Enhancement of thermoelectric performance of YbMg$_2$Bi$_2$-based materials by alloying and doping with suppressed bipolar effect

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Abstract. Here we report the enhanced thermoelectric performances of the YbMg$_2$Bi$_2$-based compounds. The formation of Yb$_{0.8-x}$Ca$_x$Mg$_{0.2}$Mg$_2$Bi$_{1.96}$ ($x = 0, 0.2, 0.4,$ and 0.6) solid solutions effectively decreases the thermal conductivity. Besides, the bandgap of the compounds is widened due to the larger bandgap of CaMg$_2$Bi$_2$ than YbMg$_2$Bi$_2$. Further doping Sn into the Bi site suppresses the bipolar effect and enhances the electrical conductivity at higher temperature by increasing the carrier concentration. And the lattice thermal conductivity is reduced due to the intensified point defects scattering. Benefiting from these results, a higher maximum $ZT$ for Yb$_{0.4}$Ca$_{0.4}$Mg$_{0.2}$Mg$_2$Bi$_{1.95}$Sn$_{0.01}$ is achieved. Our work sheds lights on enhancing the thermoelectric performance by suppressing the bipolar conduction and improving the power factor through widening the bandgap accompany by increasing the carrier concentration, and demonstrates that YbMg$_2$Bi$_2$-based Zintl are promising candidates for thermoelectric materials.

1. Introduction
Thermoelectric power generation, which can convert waste heat into electricity, is attractive in sustainable energy harvesting and relieving environmental pollution.[1, 2] The performance of the thermoelectrics is determined by the figure of merit ($ZT$), defined as $ZT = (S^2 \sigma/\kappa) T$, where $S$, $\sigma$, $\kappa$, and $T$ are the Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature, respectively. Thermal conductivity contains three parts: the electronic thermal conductivity ($\kappa_e$), lattice thermal conductivity ($\kappa_L$), and bipolar thermal conductivity ($\kappa_B$). Therefore, the optimization of the Seebeck coefficient, the electrical conductivity, and the thermal conductivity is necessary to achieve a high $ZT$ value. Many recently reported typical compounds have shown high thermoelectric performance via simultaneously optimizing the electrical transport properties and the thermal transport properties, such as Bi$_2$Te$_3$,[3] PbTe,[4] Zintl,[5, 6] and half-Heuslers.[7]

Recently, CaAl$_2$Si$_2$-structured Zintl phases AMg$_2$Bi$_2$ (A = Yb, Ca, Eu, Sm, and Mg) have been continuously studied and demonstrated for potential thermoelectric applications.[5, 6, 8-10] Here, YbMg$_2$Bi$_2$-based compounds are selected for their good thermoelectric performance due to the relatively high Hall carrier mobility.[6] In our previous study, an obviously enhanced $ZT$ value and average $ZT$ is obtained for the optimized Yb$_{0.8}$Mg$_{0.1}$Mg$_2$Bi$_{1.96}$ and Yb$_{0.8}$Mg$_{0.2}$Mg$_2$Bi$_{1.96}$ sample, ~108 % and ~ 33 % higher than the pristine YbMg$_2$Bi$_{1.96}$, respectively.[11] The enhancement is attributed to
the low lattice thermal conductivity of the YbMg2Bi2-Mg3Bi2 solid solutions. However, since Mg3Bi2 is a semimetal (i.e., with zero bandgap), the bandgap of Yb1-xMgxBi1.96 (x = 0, 0.1, 0.2, and 0.3) decreases with more Mg content. Therefore, the bipolar thermal conductivity increased at higher temperature. In order to improve the thermoelectric performances of Yb1-xMgxBi1.96 solid solutions, it is imperative to suppress the bipolar effect and reduce the bipolar thermal conductivity. The bipolar effect of the materials can be suppressed by widening the bandgap, [12, 13] increasing the Hall carrier concentration, [14, 15] and blocking the minority carrier by nano-structuring.[16, 17] Since the bandgap of CaMg2Bi2 is larger than that of YbMg2Bi2, alloying YbMg2Bi2 with CaMg2Bi2 will widen the bandgap and suppress the bipolar thermal conductivity. In addition, the doping of Sn into the Bi site will lead to higher carrier concentration and intensified point defects scattering, resulting in suppressed bipolar thermal conductivity. Therefore, enhanced thermoelectric performance might be obtained by decreasing the bipolar thermal conductivity through alloying and doping in the YbMg2Bi2-based materials.

