Journal of ELECTRONIC MATERIALS, Vol. 42, No. 7, 2013
DOI: 10.1007/s11664-012-2417-7

On the Thermoelectric Properties of Zintl Compounds $Mg_3Bi_{2-x}Pn_x$ (Pn = P and Sb)

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A series of Zintl compounds $Mg_3Bi_{2-x}Pn_x$ (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 $\sim 10^{19}$ cm^{-3} to $\sim 10^{20}$ cm^{-3} as the Bi content is increased. The Hall mobility decreases with increasing temperature (T) and reaches a more or less similar value ($\sim$45 cm^2/V s) for all substituted compositions at room temperature. Due to mass defect scattering, the lattice thermal conductivity (κ_L) is decreased to a minimum of $\sim$1.2 W/m K in Mg_3BiSb. The power factor (α^2/ρ) is found to be rather low and falls in the range 0.38 mW/m K^2 to 0.66 mW/m K^2. As expected, at a high temperature of 825 K, the total thermal conductivity (κ) of Mg_3BiSb reaches an impressive value of $\sim$1.0 W/m K. The highest dimensionless figure of merit (ZT) is realized for Mg_3BiSb and is $\sim$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 $ZT = \alpha^2\sigma T/\kappa$, where α is the Seebeck coefficient, σ 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 ($\sim$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 Mg_2Si, Mg_2Ge, and Mg_2Sn all fall between 7.9 W/m K and 5.9 W/m K at 300 K.[6] In the case of Mg_3Sb_2, κ is even lower and is $\sim$2 W/m K to 2.5 W/m K at room temperature.[7]

In addition to its low κ, Mg_3Sb_2 also exhibits a very desirable high Seebeck coefficient of $\sim$300 μV/K to 550 μV/K at around 600 K.[7,8] However, its main drawback is the high resistivity of $\sim$11 mΩ cm even at a high temperature of 750 K. Due to this high electrical resistivity, earlier investigation on the thermoelectric properties of Mg_3Sb_2 showed that the figure of merit ZT can reach only a

(Received July 5, 2012; accepted December 27, 2012; published online February 5, 2013)