Enhancement of thermoelectric performance of phase pure Zintl compounds $\text{Ca}_{1-x}\text{Yb}_x\text{Zn}_2\text{Sb}_2$, $\text{Ca}_{1-x}\text{Eu}_x\text{Zn}_2\text{Sb}_2$, and $\text{Eu}_{1-x}\text{Yb}_x\text{Zn}_2\text{Sb}_2$ by mechanical alloying and hot pressing

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Abstracts

It has been previously shown that Zintl compounds $\text{Ca}_{1-x}\text{Yb}_x\text{Zn}_2\text{Sb}_2$ and EuZn_2Sb_2 could be good candidates as thermoelectric materials. However, the conventional synthesis process via melting-solidification-annealing introduces impurities and vacancies, resulting in abnormal high carrier concentration and ultimately low thermoelectric properties. Here we report the enhanced thermoelectric performance of $\text{Ca}_{1-x}\text{Yb}_x\text{Zn}_2\text{Sb}_2$ ($x = 0, 0.25, 0.5, 0.75$, and 1) prepared by ball milling and hot pressing. XRD confirms the samples are pure Zintl phase **within its limit**. Other compounds EuZn_2Sb_2 , $\text{Eu}_{0.5}\text{Yb}_{0.5}\text{Zn}_2\text{Sb}_2$, and $\text{Eu}_{0.5}\text{Ca}_{0.5}\text{Zn}_2\text{Sb}_2$ are also prepared by ball milling and hot pressing to further understand them. The observed changes in effective mass appear to be one of the reasons for the big difference of carrier mobility in Ca and rare earth (Yb, Eu) alloyed compounds. The defects caused by alloying are the dominant phonon scattering source in these materials. The highest figure of merit of ~ 0.9 is achieved in $\text{Ca}_{0.25}\text{Yb}_{0.75}\text{Zn}_2\text{Sb}_2$, $\sim 50\%$ higher than the best reported ZT in similar materials prepared by melting-solidification-annealing method.

Keywords: Thermoelectric, mechanical alloying, pure phase, Zintl phase, vacancies

1. Introduction

Efficient use of energy will be a critical issue for human prosperity in the future, considering natural resources are gradually declining and the average efficiency from heat to electricity is less than 50% meaning more than half of energy is wasted as heat. Thermoelectric devices, which convert thermal energy to electrical energy, have been attracting a lot of attention by making use of some of the waste heat [1-5]. The conversion efficiency is quantified by the dimensionless figure of merit $(ZT) = (S^2\sigma/\kappa)T$. An ideal thermoelectric material must strike a balance between the conflicting requirements of high Seebeck coefficient S , high electrical conductivity σ , and low thermal conductivity κ [6,7].

It is well known that thermoelectric properties are dependent on chemical composition and microstructure that is sensitive to the preparation method. The traditional method such as melting-solidification-annealing (briefed as “melting” hereafter) is widely used for preparing thermoelectric samples with good thermoelectric properties in some cases [8-11]. However, for some materials with elements having high vapor pressure like Mg in $\text{Mg}_2\text{Si}_{1-x}\text{Sn}_x$ or Sb in Skutterudites, it is difficult to use high temperature melting method for accurate control of the molar ratio [12-14]. Therefore, alternatively, mechanical alloying (MA) by high-energy ball milling process is studied for the synthesis of double filled skutterudites p-type $\text{Ce}_{0.45}\text{Nd}_{0.45}\text{Fe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12}$ and n-type $\text{CoSb}_{3-x}\text{Te}_x$, $\text{Mg}_2\text{Si-Mg}_2\text{Sn}$ alloy, etc. [15-21] and has also achieved a good success to fabricate a variety of popular high-performance thermoelectric bulk materials such as Bi_2Te_3 [6], PbTe [17], and PbSe [22] without introducing noticeable impurity phases from milling process.