In this work, the thermoelectric performances of the Yb0.8-xCaxMg0.2Mg2Bi1.96 (x = 0, 0.2, 0.4, and 0.6) and Yb0.4Ca0.4Mg0.2Mg2Bi1.95Sn0.01 samples are investigated. The results show that the formation of Yb0.8-xCaxMg0.2Mg2Bi1.96 solid solutions can effectively widen the bandgap of the thermoelectric materials and reduce the thermal conductivity. Besides, with the help of further doping with Sn into Bi site for suppressing the bipolar effect by increasing carrier concentration, an increased electrical conductivity is obtained, resulting in higher ZT value.

2. Experimental details

The Yb0.8-xCaxMg0.2Mg2Bi1.96 (x = 0, 0.2, 0.4, and 0.6) and Yb0.4Ca0.4Mg0.2Mg2Bi1.95Sn0.01 samples were synthesized by ball milling and hot pressing. The raw materials Yb (ingots, 99.9%), Mg (turnings, 99.9%), Bi (ingots, 99.999%), Ca (turnings, 99.98%), and Sn (granules, 99.5%) were weighed according to the stoichiometry and loaded into a stainless-steel jar in an argon-filled glovebox. The raw materials were ball-milled for 4 h and then loaded into a graphite die and finally sintered by hot pressing at 973 K for 2 min under a pressure of ~80 MPa. The preparation process was similar with our previous work.[11]

The phase of the prepared samples was characterized by the Rigaku SmartLab X-ray diffraction with Cu Ka radiation. Scanning electron microscopy (SEM, JSM 7800F) was used to visualize the morphology, size, and elemental mapping of a representative sample. The temperature-dependent electrical resistivity (ρ, ρ=1/σ) and Seebeck coefficient from 300 to 773 K were simultaneously measured in a commercial ZEM-3 system. The thermal conductivity was calculated via \( \kappa_{\text{total}} = D C d \), where d is the volume density of the sample determined by the Archimedeans method. The thermal diffusivity (D) and specific heat (Cp) was measured using a laser flash apparatus (LFA 457, Netzsch) and a differential scanning calorimeter (DSC 404C, Netzsch), respectively. The room-temperature Hall coefficient (RH) was measured under a helium atmosphere using the van der Pauw technique under a reversible magnetic field of 1.5 T. The room-temperature Hall coefficient concentration (nH) and Hall carrier mobility (\( \mu_H \)) was obtained by \( n_i = \frac{1}{eR_H} \) and \( \sigma = e\mu_i n_i \), respectively.

3. Results and discussion

The X-ray diffraction (XRD) results of the Yb0.8-xCaxMg0.2Mg2Bi1.96 (x = 0, 0.2, 0.4, and 0.6) and Yb0.4Ca0.4Mg0.2Mg2Bi1.95Sn0.01 samples in Figure 1a can be well indexed to the crystal structure of CaAl2Si2 with a P 3 m 1 symmetry. No secondary phases are observed within the detection limit of the XRD. Since the ionic radius of Ca2+ (99 pm) is larger than that of Yb2+ (93 pm), the lattice parameters increase with increasing Ca concentration, as shown in Figure 1b.

The representative scanning electron microscopy (SEM) image for Yb0.4Ca0.4Mg0.2Mg2Bi1.96 in Figure 2a shows that the sample is densely packed. The corresponding elemental mapping of the Yb0.4Ca0.4Mg0.2Mg2Bi1.96 sample shows that the Yb, Mg, Ca, and Bi atoms are distributed nearly
uniformly with no observable micro-holes or obvious element aggregation, which also indicate that the sample is highly dense (Figure 2b).

