Enhanced thermoelectric performance in the very low thermal conductivity Ag2Se0.5Te0.5

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Citation: Applied Physics Letters 103, 143906 (2013); doi: 10.1063/1.4824353
View online: http://dx.doi.org/10.1063/1.4824353
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/103/14?ver=pdfcov
Published by the AIP Publishing
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(Received 24 July 2013; accepted 22 September 2013; published online 3 October 2013)

In this letter, we report the high-temperature thermoelectric properties of Ag$_2$Se$_{0.5}$Te$_{0.5}$. We find that this particular composition displays very low thermal conductivity and competitive thermoelectric performance. Specifically, in the temperature region 520 K ≤ T ≤ 620 K, we observe non-hysteretic behavior between the heating and cooling curves and $zT$ values ranging from 1.2 to 0.8. Higher $zT$ values are observed at lower temperatures on cooling. Our results suggest that this alloy is conducive to high thermoelectric performance in the intermediate temperature range, and thus deserves further investigation. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4824353]

Devices based on thermoelectric (TE) materials convert heat into electricity in a compact and robust package with no moving parts. Development of higher efficiency thermoelectric materials, as determined by the dimensionless figure-of-merit $zT = x^2T/ρκ$ (figure-of-merit), where $x$ is the Seebeck coefficient or thermopower, $ρ$ is the electrical resistivity, $κ$ is the thermal conductivity, and $T$ is the temperature. Maximum thermoelectric conversion efficiency can be achieved by maximizing $x$, while minimizing $ρ$ and $κ$. However, as these properties are interrelated through the physics and chemistry of the materials, it is not possible to engineer these properties separately. Certain classes of materials tend to display good thermoelectric performance; for example, the binary and ternary chalcogenides provide a low thermal conductivity platform combined with low electrical resistivity leading to high $zT$. An examination of the current state-of-the-art thermoelectric materials reveals that the chalcogenides have many representatives (PbTe, Bi$_2$Te$_3$, TAGS, Sb$_2$Te$_3$, and AgSbTe$_2$). The binary silver chalcogenides (Ag$_2$Se and Ag$_2$Te) have not gained as much attention even though previous reports indicate that they are very promising materials. For example, the thermoelectric performance of Ag$_2$Se is rather high: $zT = 0.96$ at $T = 300$ K. and recent work showed that proper synthesis procedure leads to a substantial improvement of the thermoelectric performance of Ag$_2$Te. Since, at room temperature, Ag$_2$Te stabilizes in a monoclinic structure, while Ag$_2$Se stabilizes in an orthorhombic structure, it is worth exploring the stoichiometry Ag$_2$Se$_{0.5}$Te$_{0.5}$ in order to assess whether phase competition and subsequent complexity can improve thermoelectric performance. Because of the competing structures, we expect that for specific $x$, phase separation will occur on solidification, leading to the formation of a complex composite with very low thermal conductivity possibly like those found in Refs. 17 and 18. Indeed, this is what can be inferred from the Ag$_2$Se-Ag$_2$Te phase diagram (Figure 1).

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FIG. 1. The Ag$_2$Se-Ag$_2$Te phase diagram. The dark gray vertical line corresponds to the 0.5/0.5 composition.

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According to the X-ray diffraction data (Figure 2(a), black line), the dominant structure is the orthorhombic Ag$_2$Se. The Rietveld refinement (Figure 2(a), red line) was performed using the program Rietica and the structural model $P2_12_12_1$ (space group 19). The lattice parameters obtained from the fit are $a = 4.4330$ Å, $b = 7.2345$ Å, and $c = 7.9676$ Å. The corresponding lattice parameters for the stoichiometric Ag$_2$Se (Ref. 22) are $a = 4.330$ Å, $b = 7.062$ Å, and $c = 7.764$ Å. The 2.5% increase in the lattice parameters is expected since Te is larger than Se. Traces of a secondary phase might still be present but not in a sufficient amount to be detected by X-ray diffraction. The corresponding reduction in the thermal conductivity between the stoichiometric and heavily doped phase is also shown (Figure 2(b)). The thermal conductivity of Ag$_2$Te is also shown for comparison.

FIG. 2. (a) X-ray diffraction data of an ingot sample of Ag$_2$Se$_{0.5}$Te$_{0.5}$ (black spectrum). The Rietveld refinement is also displayed for comparison (red spectrum). (b) Thermal conductivity of orthorhombic Ag$_2$Se, monoclinic Ag$_2$Te and of Ag$_2$Se$_{0.5}$Te$_{0.5}$ (sample 1).
$Ag_2Te$ is rather dramatic. Since both $Ag_2Se$ and $Ag_2Se_{0.5}Te_{0.5}$ share the same structure and undergo a similar structure transformation, it implies that the reduction in thermal conductivity in the case of $Ag_2Se_{0.5}Te_{0.5}$ is due to point defect scattering. The total thermal conductivity at room temperature remains <1 W/mK and it decreases as the sample goes through the structural phase transition. It reaches a minimum value of <0.6 W/mK at ~420 K before it starts increasing monotonically at high temperatures due to the presence of minority carriers. At approximately 575 K, the thermal conductivity value of $Ag_2Se_{0.5}Te_{0.5}$ equals that of $Ag_2Te$.