Zintl phases AM_2X_2 ($A = \text{Ca, Yb, Eu, Sr}$; $M = \text{Zn, Mn, Cd, Mg}$; $X = \text{Sb, Bi}$), especially AZn_2Sb_2 , crystalizing in CaAl_2Si_2 structure (Fig. 1), have been extensively studied as thermoelectric materials [23-28]. For many years, the dominant preparation method for AZn_2Sb_2 Zintl compounds has been melting. For example, the reported synthesis process for $\text{Ca}_{1-x}\text{Yb}_x\text{Zn}_2\text{Sb}_2$ is to first heat the samples to above 1000 °C and hold them at that temperature between 12 h and 96 h, and then cool the samples down to between 500 °C and 800 °C and hold for more than two days [23]. The total processing time of this method is more than 200 h.

Besides, all the previous reports on Zintl phase AZn_2Sb_2 via melting method have $ZnSb$, Zn_4Sb_3 or $M_9Zn_{4.5}Sb_9$ ($M = Yb, Eu$) as the secondary phases [23-28]. The recent study shows that the observed extreme high carrier concentration can be explained by the vacancies in the A-site. The initial high-temperature step may have led Yb to vaporize or react with the container [29]. The density function theory (DFT) calculation also predicated that vacancies on the A-site are most energetically favorable point defects and concentration of vacancies depends strongly on the electronegativity of A [30]. The residual vacancies and impurities have an impact on the measured thermoelectric performance and make it difficult to fully understand the fundamental thermoelectric properties in AZn_2Sb_2 series, especially when trying to study the effects caused by elemental substitutions. Considering the drawbacks of defect formation and long time process by melting method, mechanical alloying (MA) by high-energy ball milling process is studied for synthesis of these Zintl compounds.

The current study aims at exploring the effect of ball milling and hot pressing conditions on the thermoelectric performances of $Ca_{1-x}Yb_xZn_2Sb_2$, $Ca_{1-x}Eu_xZn_2Sb_2$, and $Eu_{1-x}Yb_xZn_2Sb_2$ samples. By preparing all samples without impurities phases with the detection limit of XRD, the fundamental thermoelectric properties, such as effective mass and mobility, would be explored. A significant enhancement on thermoelectric properties is achieved in $Ca_{1-x}Yb_xZn_2Sb_2$ compounds. The highest ZT value of ~ 0.9 is observed for the optimized composition $Ca_{0.25}Yb_{0.75}Zn_2Sb_2$, which is $\sim 50\%$ higher than the previously reported values [23].

2. Experimental section

Sample preparation

Calcium (Ca, Sigma Aldrich, 99.9%, pieces), ytterbium (Yb, Sigma Aldrich, 99.9%, cubes), europium (Eu, Atlantic, 99.9%, cubes), zinc (Zn, Sigma Aldrich, 99.9%, powder), and antimony (Sb, Sigma Aldrich, 99.999%, chunks) were weighed according to the stoichiometry of $Ca_{1-x}Yb_xZn_2Sb_2$ ($x = 0, 0.25, 0.5, 0.75$, and 1), $EuZn_2Sb_2$, $Eu_{0.5}Yb_{0.5}Zn_2Sb_2$, $Eu_{0.5}Ca_{0.5}Zn_2Sb_2$, and sealed directly in the stainless steel jar with stainless steel balls inside an argon-filled glove box. Then the sealed jar was taken out for mechanical alloying by a high-energy ball mill (SPEX

8000D) for 12 h. The obtained final nanopowder was then loaded into a graphite die with an inner diameter of 12.7 mm, and consolidated by hot pressing at ~ 923 K for 2 min. Ball milling process using stainless jar and balls does not have a significant Fe or other metal contamination problem since it was first reported as an efficient method to prepare high performance thermoelectric bulk materials in 2008 [6] and repeatedly demonstrated in many other materials [15-22]. Hot pressing using graphite die and rods has also been repeatedly proved that carbon contamination is not an issue either. The final hot pressed samples were cut and polished to the required dimensions for later characterizations.