Figure 1. (a) XRD patterns and (b) composition-dependent lattice parameters of the Yb$_{0.8-x}$Ca$_x$Mg$_0.2$Mg$_2$Bi$_{1.96}$ ($x = 0, 0.2, 0.4,$ and $0.6$) and Yb$_{0.4}$Ca$_{0.4}$Mg$_0.2$Mg$_2$Bi$_{1.95}$Sn$_{0.01}$ samples.

Figure 2. (a) SEM micrograph of the Yb$_{0.4}$Ca$_{0.4}$Mg$_0.2$Mg$_2$Bi$_{1.96}$ sample. (b) The corresponding elemental mapping of the Yb$_{0.4}$Ca$_{0.4}$Mg$_0.2$Mg$_2$Bi$_{1.96}$ sample.

Figure 3 shows the electrical transport properties of Yb$_{0.8-x}$Ca$_x$Mg$_0.2$Mg$_2$Bi$_{1.96}$-based samples with different Ca concentration and Sn doping. Temperature-dependent electrical resistivity of the Yb$_{0.8-x}$Ca$_x$Mg$_0.2$Mg$_2$Bi$_{1.96}$ ($x = 0, 0.2, 0.4,$ and $0.6$) samples in Figure 3a shows that the electrical resistivity increases with increasing temperature, indicating a degenerate semiconducting behavior. With the increase of Ca content, the electrical resistivity increases due to the decreased carrier concentration (see Table 1). The difference in electrical properties results from the different electronegativity. Ca is more electropositive than Yb. This will lead to a larger energy barrier and an increased defect formation enthalpy of the cation vacancies.[18] Therefore, the hole carrier concentration decreases with increasing Ca concentration in the Yb$_{0.8-x}$Ca$_x$Mg$_0.2$Mg$_2$Bi$_{1.96}$ solid solutions. Figure 3b shows the temperature-dependent Seebeck coefficient of Yb$_{0.8-x}$Ca$_x$Mg$_0.2$Mg$_2$Bi$_{1.96}$. Similar to the variation of the electrical resistivity, the Seebeck coefficient increases with increasing Ca concentration due to the decreased carrier concentration. Since CaMg$_2$Bi$_2$ has a larger bandgap than YbMg$_2$Bi$_2$, alloying CaMg$_2$Bi$_2$ with YbMg$_2$Bi$_2$ will widen the bandgap and reduce the bipolar effect.[6] The Seebeck coefficient will increase at higher temperature for higher Ca concentration. However, it is noted that the decreased carrier concentration by widened bandgap leads to the peak Seebeck coefficient shifts to lower temperature. This might be attributed to the higher maximum Seebeck coefficient at lower temperature in the Ca rich sample. The bandgap $E_g$ of the solid solution samples is estimated by the Goldsmid–Sharp formula $E_g = 2e|S|_{\text{max}}^2 T_{\text{max}}^2$, where $e$, $S_{\text{max}}$, and $T_{\text{max}}$ are the electron charge, the maximum Seebeck coefficient, and the corresponding temperature, respectively.[19, 20] Therefore,
both higher Seebeck coefficient at lower temperature and lower Seebeck coefficient at higher temperature might widen the band gap. Accordingly, a slightly broader band gap is observed for Yb$_{0.8-x}$Ca$_x$Mg$_{0.2}$Mg$_2$Bi$_{1.96}$ (see the inset of Figure 3b). Our results clearly demonstrate that CaMg$_2$Bi$_2$-YbMg$_2$Bi$_2$ is an efficient alloy for the YbMg$_2$Bi$_2$-based compound.

