On the Thermoelectric Properties of Zintl Compounds Mg₃Bi₂₋ₓPnₓ (Pn = P and Sb)

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A series of Zintl compounds Mg₃Bi₂₋ₓPnₓ (Pn = P and Sb) have been synthesized by the solid-state reaction method. While Sb can be substituted to a level as high as x = 1.0, P can be substituted only up to x = 0.5. The thermoelectric potential of these compounds has been evaluated by measuring resistivity (ρ), Seebeck (α) and Hall coefficients, and thermal conductivity between 80 K and 850 K. The measured resistivity and Seebeck coefficient values are consistent with those expected for small-bandgap semiconductors. Hall measurements suggest that the carriers are p type with concentration (p) increasing from ~10¹⁹ cm⁻³ to ~10³⁰ cm⁻³ as the Bi content is increased. The Hall mobility decreases with increasing temperature (T) and reaches a more or less similar value (~45 cm²/V s) for all substituted compositions at room temperature. Due to mass defect scattering, the lattice thermal conductivity (κₗ) is decreased to a minimum of ~1.2 W/m K in Mg₃BiSb. The power factor (α²ρ) is found to be rather low and falls in the range 0.38 mW/m K² to 0.66 mW/m K². As expected, at a high temperature of 825 K, the total thermal conductivity (κ) of Mg₃BiSb reaches an impressive value of ~1.0 W/m K. The highest dimensionless figure of merit (ZT) is realized for Mg₃BiSb and is ~0.4 at 825 K.

Key words: Thermoelectrics, Zintl phases, magnesium bismuthides, Seebeck and Hall coefficients

INTRODUCTION

In order to realize high thermal to electrical energy conversion efficiency, thermoelectric materials are required to exhibit high dimensionless figure of merit ZT = α²ρT/κ, where α is the Seebeck coefficient, ρ is the electrical conductivity, T is the absolute temperature, and κ is the thermal conductivity. Since low κ can give rise to high ZT, materials with low κ have been the desirable target for thermoelectric investigations. In fact, almost all traditional thermoelectric materials are poor conductors of heat.¹

One of the distinct advantages of considering Zintl compounds for thermoelectric applications is their low lattice thermal conductivity, which, in these complex-structured compounds, remains low (~1.1 W/m K to 1.7 W/m K at 300 K) irrespective of the mean atomic mass of the constituent atoms.²⁻⁴ Hence, Zintl compounds with light constituent elements such as Ca and P have been the focus of thermoelectric investigations in recent years.⁵ Similarly, many Mg-containing compounds are also known to exhibit moderately low thermal conductivity; For example, the thermal conductivities of Mg₂Si, Mg₂Ge, and Mg₂Sn all fall between 7.9 W/m K and 5.9 W/m K at 300 K.⁶ In the case of Mg₃Sb₂, κ is even lower and is ~2 W/m K to 2.5 W/m K at room temperature.⁷

In addition to its low κ, Mg₃Sb₂ also exhibits a very desirable high Seebeck coefficient of ~300 μV/K to 550 μV/K at around 600 K.⁷,⁸ However, its main drawback is the high resistivity of ~11 mΩ cm even at a high temperature of 750 K. Due to this high electrical resistivity, earlier investigation on the thermoelectric properties of Mg₃Sb₂ showed that the figure of merit ZT can reach only a
MODERATE VALUE OF $\sim 0.22$. Although metallic conductivity is realized in Zn$^{2+}$-substituted Mg$_3$-Zn$_x$Sb$_2$, these compositions also seem to be less promising as high-ZT materials. The electrical resistivity of Mg$_3$-Zn$_x$Sb$_2$ is too high to be a good thermoelectric material as Zn$^{2+}$ is substituted for Mg$^{2+}$. Identifying suitable doping agents to decrease the resistivity of Mg$_3$Sb$_2$ seems to be a challenge. In this regard, Mg$_3$Bi$_2$-P$_n$ (P = P and Sb) compounds are more appealing, as one would be able to fine-tune the thermoelectric properties of these compositions by varying $x$.