Sample Characterization. A PANalytical multipurpose diffractometer with an X'celerator detector (PANalytical X'Pert Pro) was used to characterize the hot pressed sample. The lattice constants of $\text{Ca}_{1-x}\text{Yb}_x\text{Zn}_2\text{Sb}_2$ ($x = 0, 0.5, \text{ and } 1$), EuZn_2Sb_2 , $\text{Eu}_{0.5}\text{Ca}_{0.5}\text{Zn}_2\text{Sb}_2$, and $\text{Eu}_{0.5}\text{Yb}_{0.5}\text{Zn}_2\text{Sb}_2$ were calculated by Rietveld refinement using the Fullprof software. Morphology and elemental ratios of the samples were characterized by scanning electron microscopy (SEM, LEO 1525) and Electron Probe Micro-Analysis (EPMA, JXA-8600), respectively. Transmission electron microscopy (TEM, JEOL 2100F) was used to analyze the detailed microstructures.

Property measurements. The electrical resistivity (ρ) and Seebeck coefficient (S) were simultaneously measured on a commercial system (ZEM-3, ULVAC) using a four-point direct current switching method and static temperature difference method. The thermal conductivity was measured by measuring the thermal diffusivity (D) on a laser flash apparatus (LFA 457, NETZSCH), specific heat (C_p) on a DSC (404 C, NETZSCH), and volumetric density (ρ_D) by Archimedes method. The carrier concentration was obtained by Hall effect measurement (Van der Pauw method) at room temperature using a modified sample puck in Physical Properties Measurement System (PPMS D060, Quantum Design) under a magnetic field of 3 Tesla. It is understood that there is a 3% error in the electrical resistivity, 5% error in the Seebeck coefficient, and 5% error in the thermal conductivity, resulting in errors of around 12% for ZT . For better readability of the figures, we have deliberately plotted the curves without the error bars.

3. Results and Discussion

The XRD patterns of $\text{Ca}_{1-x}\text{Yb}_x\text{Zn}_2\text{Sb}_2$ ($x = 0, 0.25, 0.5, 0.75$, and 1), $\text{Eu}_{0.5}\text{Yb}_{0.5}\text{Zn}_2\text{Sb}_2$, $\text{Eu}_{0.5}\text{Ca}_{0.5}\text{Zn}_2\text{Sb}_2$, and EuZn_2Sb_2 are shown in Fig. 2a and 2b. All diffraction peaks are indexed according to the reported structure of CaAl_2Si_2 (space group $P3m1$, No. 164) [31]. All the samples were found to be phase pure within the XRD detection limit. However, by using melting method, most reports show the impurity phases, such as ZnSb , Zn_4Sb_3 , and $\text{M}_9\text{Zn}_{4.5}\text{Sb}_9$ ($\text{M} = \text{Yb}, \text{Eu}$) [23-28]. The refined unit cell parameters a and c of each compound are shown in Fig. 2c (labeled as 1-5 on the x-axis). Little variation is observed in the lattice parameters of all $\text{Ca}_{1-x}\text{Yb}_x\text{Zn}_2\text{Sb}_2$ compounds because of similar atomic radius of Ca (194 pm) and Yb (197 pm). The three Eu containing samples are observed to show a larger unit cell parameters a and c (labeled as 6-8 on the x-axis), consistent with the bigger atomic radius of Eu (204 pm). As expected, the Eu-rich compound EuZn_2Sb_2 showed the largest lattice parameters a and c .

The SEM and STEM images of the optimized $\text{Ca}_{0.25}\text{Yb}_{0.75}\text{Zn}_2\text{Sb}_2$ sample are displayed in Fig. 3a and 3b. Both of them clearly indicate the sample is densely packed. A wide range of grain size from 50 to 500 nm is also observed. Fig. 3c shows a high-resolution TEM image to elucidate two grains adjacent to each other. The corresponding fast Fourier transformation (FFT) image for upper grain, as the inset of Fig. 3c, can be successfully indexed according to Pm hexagonal structure along the $[301]$ zone axis. Interestingly, some black (indicated by the black arrow) and white (indicated by the white arrow) nanoinclusions can be observed under high magnification, shown in Fig. 3d. Most of these nanoinclusions, hardly detected by XRD, ranges from 5 nm to 10 nm. To further investigate the elemental compositions of these nanoinclusions, the energy dispersive X-ray (EDX) elemental mapping has been taken to analyze the elemental distributions and are shown in Fig. 3e and Fig. 3f. It is shown that the white nanoinclusions contain a little more Yb, while the black nanoinclusions are composed of the composition with a little less concentration. Those small size of nano-precipitates could lead to extra interface and lattice distortions, thus making some contribution to lower the lattice thermal conductivity (discussed later).