Figure 3c shows the Hall-carrier-concentration-dependent Seebeck coefficient in the Bi-based Zintl compounds at room temperature. The solid line is calculated by assuming the single parabolic band (SPB) model and considering the acoustic phonon scattering based on equations (1)–(4),[21]

$$S = \pm \frac{k_F}{e} \left( \frac{2F(\zeta)}{F_0(\zeta)} - \zeta \right)$$

(1)
\[ r_{\mu} = \frac{3}{2} \frac{F_{1/2}(\zeta) F_{3/2}(\zeta)}{2F_0(\zeta)} \]  

(2)

\[ F_n(\zeta) = \int_0^\zeta \frac{x^n}{1 + \exp^{x^2}} \, dx, \quad \text{and} \]

(3)

\[ m^* = \frac{\hbar^2}{2k_B T} \left[ \frac{n_F}{4\pi F_{1/2}(\zeta)} \right]^{2/3} \]  

(4)

where \( F_n(\zeta) \) is the \( n \)th order Fermi integral, \( \zeta \) is the reduced Fermi energy, \( r_{\mu} \) is the Hall factor, \( \hbar \) is the Planck constant, \( k_B \) is the Boltzmann constant, and \( e \) is the electron charge. Except for \( Ca_{0.7-x}Ba_{0.3}Ag_{x}Mg_{2}Bi_2 \) \((m^* \approx 0.75 \, m_e)\) [22], the result of \( Yb_{0.8-x}Ca_{x}Mg_{0.2}Mg_{2}Bi_{1.96} \) and those of reference results of \( Yb_{1-x}Mg_{x}Mg_{2}Bi_{1.96} \) [11] and \( Ca_{1-x}Yb_{x}Mg_{2}Bi_{2} \) [23] are fitted well with the density of state (DOS) effective mass of \( m^* = 0.75 \, m_e \) (see Figure 3c, black solid line). The DOS effective mass of \( Ca_{0.7-x}Ba_{0.3}Ag_{x}Mg_{2}Bi_2 \) is deviated from the solid line and lower than 0.75 \( m_e \), which means it has lower Seebeck coefficient and lower power factor than our work and the former reported compounds.

Even though \( Yb_{0.8-x}Ca_{x}Mg_{0.2}Mg_{2}Bi_{1.96} \) solid solutions could widen the bandgap to a certain extent, the bipolar effect is still apparent (see Figure 3b), which is detrimental to the electrical transport properties. Therefore, it is essential to suppress the bipolar conduction to obtain the enhanced thermoelectric performance. Since increasing the carrier concentration is one of the methods to effectively suppress the bipolar effect [14, 24, 25], we further study the Sn doping at the Bi site based on the composition \( Yb_{0.4}Ca_{0.4}Mg_{0.2}Mg_{2}Bi_{1.96} \). Apparently, the carrier concentration of the \( Yb_{0.4}Ca_{0.4}Mg_{0.2}Mg_{2}Bi_{1.96}Sn_{0.01} \) sample increases to \( 4.70 \times 10^{19} \, cm^{-3} \), at least twice the value of the non-doped one. The bipolar effect disappears due to the combination of higher carrier concentration (Table 1) and widened bandgap (Figure 3b). Besides, the DOS effective mass of \( Yb_{0.4}Ca_{0.4}Mg_{0.2}Mg_{2}Bi_{1.96}Sn_{0.01} \) is also around the solid line, indicating that all samples have similar \( m^* \) and carrier mobilities. Therefore, both the electrical resistivity and the Seebeck coefficient dramatically decrease with Sn doping into the Bi site. Due to the lower electrical resistivity coupled with the higher Seebeck coefficient, higher power factor at higher temperature can be achieved in \( Yb_{0.4}Ca_{0.4}Mg_{0.2}Mg_{2}Bi_{1.96}Sn_{0.01} \) (see Figure 3d).

