Thermoelectric Performance of Ge$_{0.99-x}$Na$_{0.01}$Ag$_x$Se

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Abstract. Doped GeSe has theoretically been predicted to exhibit ultralow thermal conductivity that yields a high figure of merit (ZT) of 2.6 at 800K. However, experimental studies of the thermoelectric performance of GeSe have received little attention due to poor doping efficiency. Doping GeSe with Na is reported to reduce its thermal conductivity due to the growth of Na-rich precipitates, but the electrical resistivity remains too high. In order to suppress both thermal conductivity and resistivity, a co-doping approach was used by introducing Na and Ag. Characterization using scanning electron microscopy indicates the presence of both Ag- and Na-rich precipitates within the GeSe matrix. The resistivity decreases by ~6 times at high temperature with increasing Ag concentration. However, the thermal conductivity only decreases by ~1.5 times after Ag doping of about 0.5%. The Seebeck coefficient remains constant with doping at high temperature. Overall, the thermoelectric performance of Na,Ag co-doped GeSe is optimum at around 0.5 mol% of Ag.

1. Introduction
Thermoelectric (TE) materials that can directly convert waste heat to electricity have been widely studied to develop more environmental-friendly sources of alternative energy[1-5]. Thermoelectric performance is quantified by the dimensionless figure of merit (ZT), defined as $ZT = S^2\sigma T/\kappa$, where $S$, $\sigma$, $T$, and $\kappa$ are the Seebeck coefficient, electrical conductivity, absolute temperature and thermal conductivity, respectively.

The quantity of $S^2\sigma$ is known as the power factor (PF), while the thermal conductivity is the sum of the electronic thermal conductivity ($\kappa_{el}$) and lattice thermal conductivity ($\kappa_{latt}$). Good TE materials require a high PF and a low thermal conductivity. However, the efficiency of the best TE devices is still far below the Carnot efficiency[6-7]. Many studies to improve the Seebeck coefficient and reduce the thermal conductivity have been performed recently in bulk materials, nanomaterials and bulk nanostructured thermoelectric materials[8-13]. The PF and thermal conductivity are both related to the carrier concentration ($n$). The optimum carrier concentration for TE materials is generally in the range $10^{19} - 10^{20}$ cm$^{-3}$, which corresponds to the heavily doped semiconductor regime[14], and in suitable systems.

Semiconductor material allows a high Seebeck coefficient and low thermal conductivity to be simultaneously obtained[15-17]. Recently, single crystal SnSe with low thermal conductivity has been
reported to show a record ZT of 2.6 at 973 K measured along the b-axis [18]. Doping single crystal SnSe with Na was reported to show an increased average ZT of ~1.34[19]. Furthermore, polycrystalline SnSe also exhibits a low thermal conductivity and high ZT[6,20-23]. Theoretical studies on the thermoelectric properties of the isostructural orthorhombic IV-VI compounds SnS, GeS, and GeSe have also been reported[24-26]. GeSe was theoretically predicted to have a lower thermal conductivity and similar ZT to SnSe (2.6 at 800 K) if the carrier concentration can be increased to an appropriate level[24]. Nevertheless, experimental studies on the thermoelectric properties of GeSe are few due to the high resistivity of undoped GeSe and the apparent difficulty in doping it.

In this study, we have synthesized 1% Na-doped GeSe and co-doped it with various concentrations of Ag in an attempt to suppress both thermal conductivity and resistivity. Doping GeSe with Na was recently reported to strongly reduce its thermal conductivity due to the formation of Na-rich precipitates [26]. However, the power factor remained low due to a high resistivity. On the other hand, Ag-doped GeSe is reported to exhibit an increased carrier concentration of \( \sim 10^{18} \text{cm}^{-3} \), with an improved ZT [27].