The temperature dependence of electrical resistivity and Seebeck coefficient of all ball milled and hot pressed $\text{Ca}_{1-x}\text{Yb}_x\text{Zn}_2\text{Sb}_2$ compounds are shown in Fig. 4a. and 4c. They behave like typical degenerated semiconductor: increase with temperature. In Fig. 4a, by increasing Yb content, the resistivity is decreased for $x < 0.5$ and then increased a little. For comparison, the resistivity and Seebeck coefficient of three representative samples by melting method (CaZn_2Sb_2 , YbZn_2Sb_2 , and $\text{Ca}_{0.25}\text{Yb}_{0.75}\text{Zn}_2\text{Sb}_2$) reported by Gascoin *et al.* are also shown [23]. Clearly, CaZn_2Sb_2 ($x = 0$) prepared by melting shows much higher resistivity and also higher Seebeck coefficient, while YbZn_2Sb_2 ($x = 1$) by melting method exhibits lower resistivity and much lower Seebeck coefficient. The optimized sample $\text{Ca}_{0.25}\text{Yb}_{0.75}\text{Zn}_2\text{Sb}_2$ ($x = 0.75$) via ball milling shows a lower resistivity and higher Seebeck coefficient than the same composition by melting. For $\text{Ca}_{1-x}\text{Yb}_x\text{Zn}_2\text{Sb}_2$ samples made by melting, the electric resistivity drops sharply from $23.7 \text{ m}\Omega \text{ m}$ to $3.2 \text{ m}\Omega \text{ m}$ as Yb content increases, which might attribute to the increased Yb vacancies. The melting method would introduce A-site vacancies to form **probably because of** heavy loss of atom A during the ball milling processing. Deficiency of A-site cations leads to fewer electrons in the bonding and anti-bonding states, which would contribute to the lower resistivity by increasing the hole carrier concentration. At the same time, the increased carrier concentration would contribute to the reduction in Seebeck coefficient for samples made by melting based on Pisarenko relations with the assumption of similar effective mass [23] (further discussed later). The electric transport properties of ball milled and hot pressed Eu-containing samples EuZn_2Sb_2 and $\text{Eu}_{0.5}\text{A}_{0.5}\text{Zn}_2\text{Sb}_2$ ($\text{A} = \text{Yb, Ca}$) are also shown in comparison with CaZn_2Sb_2 , YbZn_2Sb_2 , and $\text{Ca}_{0.5}\text{Yb}_{0.5}\text{Zn}_2\text{Sb}_2$ in Fig. 4b and Fig. 4d. The resistivity of EuZn_2Sb_2 is higher than YbZn_2Sb_2 but lower than CaZn_2Sb_2 . The Eu alloyed compounds ($\text{Eu}_{0.5}\text{Ca}_{0.5}\text{Zn}_2\text{Sb}_2$ and $\text{Eu}_{0.5}\text{Yb}_{0.5}\text{Zn}_2\text{Sb}_2$) appear to have intermediate properties. The resistivity and Seebeck coefficient of EuZn_2Sb_2 appear not much different from the reported melting samples [24]. **The tendency for Eu to form the vacancies is low, as calculated by G. S. Pomrehn *et al.* [30],** which might be the reason why the electric transport properties appear similar between two different synthesis methods. Power factor ($PF = S^2/\rho$) calculated from the measured electrical resistivity and Seebeck coefficient is plotted in Fig. 4e and 4f. In Fig. 4e, with higher Yb concentration, the power factor in $\text{Ca}_{1-x}\text{Yb}_x\text{Zn}_2\text{Sb}_2$ samples increases. Compared with the three samples prepared by melting method, the power factors of all our samples are $\sim 100\%$ higher, mainly **attribute to** the higher phase

purity by eliminating the A-site vacancies. Among all the samples shown in Fig. 4f, EuZn_2Sb_2 possesses the highest power factor of $\sim 21 \mu\text{W cm}^{-1} \text{K}^{-2}$.

