, as shown in Fig. 3a. In the undoped sample, n_H increases exponentially due to intrinsic carrier activation, resulting in a change in the majority carrier type above 650 K (unfilled blue symbols indicate negative data). This explanation relies on the assumption that the electrons have higher mobility than the holes, and thus dominate the Hall coefficient. A detailed discussion of this behavior can be found in Zevalkink et al. In contrast, the temperature independent carrier concentrations of the doped samples are indicative of metallic behavior with transport dominated by extrinsic carriers. For comparison, we have included a representative Ca₅Al₁ₓZnₓSb₆ sample with x = 0.1. In both the Al and Ga analogues with x = 0.1, the carrier concentration values and trends are in agreement.

As shown in Fig. 3b, with increasing x, the resistivity (ρ) decreases by nearly two orders of magnitude due to the increase in hole concentration. In the doped samples, resistivity increases with temperature due to decreasing hole mobility (Fig. 3c). In contrast, the undoped sample has resistivity that decreases with temperature due to the competing effect of intrinsic carrier activation. As discussed in ref. 24, a reversible discontinuity in the data around 600 K (also observed in Ca₅In₁ₓSb₆) may be due to a phase transition. The resistivity of Ca₅Al₁ₓZnₓSb₆ is shown for comparison.
The Hall mobility ($\mu$), calculated from $\rho = 1/ne$, is shown in Fig. 3c. At room temperature, $\mu$ in the undoped sample is more than twice that of the doped samples. The mobility of the doped samples, in general, decreases with increasing $x$, though still remains higher than observed in either Na- or Zn-doped Ca$_5$Al$_2$Sb$_6$. Note that the Al-based reference sample synthesized for this study has higher mobility than the samples in our previous report on Zn-doped Ca$_5$Al$_2$Sb$_6$. This may be due to improved microstructure (larger grain size) resulting from the increased hot pressing temperature used in the current study. Compared with Ca$_5$Al$_{1.9}$Zn$_{0.1}$Sb$_6$, the mobility of Ca$_5$Ga$_{1.9}$Zn$_{0.1}$Sb$_6$ is improved by ~20%, which is beneficial to the compound’s performance and figure of merit. In all doped samples, the temperature dependence of $\mu$ is indicative of acoustic phonon scattering (described by $\mu \propto T^{-\nu}$, where $\nu$ ranges from 1 to 1.5 for degenerate and non-degenerate semiconductors, respectively). For all Zn-doped samples in this study, $\nu$ ranges from 1.3 to 1.7. Note that the near-zero mobility above 600 K in the undoped sample stems from the assumption of a single carrier type, and does not represent the true drift mobility of the holes.

The Seebeck coefficients ($\alpha$) are shown in Fig. 4 up to 873 K. The undoped sample displays a large room temperature Seebeck coefficient characteristic of a nondegenerate semiconductor. It then rapidly decreases with increasing temperature due to the thermally activated minority carriers observed in the Hall effect. With increasing $x$, the Seebeck coefficients decrease and exhibit increasingly linear temperature dependences. Relative to Ca$_5$Al$_{2-x}$Zn$_x$Sb$_6$ (plotted for $x = 0.10$ case), the reduction of $\alpha$ in Ca$_5$Ga$_{2-x}$Zn$_x$Sb$_6$ samples due to minority carriers begins at lower temperature. The magnitude and temperature at which the Seebeck coefficient peaks ($\alpha_{\text{max}}$ and $T_{\text{max}}$) can be used to roughly estimate the band gap $E_g$. This estimate yields $E_g = 0.2$–0.3 eV, in contrast to the larger estimate of 0.4 eV in Ca$_5$Al$_2$Sb$_6$.

The relationship between $\alpha$ and $n_y$ (shown in Fig. 5) is well described by a single parabolic band model (SPB), assuming an effective mass of $1.6m_e$ and that acoustic phonons are the primary scattering source. A more detailed description of this model can be found in ref. 13 and 19. A single band model cannot account for minority carriers effects at high temperature, and is thus only used to 500 K. Consistent with prior DFT results, which predicted a lighter valence band in Ca$_5$Ga$_2$Sb$_6$, relative to both the In and Al analogues, our experimental effective mass of $1.6m_e$ is significantly lower than that observed in Ca$_5$Al$_2$Sb$_6$ samples ($2.2m_e$). In all Ca$_5$M$_2$Sb$_6$ compounds, the calculated band structures predict significant deviations from parabolic behavior when the Fermi energy is far from the band edge, as expected from heavy doping. Since Ca$_5$Ga$_2$Sb$_6$ can be doped to higher hole concentrations than the Al analogue, it provides an opportunity to experimentally probe deeper into the valence band. However, we are unable to confirm the expected non-parabolic behavior, as even the most heavily doped samples are reasonably well described by a constant effective mass, within experimental error.

**Thermal transport properties**

The total thermal conductivity, shown in Fig. 6a, is calculated from the measured thermal diffusivity ($D$) according to the equation $\kappa_{\text{total}} = C_pD\rho$, where in this case $\rho$ is the geometric density and $C_p$ is the Dulong–Petit heat capacity. Note that our use of the Dulong–Petit heat capacity may underestimate the heat capacity, and thus the thermal conductivity, by 10–20% at very high temperatures. The total thermal conductivity is the sum of three components: the electronic ($\kappa_e$), bipolar ($\kappa_B$), and lattice ($\kappa_l$) contributions. The electronic component has been estimated from the Wiedemann–Franz equation, $\kappa_e = \frac{L}{T} \frac{\rho}{\pi}$, where $L$ is the Lorenz number calculated using the SPB model (shown in the inset in Fig. 6). Thus, the total thermal conductivity tends to increase with increasing dopant concentration, as $\rho$ decreases. Comparison with the $x = 0.1$ case of Ca$_5$Al$_{2-x}$Zn$_x$Sb$_6$ is shown as well.