![Figure 4](image-url)

**Figure 4.** Temperature-dependent (a) total thermal conductivity and (b) sum of lattice and bipolar thermal conductivity of the \( Yb_{0.8-x}Ca_{x}Mg_{0.2}Mg_{2}Bi_{1.96} \) \((x = 0, 0.2, 0.4, \) and \(0.6) \) and \( Yb_{0.4}Ca_{0.4}Mg_{0.2}Mg_{2}Bi_{1.95}Sn_{0.01} \) samples.

The effect of Ca content on the thermal conductivities of \( Yb_{0.8-x}Ca_{x}Mg_{0.2}Mg_{2}Bi_{1.96} \) \((x = 0, 0.2, 0.4, \) and \(0.6) \) and \( Yb_{0.4}Ca_{0.4}Mg_{0.2}Mg_{2}Bi_{1.95}Sn_{0.01} \) is shown in Figure 4. The total thermal conductivity decreases significantly with the increase of Ca concentration, as shown in Figure 4a. The room temperature total thermal conductivity of \( Yb_{0.4}Mg_{0.2}Mg_{2}Bi_{1.96} \) is \( \sim 1.35 \, W \, m^{-1} \, K^{-1} \) but only \( \sim 0.85 \, W \, m^{-1} \, K^{-1} \) for \( Yb_{0.2}Ca_{0.8}Mg_{0.2}Mg_{2}Bi_{1.96} \), a reduction of \(~37\%). In addition, the formation of solid solutions between \( CaMg_2Bi_2 \) and \( YbMg_2Bi_2 \) not only widens the bandgap, but also decreases the
lattice thermal conductivity by intensifying the alloy scattering because of the lighter element Ca. The sum of lattice thermal conductivity and bipolar thermal conductivity shown in Figure 4b is obtained by subtracting the electronic thermal conductivity \( \kappa_e \) (\( \kappa_e = \sigma T \), where \( \sigma \) is the Lorenz number) from total thermal conductivity. In Figure 4b, the room temperature sum of lattice thermal conductivity and bipolar thermal conductivity is ~ 1.05 W m\(^{-1}\) K\(^{-1}\) for Yb\(_{0.8}\)Mg\(_{0.2}\)Mg\(_2\)Bi\(_{1.96}\) but only ~ 0.8 W m\(^{-1}\) K\(^{-1}\) for Yb\(_{0.2}\)Ca\(_{0.6}\)Mg\(_{0.2}\)Mg\(_2\)Bi\(_{1.96}\), a decrease of ~ 23%. As expected, the lattice thermal conductivity decreases with increasing Ca concentration, which can be ascribed to the mass difference between the two atoms (Ca 40.08 g mol\(^{-1}\) and Yb 173.04 g mol\(^{-1}\)). It is worth noting that the bipolar thermal conductivity is obvious for Yb\(_{0.8-x}\)Ca\(_{x}\)Mg\(_{0.2}\)Mg\(_2\)Bi\(_{1.96}\) at higher temperature, in accordance with the variation of Seebeck coefficient. Since doping Sn into the Bi site can suppress the bipolar effect, the bipolar thermal conductivity of Yb\(_{0.4}\)Ca\(_{0.4}\)Mg\(_{0.2}\)Mg\(_2\)Bi\(_{1.95}\)Sn\(_{0.01}\) will decrease. Indeed, as shown in Figure 4, the diminished bipolar effect in the Sn-doped sample contributes to lower thermal conductivity at higher temperature. The decrease of the thermal conductivity can be partially ascribed to the phonon scattering by point defects. This further indicates that Sn is an efficient dopant for Yb\(_{0.4}\)Ca\(_{0.4}\)Mg\(_{0.2}\)Mg\(_2\)Bi\(_{1.96}\), which is similar to the previous reports.[26-28]

Figure 5. (a) Temperature-dependent \( ZT \) values of the Yb\(_{0.8-x}\)Ca\(_{x}\)Mg\(_{0.2}\)Mg\(_2\)Bi\(_{1.96}\) \( (x = 0, 0.2, 0.4, \) and \( 0.6) \) and Yb\(_{0.4}\)Ca\(_{0.4}\)Mg\(_{0.2}\)Mg\(_2\)Bi\(_{1.95}\)Sn\(_{0.01}\) samples in comparison with those of YbMg\(_2\)Bi\(_2\),[9] YbMg\(_2\)Bi\(_{1.96}\),[11] Yb\(_{0.5}\)Ca\(_{0.5}\)Mg\(_2\)Bi\(_2\),[23] and Ca\(_{0.68}\)Ba\(_{0.3}\)Ag\(_{0.015}\)Mg\(_2\)Bi\(_2\).[22] samples. (b) Comparison between the average \( ZT \) among our work and previous results.