In the case of the thermopower (Figure 3(a)), the absolute value of the Seebeck coefficient decreases considerably after the first temperature cycle. However, it assumes a relatively constant value ($\approx 160 \mu V/K$) for a wide temperature range. During all cycles, the magnitude of the Seebeck coefficient increases as we cross the structural phase transition and continues to increase with temperature until the presence of a downturn due to minority carrier contribution. The point at which the minority carrier contribution becomes significant shifts to a lower temperature during cooling. This feature remains regardless of the cycling and it presumably relates to the changes in composition as the sample traverses the phase diagram.

Finally, the resistivity values (Figure 3(c)) also decrease considerably after the first temperature cycle. During the third cycle, the resistivity values below the structural phase transition are $\rho \leq 1 \text{ m}\Omega\text{-cm}$, and above the transition the resistivity values on cooling remain <2 m\Omega\text{-cm}. Above the structural phase transition, we also observe a consistent increase in the carrier concentration (Figure 3(b)) and a large drop in mobility (Figure 3(d)) that continues to decrease monotonically with increasing temperature. The mobility reduction explains the increase in the resistivity in the presence of increasing carrier concentration as the sample moves through the structural phase transition, and it is most likely due to the presence of mobile Ag ions. The carrier concentration at room temperature is $n = 4 \times 10^{18} \text{ cm}^{-3}$ and at $T = 620 \text{ K}$ it reaches a value of $n = 1 \times 10^{19} \text{ cm}^{-3}$. The mobility of $Ag_2Se_{0.5}Te_{0.5}$ is very high; the mobility values obtained are $\mu > 2000 \text{ cm}^2/\text{Vs}$ at room temperature and $\mu > 350 \text{ cm}^2/\text{Vs}$ at $T = 620 \text{ K}$. Thus, the mobility of this highly disordered alloy is much greater than that of other state-of-the-art n-type thermoelectric materials. For comparison, the mobility of Te-doped Bi$_2$Te$_3$ is $\mu = 212 \text{ cm}^2/\text{Vs}$ and that of La$_3AsTe_4$ is $\mu = 4 \text{ cm}^2/\text{Vs}$. We only observe very small hysteresis in the mobility data above the phase transition, and the mobility values in that region do not vary with cycling. Hysteresis is only observed below the phase transition as the mobility in that region decreases with cycling. The carrier concentration on the other hand increases with cycling, in agreement with the reduction in resistivity, and the crossover temperature (temperature for which $n_{\text{cooling}} > n_{\text{heating}}$ on cooling) decreases. This crossover temperature appears to correlate with the temperature at which the bipolar contribution becomes significant.

The dimensionless figure-of-merit ($zT$) as a function of temperature is shown in Figure 4. The $zT$ was calculated in the temperature region extending from 420 K to 610 K since this is the region of high thermoelectric efficiency (the $zT$ values below the transition are of the order of ~0.5 to 0.6). The large hysteresis observed between the heating and cooling curves is due to the hysteresis present in the Seebeck coefficient; the hysteresis in the electrical resistivity is reduced by cycling and the hysteresis in the thermal conductivity data remains small, but in the case of the Seebeck coefficient the hysteresis remains pronounced and persistent. As a result, significant hysteresis can be observed in the temperature region <520 K. The highest $zT$ values are observed on cooling and in the temperature region <520 K. A consistent maximum $zT = 1.2$ is observed at $T = 440 \text{ K}$. The maximum $zT$ on cooling is observed in the case of sample 2 for which $zT = 1.4$ at 420 K, mainly due to a smaller value in the total thermal conductivity versus sample 1 at 420 K (on cooling, 0.47 W/mK versus 0.51 W/mK). Nonetheless, the large hysteresis observed in that temperature region suggests that the
high $zT$ values might be due to the formation of a metastable phase or kinetic effects resulting from the structural phase transition. However, $zT$ in the non-hysteretic temperature region is very competitive ($zT = 1.0$ at $T = 520$ K and $zT = 0.8$ at $T = 610$ K) and the lack of hysteresis between the heating and cooling curves suggests a stable alloy configuration. More importantly, the slow decrease in $zT$ versus temperature ($\frac{dzT}{dT} \approx 0.0015$ K$^{-1}$) enables the potential for substantial waste heat recovery through a wide temperature region.

These results confirm that Ag$_2$Se$_{1-x}$Te$_x$ offers a very appealing compositional space that is conducive to high thermoelectric performance in the intermediate temperature regime. Specifically, the discussed composition (0.5/0.5) outperforms many of the state-of-the-art thermoelectric materials in the corresponding temperature range. In addition, it provides an alternative system for the formation of biphasic alloys and the study of the effects of structural complexity and disorder on thermoelectric performance. Further studies are required in order to establish a correlation between the microstructure and the electrical and thermal transport behavior of these alloys to ultimately optimize their thermoelectric performance.

The authors would like to thank the U.S. Air Force Office of Scientific Research for supporting this work.