ABSTRACT

AgPb\textsubscript{10}SbTe\textsubscript{12} is one member of the cubic family of materials AgPb\textsubscript{m}SbTe\textsubscript{m+2}, which adopts NaCl structure where Ag, Pb and Sb atoms occupy the Na site and Te atoms occupy the Cl site. Ingots of this compound were prepared by a solid state reaction for thermoelectric measurements. AgPb\textsubscript{10}SbTe\textsubscript{12} is a narrow band gap semiconductor with Eg~0.26 eV. In order to optimize the ZT of this member, compositions with deficiency of Ag and Bi-substitution were examined and found to exhibit enhanced power factor at 300 K. The Bi-substituted ingot had ZT~0.39 at 300 K and ZT~0.68 at 400 K. Carrier concentration and the mobility measurements are reported.

INTRODUCTION

Recently, several new materials have been discovered to possess high ZT values at the medium high temperature. Rare earth-filled skutterudites RECo\textsubscript{4}Sb\textsubscript{12} (RE = Yb, Eu) were reported to reach ZT >1 at 700 K due to the lower low lattice thermal conductivity caused by the ion rattling effect.\textsuperscript{1,2} ZrNiSn-based half-Heusler compounds were reported to have ZT = 0.7 at 800 K.\textsuperscript{3} The Sr\textsubscript{8}Ga\textsubscript{16}Ge\textsubscript{30} clathrates\textsuperscript{4} and Na\textsubscript{x}Co\textsubscript{2}O\textsubscript{4} oxides\textsuperscript{5} were also found to have potential thermoelectric applications at high temperature. Furthermore, low dimensional supperlattice materials were reported to enhance ZT values caused by the effects of increasing electronic density of states and lower lattice thermal conductivity within the supperlattice structures.\textsuperscript{6,7,8} Lead telluride is a well-known thermoelectric material used for power generation up to 900 K with a maximum ZT of ~0.8\textsuperscript{9}, while remarkably, PbTe-based QD superlattice materials were reported to reach ZT~2 around 500-700 K.\textsuperscript{10,11}

We have focused on discovering high performance bulk thermoelectric materials suitable for different temperature ranges. One of the approaches is to search for new compounds with low dimensional structures based on the transport theory that ZT scales with a parameter B defined as:

$$B = \gamma \frac{1}{3\pi^2} \left( \frac{2k_B T}{\hbar^2} \right)^{3/2} \sqrt{m_x m_y m_z} \frac{k_B^2}{e \kappa_L} \mu \mu_x \frac{x}{y}$$

Eq. (1)

where $\gamma$ is the band degeneracy, $m_i$ is the effective mass of the carriers (electrons or holes) in the $i$th direction, $\mu$ is the carrier mobility along the transport direction, and $\kappa_L$ is the lattice contribution to the thermal conductivity. Thus, for high ZT, large effective mass, high carrier mobility, and low lattice thermal conductivity are desirable.\textsuperscript{12} Along these lines we identified layered CsBi\textsubscript{4}Te\textsubscript{6} a promising system showing a ZT of 0.8 at 225 K, which is 40% greater than that of the Bi\textsubscript{2-x}Sb\textsubscript{x}Te\textsubscript{3}. [10,11]
γSe₂ alloys. These low dimensional systems are taking advantage of the large anisotropy in carrier effective masses associated with high carrier mobility.

Another approach to significantly increase ZT (mainly through enhancing thermopower) is to take advantage of a large number of valleys (or peaks) in the bands near the Fermi level (i.e. a large γ in eq (1)). High band degeneracy γ is likely to exist in compounds of the highest possible crystal symmetry such as hexagonal or cubic. We have examined an interesting and highly attractive family of bulk cubic compounds with complex composition and general formula AgPbₘSbTeₙ₊₂ materials, which adopt NaCl structure with *Fm3m* symmetry. One interesting member of this family is AgPb₁₀SbTe₁₂ which we discovered shows a promising figure of merit at 300 K. In order to optimize the ZT value of this compound, we investigated non-stoichiometric compositions and Bi-substituted compositions. We find that these are important parameters and play an important role in reaching optimum thermoelectric performance. The thermopower, electrical conductivity, thermal conductivity, power factor, ZT, carrier concentration and mobility of the optimized materials Ag₁₋δPb₁₀SbTe₁₂ and Ag₁₋δPb₁₀Sb(Bi)Te₁₂ are presented in this paper.

RESULTS AND DISCUSSION

A silver shiny metallic ingot with the composition of AgPb₁₀SbTe₁₂ was prepared by a solid state reaction. The powder X-ray pattern indicated that the material possesses the NaCl-type structure with *Fm3m* symmetry, see Figure 1. The cell parameter of AgPb₁₀SbTe₁₂ was 6.396(3) Å. The IR diffuse reflectance spectroscopic measurements showed that AgPb₁₀SbTe₁₂ is a narrow band gap semiconductor with E_g~0.26 eV at room temperature, see Figure 2.

Figure 1. The NaCl-type structure of AgPb₁₀SbTe₁₂.
Figure 2. Energy band gap of Ag$_{1-\delta}$Pb$_{10}$SbTe$_{12}$.