The carrier concentration (n) and Hall mobility (μ) are listed in Table 1, and related to electrical resistivity by $1/\rho = ne\mu$. The effect of Yb concentration on resistivity and carrier concentration is plotted in Fig. 5a. With increasing Yb concentration, the carrier concentration of samples by melting increases from 3.1×10^{19} to $15 \times 10^{19} \text{ cm}^{-3}$ and resistivity decreases sharply, as a result of increased vacancies in Yb-site by melting method. However, our samples prepared by ball milling and hot pressing method showed lower carrier concentrations, with the highest of $\sim 8.75 \times 10^{18} \text{ cm}^{-3}$ in $\text{Ca}_{0.5}\text{Yb}_{0.5}\text{Zn}_2\text{Sb}_2$, about half of that in YbZn_2Sb_2 by melting.

The single parabolic band model that has been successfully applied in Zintl AZn_2Sb_2 system and DFT calculation has also demonstrated that AZn_2Sb_2 contains three bands at the valence band edge that are degenerate at Γ point, which can be modeled as a single parabolic band with a single combined effective mass [27]. Previous studies show those Zintl compounds have similar effective mass of $\sim 0.6 m_e$ [27-29]. The Pisarenko relations are plotted in Fig. 5b by using a density of states (DOS) effective mass $m^* = 0.6 m_e$ and assuming acoustic phonons are the primary scattering sources [32,33]. The well-established Pisarenko relations between the Seebeck coefficient and carrier concentration gives a good description of the experimental data for rare earth alloyed AZn_2Sb_2 samples. However, for Ca-rich AZn_2Sb_2 , the enhanced Seebeck coefficient lying above the Pisarenko line indicates an increase in the density of state mass.

SPB model is used to calculate each sample's DOS effective mass [32-34]. The Ca-rich compound shows higher effective mass than the rare earth-rich compounds, and with more Ca, the effective mass gradually increases (Table 1). With increasing Ca concentration, the Hall mobility gradually decreases to $85.9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in CaZn_2Sb_2 . The highest mobility of $\sim 240 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is found in EuZn_2Sb_2 . Although higher concentration would lead to lower mobility, the big difference in mobility between the rare earth and Ca alloyed AZn_2Sb_2 is surprising. The classical definition of mobility is ($= e\hbar/m^*$) [35,36]. Previous studies assume the effective masses for all AZn_2Sb_2 samples are almost similar, the difference in mobility is most likely interpreted by the changes in $\hbar$ arising from differences in microstructure and/or bonding

features. Here, the experimental data from our samples by ball milling and hot pressing shows that the Hall mobility (μ) decreases with increased effective mass (Fig. 5c). Therefore, it is also possible that the change of effective mass would also change the mobility.