Temperature-dependent \( ZT \)s for Yb\(_{0.8-x}\)Ca\(_{x}\)Mg\(_{0.2}\)Mg\(_2\)Bi\(_{1.96}\) \( (x = 0, 0.2, 0.4, \) and \( 0.6) \) and Yb\(_{0.4}\)Ca\(_{0.4}\)Mg\(_{0.2}\)Mg\(_2\)Bi\(_{1.95}\)Sn\(_{0.01}\) are shown in Figure 5a. Due to the widened bandgap and increased carrier concentration, enhanced electrical transport properties along with reduced thermal conductivity at higher temperature are obtained, resulting in a peak \( ZT \) of ~ 0.85 at 733 K for Yb\(_{0.4}\)Ca\(_{0.4}\)Mg\(_{0.2}\)Mg\(_2\)Bi\(_{1.95}\)Sn\(_{0.01}\), which is higher than that of the recently reported Bi-based Zintl compounds[9, 11, 22] and other Zintl compounds such as Yb\(_{13}\)CaMnSb\(_{11}\) \( (ZT \sim 0.9, 773 \text{ K})[29]\), Sr\(_3\)In\(_1\)sZn\(_{0.1}\)Sb\(_6\) \( (ZT \sim 0.4, 750 \text{ K})[30]\), Eu\(_3\)Cd\(_{3.75}\)Ag\(_{1.42}\)Sb\(_6\) \( (ZT \sim 0.32, 750 \text{ K})[31]\), Ba\(_{0.93}\)Na\(_{0.06}\)Sr\(_{0.02}\)Zn\(_{0.02}\)Sb\(_2\) \( (ZT \sim 0.58, 704 \text{ K})[32]\). In addition, the average figure of merit \( (ZT)_{\text{avg}} \) in the temperature range from 300 to 773 K is shown in Figure 5b. The \( (ZT)_{\text{avg}} \) of the alloyed and doped sample is obviously higher than that of the pristine YbMg\(_2\)Bi\(_2\).

4. Conclusions

In summary, the thermoelectric performances of the YbMg\(_2\)Bi\(_2\)-based materials are studied. The results show that the thermal conductivity is effectively reduced in the Yb\(_{0.8-x}\)Ca\(_{x}\)Mg\(_{0.2}\)Mg\(_2\)Bi\(_{1.96}\) \( (x = 0, 0.2, 0.4, \) and \( 0.6) \) solid solutions and the bandgaps of them are expectedly widened due to the larger bandgap of CaMg\(_2\)Bi\(_2\). Upon further Sn doping, both the bipolar effect and electrical resistivity are suppressed at higher temperature due to the increasing carrier concentration, accompanying by decreased lattice thermal conductivity due to the intensified point defects scattering. Finally, a relatively higher peak \( ZT \) of ~ 0.85 at 773 K is obtained for Yb\(_{0.4}\)Ca\(_{0.4}\)Mg\(_{0.2}\)Mg\(_2\)Bi\(_{1.95}\)Sn\(_{0.01}\), which is
higher than that of the previously reported Bi-based compounds and other Zintl compounds. Our work sheds lights on enhancing the thermoelectric performance by suppressing the bipolar conduction and improving the power factor through widening the bandgap accompany by increasing the carrier concentration, and demonstrates that YbMg₂Bi₂-based Zintl compounds are promising thermoelectric materials.

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