Mg$_3$Sb$_2$ crystallizes in the hexagonal La$_2$O$_3$-type structure. In this inverse $z$-La$_2$O$_3$ structure with one formula unit per primitive unit cell, Mg occupies two crystallographically inequivalent sites. The lattice parameters are $a = 4.568$ Å and $c = 7.229$ Å. While Mg$_3$Bi$_2$ is isostructural, Mg$_3$P$_2$ exhibits the cubic Mn$_2$O$_3$-type structure. With regard to electronic structure, earlier works indicated that Mg$_3$Sb$_2$ is a semiconductor with a bandgap ($E_g$) in the range of 0.6 eV to 0.82 eV. However, recent band structure calculations predict a smaller $E_g$ of $\sim 0.41$ eV for Mg$_3$Sb$_2$. As expected, the calculated bandgap ($E_g$) of Mg$_3$P$_2$ is larger and is $\sim 1.73$ eV. Mg$_3$Bi$_2$ is a semimetal. Hence, a systematic change in the bandgap is expected in the compound series Mg$_3$Bi$_2$-P$_n$ (P = P and Sb), as $x$ is varied. In addition, mass defect scattering present in these compositions should reduce the thermal conductivity further.

EXPERIMENTAL PROCEDURES

Mg$_3$Bi$_2$-P$_x$ with $0.0 < x < 1.0$ and Mg$_3$Bi$_{1.5}$P$_{0.5}$ were prepared by solid-state reaction of high-purity elements: Mg turnings (3 N), Bi shot (5 N), and red phosphorus powder (98.9%). Appropriate quantities of elements were first loaded into graphite crucibles and then sealed in evacuated quartz ampoules. These ampoules were then loaded into a furnace to carry out the solid-state reaction at higher temperatures for a period of 5 days to 7 days. The reaction temperatures were between $\sim 675$°C and 750°C, depending on the composition. While Mg$_3$Bi$_2$ was prepared at $\sim 675$°C, Mg$_3$Sb$_2$ and Mg$_3$Bi$_{1.5}$P$_{0.5}$ were prepared at $\sim 750$°C. After 1 day of reaction, the quartz ampoules were taken out of the furnace and water quenched. The reacted mixtures were then removed from the quartz ampoules, ground well to promote homogeneous mixing, and subjected to powder x-ray diffraction (Rigaku, Miniflex unit) to check phase purity. For all compositions, this process had to be repeated for several times to obtain phase-pure compounds. Mg evaporated readily. Hence, excess Mg, $\sim 5\%$ to 10%, was added during every intermediate grinding. The phase-pure compounds were then compacted into dense, half-inch-diameter discs ($\sim 97\%$ of theoretical density) using the pulsed electric current sintering (PECS) technique. PECS processing was employed for a duration of 30 min at pressure and temperature of 60 MPa and 625°C, respectively. The PECS heating rate was 20 K/min.

Rectangular bars ($\sim 3$ mm x 3 mm x 10 mm) cut from the discs were used to measure resistivity ($\rho$), Seebeck coefficient ($\alpha$), and thermal conductivity ($\kappa$). Below 300 K, a cryostat was used to measure $\rho$, $\alpha$, and $\kappa$ simultaneously. Above 300 K, a commercial unit (ZEM-3; ULVAC-RIKO) was used to collect $\rho$ and $\alpha$ data up to 850 K. Thin slabs ($\sim 1$ mm thick) were used to collect Hall data from 80 K to 300 K. The Hall resistance was measured by varying the magnetic field ($H$) from $-2.1$ T to $+2.1$ T, in steps of 0.5 T. The Hall resistance was found to vary linearly with $H$, and the Hall coefficient was calculated from the slope. The Hall coefficient $R_H$ was found to be positive, suggesting that holes are the dominant charge carriers. The carrier concentration was calculated using the expression $R_H = 1/p_e$, where $p$ is the hole concentration and $e$ is the electronic charge.

The lattice part of the thermal conductivity is calculated by subtracting the electronic part $\kappa_e = L_0T$ (where we choose the Lorenz number $L$ to be equal to its Sommerfeld value, $2.45 \times 10^{-8}$ V$^2$/K$^2$) from the measured total thermal conductivity ($\kappa$).

In order to calculate high-temperature thermal conductivity, thermal diffusivity ($D$) data were collected on thin discs (1.5 mm to 2.0 mm thick) over a temperature range of 300 K to 850 K, using a laser flash unit (LFA-457; NETZSCH). The thermal conductivity was calculated using the relation $\kappa = D\rho_mC_p$, where $\rho_m$ is the sample density and $C_p$ is the heat capacity, for which the Dulong–Petit limit value was used.

RESULTS AND DISCUSSION

Powder x-Ray Diffraction

Powder x-ray diffraction (XRD) patterns are given in Fig. 1. The patterns show systematic shift with Sb content without any additional reflections. Hence, it can be concluded that single phase formation is possible for the entire composition range.