Fig. 6 shows the temperature-dependent thermal transport behavior of $\text{Ca}_{1-x}\text{Yb}_x\text{Zn}_2\text{Sb}_2$ and Eu alloyed AZn_2Sb_2 samples. Specific heat (C_p) for all samples is shown in Fig. 6a and it decreases gradually from Ca rich samples to Yb/Eu rich samples because of the increased atomic mass. All the specific heat curves increase with temperature. Fig. 6b shows the thermal diffusivity of all samples. With increasing temperature, the diffusivity (D) of all samples shows a gradually decreasing tendency. C_p and D are used to calculate the total thermal conductivity (κ) of all the samples by $\kappa = D\rho_D C_p$, where ρ_D is the measured density of samples. Densities of samples $\text{Ca}_{1-x}\text{Yb}_x\text{Zn}_2\text{Sb}_2$ with $x = 0, 0.25, 0.5, 0.75$, and 1 are $5.25, 5.74, 6.23, 6.61, 7.05 \text{ g cm}^{-3}$, and densities for samples $\text{Eu}_{0.5}\text{Yb}_{0.5}\text{Zn}_2\text{Sb}_2$, $\text{Eu}_{0.5}\text{Ca}_{0.5}\text{Zn}_2\text{Sb}_2$, and EuZn_2Sb_2 are $6.90, 6.04$, and 6.81 , respectively, $\sim 98\%$ of the theoretical densities. As shown in Fig. 6c, the total thermal conductivity decreases dramatically in the mixed Ca/Yb compounds $\text{Ca}_{1-x}\text{Yb}_x\text{Zn}_2\text{Sb}_2$ made by different methods, indicating alloying is quite effective in lowering the lattice thermal conductivity. The much high thermal conductivity in sample YbZn_2Sb_2 by melting might attribute to the increased electronic contribution κ_e , estimated using the Wiedemann–Franz relationship ($\kappa_e = LT/\rho$), where L is the Lorenz number, approximated using a single parabolic band model [34]. In Fig. 6d, it is clear that the samples with Ca and Yb/Eu have lower thermal conductivity because of the mass fluctuations, while samples with mixed Eu/Yb isn't influenced by point defect scattering because of the similar atomic mass. However, given the considerable amounts of impurity phases $\text{Eu}_9\text{Zn}_{4.5}\text{Sb}_9$ [24], the EuZn_2Sb_2 sample by melting shows a little lower thermal conductivity. By directly subtracting the electronic contribution from the total thermal conductivity, the lattice thermal conductivity (κ_L) were obtained and shown in Fig. 6e and 6f. It is observed that lattice thermal conductivity of CaZn_2Sb_2 prepared by different methods appear to be similar, while the Yb-containing samples via ball milling show a little lower lattice thermal conductivity. As detected by EDX in Fig. 3f, Yb-rich nano precipitates might have some effects on scattering the phonons with short mean free path to lower the lattice thermal conductivity. For the alloyed $\text{Ca}_{0.5}\text{Yb}_{0.5}\text{Zn}_2\text{Sb}_2$ sample, the lattice thermal conductivity reaches as low as $0.4 \text{ W m}^{-1} \text{ K}^{-1}$ mainly because of the point defects. This point defects scattering

also lower the lattice thermal conductivity in $\text{Eu}_{0.5}\text{Ca}_{0.5}\text{Zn}_2\text{Sb}_2$, but not in $\text{Eu}_{0.5}\text{Yb}_{0.5}\text{Zn}_2\text{Sb}_2$ because of the dominating mass disorder scattering effect. The data reported before on EuZn_2Sb_2 suggested a significant lower lattice thermal conductivity [24], which is not really correct since they overestimated the κ_e by using higher L .

Combining the electrical and thermal properties, the corresponding ZT values are shown in Fig. 7a and 7b. With increasing temperature, ZT increases continuously. Ball milling and hot pressing method doesn't make too much difference in ZT for EuZn_2Sb_2 . However, for $\text{Ca}_{0.25}\text{Yb}_{0.75}\text{Zn}_2\text{Sb}_2$, we obtained the highest $ZT \sim 0.9$ at 773 K, an improvement of $\sim 50\%$ over that of the best reported sample by melting. The obtained enhancement is even more obvious for YbZn_2Sb_2 via ball milling, indicating adjusting electrical conductivity (e.g., controlling vacancies) is very crucial in optimizing properties for the compounds especially within AZn_2Sb_2 system. In addition, given that the lattice thermal conductivity has been regarded as the only one independent material properties, in order to further increase ZT , it is important to optimize the electrical part to strike a balance between conflicting factor of high electrical conductivity and low electron thermal conductivity.