Charge transport properties were measured on rectangular samples sliced from the prepared ingots with dimensions ~3 x 3 x 4 mm$^3$. The “as-prepared” undoped AgPb$_{10}$SbTe$_{12}$ ingot had electrical conductivity over 520 S/cm and thermopower (i.e. Seebeck coefficient) of -154 $\mu$V/K at the room temperature. The resulting power factor of 12.3 $\mu$V/cm-K$^2$ is significant and makes this material a potential n-type candidate thermoelectric system. In order to optimize the ZT value, an effort of compositional tuning was then made. Interestingly, an ingot with Ag deficient composition Ag$_{1-\delta}$Pb$_{10}$SbTe$_{12}$ was characterized with a higher power factor by virtue of an enhancement of the electrical conductivity without great loss of thermopower, see Figure 3A.

The negative Seebeck coefficient indicates that Ag$_{1-\delta}$Pb$_{10}$SbTe$_{12}$ ingot is a n-type conductor. The thermopower S increases with rising temperature and reaches -135 $\mu$V/K at 300 K. (Figure 3A) The power factor PF also increases from 4.8 K to 300 K, see Figure 2B. The power factor of Ag$_{1-\delta}$Pb$_{10}$SbTe$_{12}$ is promoted to 14.9 $\mu$W/cm-K$^2$ at 300 K as compared with 12.3 $\mu$V/cm-K$^2$ of AgPb$_{10}$SbTe$_{12}$.

The measured thermal conductivity $\kappa$ of Ag$_{1-\delta}$Pb$_{10}$SbTe$_{12}$ is ~1.8 W/mK at 300 K, see Figure 3C. Based on the Wiedemann-Franz law, the measured thermal conductivity $\kappa$ can be separated into electronic $\kappa_e$ and lattice components $\kappa_L$. The obtained lattice thermal conductivity $\kappa_L$ was ~1.2 W/mK at 300 K, which is comparable to that of PbTe$_{1-x}$Se$_x$ solid solutions. The ZT was obtained as 0.25 at 300 K, see Figure 3D.
The Bi substituted Ag$_{1-x}$Pb$_{10}$Sb(Bi)Te$_{12}$ ingot was also found to have a higher electrical conductivity and considerable thermopower as compared with the AgPb$_{10}$SbTe$_{12}$ ingot. The electrical conductivity $\sigma$ of Ag$_{1-x}$Pb$_{10}$Sb(Bi)Te$_{12}$ decreases with the rising temperature where $\sigma \approx 830$ S/cm at 300 K and $\sigma \approx 515$ S/cm at 400 K, Figure 4A. The thermopower indicates that Ag$_{1-x}$Pb$_{10}$Sb(Bi)Te$_{12}$ is also a n-type conductor and increases almost linearly with the rising temperature from a value of -153 $\mu$V/K at 300 K to -209 $\mu$V/K at 400 K. (Figure 4A) The power factor is increased to 19.3 $\mu$W/cm$^2$K at 300 K, see Figure 4B.

The measured thermal conductivities of Ag$_{1-x}$Pb$_{10}$Sb(Bi)Te$_{12}$ is $\approx 1.5$ W/mK at 300 K, see Figure 4C. Based on this the ZT is 0.39 at 300 K and reaches 0.68 at 400 K, see Figure 4D. The Bi-substituted Ag$_{1-x}$Pb$_{10}$Sb(Bi)Te$_{12}$ material has a lower lattice thermal conductivity than AgPb$_{10}$SbTe$_{12}$ which helps to achieve a higher ZT value.

Hall measurements of Ag$_{1-x}$Pb$_{10}$Sb(Bi)Te$_{12}$ as function of temperature led carrier concentration (electrons) at room temperature of $\approx 7.8 \times 10^{18}$ cm$^{-3}$, Figure 4E, electron mobility of $\approx 570$ cm$^2$/V-s, Figure 4F.
CONCLUSIONS

The member m = 10 in the cubic family AgPbₘSbTeₘ₊₂ is a promising n-type thermoelectric candidate. The non-stoichiometric composition based on AgPb₁₀SbTe₁₂ plays an important role to magnify its thermoelectric properties. Furthermore, the Bi-substituted compound improves the ZT.
value by achieving a lower lattice thermal conductivity. The investigation of higher members in this family and the modification of p-type materials is under way.

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REFERENCES

12 Systems with many band extrema, characterized by a degeneracy parameter γ, have higher thermoelectric power than those with a single extrema. This is because, for the same total carrier concentration, the concentration in each pocket is smaller for larger γ. This increases the value of S associated with each pocket compared to the value obtained for the single band case because S increases with decreasing carrier concentration. The amount of increase, however, depends on γ, the temperature, band gap, and other band parameters.
14 This is true if the carrier scattering between valleys is absent or minimized.
15 The electronic thermal conductivity can be accurately estimated over all temperatures using the electrical conductivity data by the Wiedemann-Franz (WF) law (using a Lorenz number L of 2.45 x10⁻⁸ W·ohm·K²).