Lattice thermal conductivity (Fig. 6b) is obtained by subtracting $\kappa_e$ from $\kappa_{\text{total}}$, providing that the bipolar contribution is
negligible. This is clearly not the case for the undoped material, in which $\kappa_{\text{total}} - \kappa_\text{e}$ rises with temperature above 600 K, indicating that there is a significant bipolar contribution. In contrast, the Zn-doped samples show no obvious indication of a bipolar contribution; in these, $\kappa_{\text{total}} - \kappa_\text{e}$ decreases with temperature approximately as $1/T$, characteristic of lattice thermal conductivity limited by Umklapp phonon–phonon scattering.\(^7\)

The minimum lattice thermal conductivity ($\kappa_{\text{min}}$)\(^3, 7\) places a theoretical lower limit on $\kappa_\text{e}$, which derives from the minimum allowed scattering distance ($l = \lambda/2$) for phonons with wavelength $\lambda$. At high temperatures, $\kappa_{\text{min}}$ can be approximated by eqn (1), where $V$ is the average volume per atom and $\nu_T$ and $\nu_L$ are the transverse and longitudinal sound velocities, respectively. Ultrasonic measurements of $\nu_T$ and $\nu_L$ for undoped Ca$_5$M$_2$Sb$_6$ compounds (M = Al, Ga, In) are detailed in ref. 24. Relative to Ca$_5$Al$_2$Sb$_6$, the higher density and lower stiffness in Ca$_5$Ga$_2$Sb$_6$ lead to lower speed of sound, and thus lower $\kappa_{\text{min}}$

$$\kappa_{\text{min}} = \frac{1}{2} \left( \frac{\pi}{6} \right)^{1/3} k_B V^{-2/3} (\nu_T + \nu_L).$$ (1)

The dashed line in Fig. 6b denotes the estimated $\kappa_{\text{min}}$ for Ca$_5$Ga$_2$Sb$_6$. Unlike in doped Ca$_5$Al$_2$Sb$_6$ samples (of which the $x = 0.10$ case is plotted), which actually reach the predicted $\kappa_{\text{min}}$ at high temperatures, $\kappa_\text{e}$ in Zn-doped Ca$_5$Ga$_2$Sb$_6$ remains

conspicuously high. This may suggest that a small, but not negligible, bipolar contribution is present even in the most heavily Zn-doped samples. This is likely an additional adverse effect of the small band gap in Ca$_5$Ga$_2$Sb$_6$, limiting the potential of this compound for high temperature applications.

**Figure of merit**

The figures of merit for Ca$_5$Ga$_2$$_x$Zn$_x$Sb$_6$ samples, calculated using polynomial fits to the experimental data, are shown in Fig. 7. At low temperatures, the effect of the increased mobility in the Ga compound dominates, leading to an apparent improvement in $zT$ from 400 to 750 K relative to the Al-based material. This may be due to the reduced effective mass in Ca$_5$Ga$_2$Sb$_6$: when acoustic phonons dominates the charge carrier scattering, the quality factor, which determines the $zT$ of optimally doped materials, is given by $B = \frac{N_e}{m^*_{\text{e}} \kappa_L}$ ($m^*_\text{e}$ is the mass of a single hole pocket along the conduction direction and $N_e$ is the number of bands contributing to transport). Note however that the $zT$ improvement in this study is within the generally accepted uncertainty in $zT$ of about 20%.

Compared with optimally Zn-doped Ca$_5$Al$_2$Sb$_6$, the $zT$ in Zn-doped Ca$_5$Ga$_2$Sb$_6$ is detrimentally affected by minority carriers at high temperature, leading to a lower peak $zT$. A maximum $zT$ of about 0.35 is reached at 775 K in the samples with $x = 0.05$ and $x = 0.1$. Beyond $x = 0.1$, the maximum $zT$ decreases, suggesting that the optimal doping level for this compound is surpassed. Using an SPB model at 500 K with $m^* = 1.6m_0$, and an intrinsic mobility of 9 cm$^2$ V$^{-1}$ s$^{-1}$, we estimate an optimal carrier concentration of $\sim 10^{20}$ cm$^{-3}$. This corresponds to the most lightly doped sample ($x = 0.05$), consistent with the experimental results.

**Conclusion**

In this study, Ca$_5$Ga$_2$Sb$_6$ was successfully p-doped with Zn, leading to metallic behavior and greatly improved
thermoelectric properties. The Ga-based material, when optimally doped, exhibits an increased mobility over the Al analogue, attributed to the reduced effective mass predicted by DFT calculations. The reduction in effective mass was also reflected in the measured Seebeck coefficients at 300 K and 500 K; a single band model yielded \( m^* = 1.6 m_e \) in Zn-doped Ca₅Ga₂Sb₆ in contrast to \( m^* = 2.0 m_e \) in Ca₅Al₂Sb₆. Additionally, detrimental effects from the smaller band gap in Ca₅Ga₂Sb₆ were observed: minority carrier activation leads to both compensated Seebeck coefficients and bipolar thermal conductivity at high temperatures. The high cost of Ga must also be considered. Ultimately, the improved electronic mobility of the Ga compound yields an increase in \( zT \) between 400 and 800 K relative to the Al analogue. However, due to the reduced band gap, and hence reduced Seebeck coefficient and high bipolar thermal conductivity, of Ca₅Ga₁₋ₓZnxSb₆, the peak \( zT \) is lower than the Al analogue.

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