Up to very recently, the conventional ZT and PF especially the peak ZT and PF have been used as the criteria to guide the thermoelectric materials performance. However, for thermoelectric devices that work at a large temperature difference, cumulative ZT and PF over the whole temperature range are more important, not the peak ZT and PF , in determining the possible efficiency and output power density, respectively. Recently, Kim *et al.* took another big step and proposed the engineering figure of merit $(ZT)_{eng}$ as a function of thermal boundaries, i.e., the temperatures of hot side T_h and cold side T_c to reliably predict the possible efficiency and output power density [37]. Fig. 8 shows the calculated $(ZT)_{eng}$ and $(PF)_{eng}$ dependence of the hot side temperature up to 773 K while the cold side temperature is kept at 323 K. It shows that the optimized sample $\text{Ca}_{0.25}\text{Yb}_{0.75}\text{Zn}_2\text{Sb}_2$ improves the materials' performance by 45% in terms of $(ZT)_{eng}$ over CaZn_2Sb_2 . Compared with the same composition $\text{Ca}_{0.25}\text{Yb}_{0.75}\text{Zn}_2\text{Sb}_2$ prepared by melting, our sample $\text{Ca}_{0.25}\text{Yb}_{0.75}\text{Zn}_2\text{Sb}_2$ has $(ZT)_{eng}$ doubled. EuZn_2Sb_2 exhibits the highest $(PF)_{eng} \sim 0.86 \text{ W m}^{-1} \text{ K}^{-1}$. Assuming $T_c = 323 \text{ K}$ and 2 mm of leg length, we have calculated the maximum efficiency η_{max} and its corresponding output power density P_d using $(ZT)_{eng}$ and $(PF)_{eng}$. The conversion efficiency of the optimized $\text{Ca}_{0.25}\text{Yb}_{0.75}\text{Zn}_2\text{Sb}_2$ is about 8.4% at $\Delta T = 450$

°C, almost twice that of the similar composition by melting method. EuZn_2Sb_2 shows the best output power density of 2.1 W cm^{-2} .

4. Conclusion

Ball milling and hot pressing has been demonstrated to be effective to fabricate phase pure Zintl compounds AZn_2Sb_2 , especially $\text{Ca}_{1-x}\text{Yb}_x\text{Zn}_2\text{Sb}_2$ with enhanced thermoelectric properties. The larger carrier mobility in the rare earth alloyed compounds appears to be an inherent feature of these materials, but the experimentally measured smaller effective mass may also be a reason for the increased Hall mobility with increasing Yb/Eu concentration in AZn_2Sb_2 . The highest ZT value achieved is ~ 0.9 for $x = 0.75$ at 773 K, $\sim 50\%$ higher than the best of the sample made by melting method.

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Figure Captions

Figure 1. The crystal structure of AZn_2Sb_2 .

Figure 2. (a) XRD patterns for $\text{Ca}_{1-x}\text{Yb}_x\text{Zn}_2\text{Sb}_2$ ($x = 0, 0.25, 0.5, 0.75$, and 1); (b) XRD patterns for EuZn_2Sb_2 , $\text{Eu}_{0.5}\text{Ca}_{0.5}\text{Zn}_2\text{Sb}_2$, and $\text{Eu}_{0.5}\text{Yb}_{0.5}\text{Zn}_2\text{Sb}_2$. (c) Refined lattice parameters a and c for $\text{Ca}_{1-x}\text{Yb}_x\text{Zn}_2\text{Sb}_2$ ($x = 0, 0.25, 0.5, 0.75$, and 1), EuZn_2Sb_2 , $\text{Eu}_{0.5}\text{Ca}_{0.5}\text{Zn}_2\text{Sb}_2$, and $\text{Eu}_{0.5}\text{Yb}_{0.5}\text{Zn}_2\text{Sb}_2$.

Figure 3. Typical microstructure for $\text{Ca}_{0.25}\text{Yb}_{0.75}\text{Zn}_2\text{Sb}_2$. (a) SEM image; (b) STEM image; (c) high magnification TEM with grain boundary with Fast Fourier transformation (FFT) image for right side grain; (d) high magnification TEM images with black and white nanoinclusions; (e) and (f) EDS mapping for the selected enlarged nanoinclusions.

Figure 4. Temperature dependent thermoelectric properties of $\text{Ca}_{1-x}\text{Yb}_x\text{Zn}_2\text{Sb}_2$ ($x = 0, 0.25, 0.5, 0.75$, and 1), EuZn_2Sb_2 , $\text{Eu}_{0.5}\text{Ca}_{0.5}\text{Zn}_2\text{Sb}_2$, and $\text{Eu}_{0.5}\text{Yb}_{0.5}\text{Zn}_2\text{Sb}_2$: (a) and (b) electrical resistivity; (c) and (d) Seebeck coefficient; (e) and (f) power factor. Four typical compounds from literature are included for comparison.