2. Experimental Details

Polycrystalline Ge\(_{0.99-x}\)Na\(_{0.01}\)Ag\(_x\)Se samples (with \( x=0 \), \( x=0.005 \), and \( x=0.01 \)) were synthesized by solid-state reaction using high purity elements (>99.99%). Stoichiometric ratios of Ge powder (99.999%, Alfa Aesar), Se shot (99.999%, Alfa Aesar), Na powder and Ag powder were weighed in an Argon atmosphere glovebox. With a total mass of 10 g, these elements were sealed in carbon-coated quartz tubes under vacuum. The samples were then melted at 1223 K for 10 h and quenched in cold water. The samples were subsequently annealed at 673 K for 72 h. The obtained ingots were then hand-ground into fine powders and characterized using a Bruker D8 Advance X-ray diffractometer to identify the structure and the crystalline phases present. The X-ray diffraction (XRD) patterns were fitted using the GSAS software.

Fine powder samples of Ge\(_{0.99-x}\)Na\(_{0.01}\)Ag\(_x\)Se were placed into a 10 mm diameter or 20 mm diameter graphite die and cold-pressed into pellets. The 20 mm pellets were then cut and polished into a parallelepiped shape for resistivity and Seebeck coefficient measurements using a Linseis LSR-3 instrument under 0.1 atm helium. The 10 mm pellets were used for thermal diffusivity measurement by the laser flash method (Linseis LFA 1000). Thermal conductivity was calculated using \( \kappa = \rho \lambda C_p \), where \( \rho \), \( \lambda \), and \( C_p \) are the density, thermal diffusivity, and heat capacitance, respectively. The density of our samples was calculated by measuring the mass and dimensions, and the heat capacity was calculated using the equation \( C_p = 46.77 + (15.099 \times 10^{-3} \, T^- \, (0.0316 \times 10^{-6} \, T^2) \) J/K.mol[28]. The morphology and elemental distribution of the samples was studied using a scanning electron microscope (SEM) JEOL JSM-7001, equipped with an EDAX (energy-dispersive X-ray) spectrometer.

3. Results and Discussion

GeSe has an orthorhombic structure at room temperature with the Pnma space group formed from zigzag chains of Ge-Se along the b-axis[30,31]. The unit cell contains eight atoms as shown in figure1(b). The dopant and co-dopant are expected by electronegativity considerations to occupy the Ge site in the GeSe structure. The XRD patterns of our Ge\(_{0.99-x}\)Na\(_{0.01}\)Ag\(_x\)Se samples (\( x=0 \), \( x=0.005 \), and \( x=0.01 \)) are compared to a reference pattern[31] in figure1 (a). The main peaks are indexed in the orthorhombic structure of GeSe[32], with the most intense 400 peak at ~32.7°. The bond distances and lattice parameters of all the samples are shown in table 1. There is no significant difference in structure to the reference[31] due to the small amount of dopants.
Figure 1. (a) XRD patterns of Ge$_{0.99-x}$Na$_{0.01}$Ag$_x$Se ($x=0$, $x=0.005$, and $x=0.01$) compared to a reference GeSe pattern[31]. (b) Orthorhombic unit cell of Ge$_{0.99-x}$Na$_{0.01}$Ag$_x$Se

Table 1. Refined lattice parameters and bond distances of Ge$_{0.99-x}$Na$_{0.01}$Ag$_x$Se ($x=0$, $x=0.005$, and $x=0.01$)

| Samples           | Lattice Parameters (Å) | Ge-Se bond distance (Å) |
|-------------------|------------------------|-------------------------|
|                   | a         | b      | c      |                       |
| GeNaSe            | 10.837(6) | 3.838 (3) | 4.392 (3) | 2.577                 |
| GeNaAgSe, Ag:0.5% | 10.832(6) | 3.836(3) | 4.391(4) | 2.576                 |
| GeNaAgSe, Ag:1%   | 10.830(6) | 3.835(3) | 4.391 (5) | 2.576                 |
| GeSe[31]          | 10.83     | 3.83   | 4.39   | -                     |