Figure 5. (a) Room temperature resistivity and carrier concentration comparison between samples of $\text{Ca}_{1-x}\text{Yb}_x\text{Zn}_2\text{Sb}_2$ ($x = 0, 0.25, 0.5, 0.75$, and 1) made by ball milling and melting; (b) Seebeck coefficients dependence of carrier concentration n in accordance with a single band model with $m^* = 0.6 m_e$ at 300K ; (c) Carrier mobility verses effective mass for all samples.

Figure 6. Temperature dependent thermal transport properties of $\text{Ca}_{1-x}\text{Yb}_x\text{Zn}_2\text{Sb}_2$ ($x = 0, 0.25, 0.5, 0.75$, and 1), EuZn_2Sb_2 , $\text{Eu}_{0.5}\text{Ca}_{0.5}\text{Zn}_2\text{Sb}_2$, and $\text{Eu}_{0.5}\text{Yb}_{0.5}\text{Zn}_2\text{Sb}_2$: (a) Specific heat; (b) thermal diffusivity; (c) and (d) total thermal conductivity; and (e) and (f) lattice

thermal conductivity. Four typical compounds from literature are included in (c), (d) and (f) for comparison.

Figure 7. Temperature dependent ZT for $\text{Ca}_{1-x}\text{Yb}_x\text{Zn}_2\text{Sb}_2$ ($x = 0, 0.25, 0.5, 0.75, \text{ and } 1$) EuZn_2Sb_2 , $\text{Eu}_{0.5}\text{Ca}_{0.5}\text{Zn}_2\text{Sb}_2$, and $\text{Eu}_{0.5}\text{Yb}_{0.5}\text{Zn}_2\text{Sb}_2$. Four typical compounds from literature are included in (a) and (b) for comparison.

Figure 8. Calculated $(ZT)_{\text{eng}}$ (a) and $(PF)_{\text{eng}}$ (b) dependence of T_h up to 773 K and T_c at 323 K for $\text{Ca}_{1-x}\text{Yb}_x\text{Zn}_2\text{Sb}_2$ ($x = 0, 0.25, 0.5, 0.75, \text{ and } 1$), EuZn_2Sb_2 , $\text{Eu}_{0.5}\text{Ca}_{0.5}\text{Zn}_2\text{Sb}_2$, and $\text{Eu}_{0.5}\text{Yb}_{0.5}\text{Zn}_2\text{Sb}_2$, efficiency (c) and output power density (d) as a function of hot side temperature. The data of the best performance of $\text{Ca}_{0.25}\text{Yb}_{0.75}\text{Zn}_2\text{Sb}_2$ from literature are included for comparison.

Figure 1. Jing Shuai *et al.*

Figure 2

Figure 2. Jing Shuai *et al.*

Figure 3. Jing Shuai *et al.*

Figure 4. Jing Shuai *et al.*

Figure 5. Jing Shuai *et al.*

Figure 6. Jing Shuai *et al.*

Figure 7. Jing Shuai *et al.*

Figure 8. Jing Shuai *et al.*

Table 1. Room-temperature thermoelectric transport properties of $\text{Ca}_{1-x}\text{Yb}_x\text{Zn}_2\text{Sb}_2$, EuZn_2Sb_2 , $\text{Eu}_{0.5}\text{Ca}_{0.5}\text{Zn}_2\text{Sb}_2$, and $\text{Eu}_{0.5}\text{Yb}_{0.5}\text{Zn}_2\text{Sb}_2$.

$\text{Ca}_{1-x}\text{Yb}_x\text{Zn}_2\text{Sb}_2$	x = 0	x = 0.25	x = 0.5	x = 0.75	x = 1
Carrier concentration (10^{19} cm^{-3})	5.92	6.91	8.72	6.08	4.14
Hall mobility ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	85.9	105	115	152	209
Effective mass (m_e)	1.02	0.85	0.81	0.73	0.66

AZn_2Sb_2	Eu	$\text{Eu}_{0.5}\text{Ca}_{0.5}$	$\text{Eu}_{0.5}\text{Yb}_{0.5}$
Carrier concentration (10^{19} cm^{-3})	3.60	5.11	4.49
Hall mobility ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	240	153	210
Effective mass (m_e)	0.69	0.79	0.69