The enlarged XRD pattern with 2θ range from ~25°-35° in figure 2 shows the presence of impurities in our samples. The impurity peak at ~26.5° indicated by the red circle is consistent with graphite, which originates from the carbon-coated quartz tube. The peak at ~28.7° indicated by the blue circle belongs to the sample holder, and there are further small impurity peaks that could not be matched to any reported phase. The EDAX elemental mapping of the ingots (figure 3) indicates the presence of Ag-rich precipitates after Ag co-doping (lighter colour corresponds to heavier elements). The additional peaks in the XRD patterns might thus belong to Ag-rich secondary phases.
The thermoelectric transport properties were measured in pellets with densities of ~89%, which is lower than in previous studies[26,27] where pellets are prepared by hot pressing. The high resistivity of all the samples (figure 4 (a)) indicates that they are not heavily doped. However, co-doping with Ag successfully decreases the resistivity from ~10 Ωm at 600 K for x=0 to ~1.5 Ωm for x=0.01. The Seebeck coefficient (S) exhibits a constant, positive value (figure 4 (b)) of ~700μV/K throughout the temperature range measured, indicating p-type conduction. There is no indication of any bipolar conduction in our samples. Generally, the bipolar effect represents a “conductivity-limit” due to the rising contribution of minority carriers with temperature to the transport properties in extrinsic semiconductors[34]. This effect was previously reported for Ag-doped GeSe at temperatures above 600 K[27]. The absence of the bipolar effect in our samples indicates that the thermal energy is too low to excite minority carriers (electrons) to the conduction band below 600 K.
Figure 5. (a) Total thermal conductivity, (b) electronic thermal conductivity, and (c) lattice thermal conductivity of Ge$_{0.99-x}$Na$_{0.01}$Ag$_x$Se samples

Figure 5 (a), (b), and (c) show the total thermal conductivity ($\kappa_{\text{tot}}$), electronic thermal conductivity ($\kappa_{\text{el}}$), and lattice thermal conductivity ($\kappa_{\text{lat}}$), respectively. The correlation between these three parameters is given by $\kappa_{\text{tot}} = \kappa_{\text{el}} + \kappa_{\text{lat}}$. Here, $\kappa_{\text{el}}$ was estimated by the equation $\kappa_{\text{el}} = L\sigma T$, where $L$ is the Lorentz number and $\sigma$ is the electrical conductivity. The electronic thermal conductivity is several orders of magnitude smaller than the lattice thermal conductivity due to a low carrier concentration, thus the main contribution to the total thermal conductivity is from phonon transport through the crystal lattice. At room temperature, the total thermal conductivity is 0.52 Wm$^{-1}$K$^{-1}$, 0.40 Wm$^{-1}$K$^{-1}$, and 0.69 Wm$^{-1}$K$^{-1}$ for $x$ = 0, $x$ = 0.01, and $x$ = 0.005, respectively. These small values of $\kappa_{\text{tot}}$ are likely due to strong anharmonicity. The dopant and co-dopant are expected to occupy the Ge site in the GeSe structure. The resulting atomic displacements generate changes in the spring constant, which leads to increased phonon-phonon scattering and reduces the lattice thermal conductivity without affecting the electronic properties of the samples[7].

The total thermal conductivity shows a negative slope with temperature, which indicates strong phonon-phonon interactions in our samples. Adding 0.5% Ag to Ge$_{0.99}$Na$_{0.01}$Se reduces the total thermal conductivity over the entire temperature range. However, the sample with 1% Ag doping has the highest total thermal conductivity of all three. Compared to the variation in resistivity with doping shown in figure 4(a), the dependence of the total thermal conductivity with Ag concentration is
inconsistent. This might indicate that the doping limit is reached below 1% Ag; thus, the optimum Ag concentration is around 0.5%.

4. Conclusion

Polycrystalline samples of Ge$_{0.99-x}$Na$_{0.01}$Ag$_x$Se with x=0, x=0.005, and x=0.01 have been successfully synthesized by solid-state reaction. The obtained samples contain impurities corresponding to Ag-rich secondary phases. The thermoelectric properties of all samples have been measured, showing a positive Seebeck coefficient that is essentially constant with temperature. The resistivity decreases as the Ag dopant concentration increases. However, there is an inconsistent dependency of the Ag concentration on the thermal conductivity. Overall, the effect of the variation of Ag on the thermoelectric performance of Na-doped GeSe is optimum at around 0.5% concentration.

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