Thermoelectric and thermal stability improvements in Nano-Cu$_2$Se included Ag$_2$Se

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ABSTRACT

Recently, silver chalcogenides have attracted great attention due to their potential application for room temperature power generation and local cooling. In this work, we report the thermoelectric properties and thermal stability of bulk Ag$_2$Se with nano-Cu$_2$Se inclusions ($(\text{Ag}_2\text{Se})_{1-x} (\text{Cu}_2\text{Se})_x$ where $x = 0, 0.02$ and $0.05$). Ag$_2$Se samples were prepared via melting, annealing and the nanocomposite was prepared by ball milling this material with required amount of nano-Cu$_2$Se; finally, the samples were consolidated by spark plasma sintering. High temperature and low temperature transport properties were assessed by the measurements of the Seebeck coefficient, electrical conductivity, thermal conductivity, and Hall coefficient. The phase composition and microstructure were explored by powder X-ray diffraction (PXRD) and scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) analysis, while the thermal stability of samples was investigated via heating microscopy and heat capacity measurement. Room temperature PXRD and SEM indicated that two separate phases of Ag$_2$Se and Cu$_2$Se form in nano-Cu$_2$Se included composites. Heating microscopy and the heat capacity measurement indicate that the thermal stability of Ag$_2$Se is enhanced with increasing nano-Cu$_2$Se inclusions. The sign of the Seebeck coefficient, in agreement with the Hall coefficient, shows that electrons are the dominant carriers in all samples. The electrical conductivity of the samples increases and the Seebeck coefficient decreases with increasing amount of the nano-Cu$_2$Se inclusion, likely due to augmented carrier concentration. Despite the larger electrical conductivity, the thermal conductivity is suppressed with nano-Cu$_2$Se inclusions. A high power factor and reduced thermal conductivity lead to a maximum $ZT$ value of 0.45 at 875 K for $(\text{Ag}_2\text{Se})_{1-x} (\text{nano-Cu}_2\text{Se})_x$ sample where $x = 0.05$.

1. Introduction

Today almost 60% of world energy use globally is rejected to the atmosphere as waste heat, much of it coming from automobiles and industrial settings [1]. Thermal-to-electric power conversion via thermoelectric (TE) materials is one of the most promising technologies to convert a part of this energy to useful electric power [2,3]. TE materials are capable of converting heat energy directly into electricity, and vice versa, with very little maintenance, noiseless operation and fully solid-state means. The efficiency of a TE material is determined by the TE figure of merit, $Z$. Its dimensionless form, $ZT$, is characterized by three parameters, $ZT = S^2\sigma T/\kappa$ where $S$, $\sigma$, and $\kappa$ are the Seebeck coefficient, electrical conductivity, and total thermal conductivity ($\kappa = \kappa_e + \kappa_L$ where $\kappa_e$ is the electronic contribution and $\kappa_L$ the lattice contribution), respectively, and $T$ is the absolute temperature. An ideal TE material should have a high power factor ($S^2\sigma$) as well as low thermal conductivity. However, because of the interrelation between transport parameters, it is very challenging to achieve high $ZT$ values > 2 in bulk materials. A general method to design a TE material with high $ZT$ is to select an extrinsic semiconductor with good electronic properties (high charge carrier mobility) and attempt to reduce its thermal conductivity as much as possible. In recent years, several novel approaches, such as the Phonon-Glass-Electron-Crystal (PGEC) paradigm [4,5], formation of bulk nanocomposite structures [6,7], the use of electronic energy band
resonant states [8], composition and temperature induced band convergence [9,10], seeking materials with extremely unharmonic lattice vibrations [11], using ultra-fast solidification techniques [12], the Phonon-Liquid-Electron-Crystal (PLEC) concept [13,14] and even synergistic band engineering have been implemented to enhance the efficiency of TE materials [15]. Among the TE families, chalcogenides such as PbTe, alloys of PbTe and AgSbTe2 (called LAST materials), alloys of GeTe and AgSbTe2 (called TAGS), Bi2Te3, Cu2Se, and Ag2Se have been widely studied due to their high electrical conductivity and low thermal conductivity [6,16,17]. In particular, n-type Ag2Se is known for superionic compound [18], similar to Cu2Se, with an alpha (α) to beta (β) phase transition around 400 K through which the crystal structure turns from the orthorhombic α-phase to the cubic superionic β-phase [19]. The small electronic energy band gap of Ag2Se (~0.20 eV) leads to easy modification of the transport properties for different applications [19–22]. The main problem facing Cu- and Ag-based chalcogenides for TE device applications is the migration of Cu and Ag ions into the electrodes under applied current (for cooling applications) or a large temperature gradient (for power generation) [23]. Regarding this problem, recently a few research groups reported on Cu-based chalcogenides. The thermal stability of Cu2Se was recently modified by changing the Cu:Ag ratio or by doping with small quantities of In Refs. [24,25]. Besides, P. Qiu et al. proposed that electrically conducting interfaces can be used to block Cu diffusion [26]. However, there is no detailed report on the high temperature thermal stability of Ag2Se in spite of extensive studies on the low temperature TE properties, reporting ZT values in the range of 0.1–1 in the past few years [27–31].

In this work, we report on both low and high temperature TE properties of bulk Ag2Se with nano-grained Cu2Se inclusions ((bulk Ag2Se)1-x(Cu2Se)x samples, where x = 0, 0.02 and 0.05). The thermal stability of the samples was examined via heating microscopy, and the heat capacity as a function of temperature.

2. Experimental methods

2.1. Sample preparation

Bulk Ag2Se was prepared by the conventional method of melting and annealing [32]. Nano-grained Cu2Se powders (referred to as “nano-Cu2Se powder” hereon) were prepared with a microwave assisted thermolysis presented in detail in our earlier work [33]. Obtained ingots of Ag2Se were ground by hand into nano-powder and mixed with nano-Cu2Se powder in the ratio of 2% and 5% of mol of Ag2Se. Powdering and mixing processes were carried out in a nitrogen-filled glove box. The mixtures were then loaded into agate jars containing agate milling balls at a 5:1 ball-to-powder mass ratio. The jars were sealed in nitrogen filled glove box to minimize oxygen contamination during the milling process. The sealed jars were mounted on a planetary ball mill (Optosense), and the powders were then mechanically alloyed for 1 h to obtain homogenous solid solutions. Finally, mixed powders were compacted with SPS under 50 MPa of pressure with 15 min holding time.

2.2. Structural characterization

Room temperature powder X-ray diffraction (PXRD) analysis was carried out with a Rigaku Ultima X-ray diffractometer equipped with graphite monochromated Cu Ka radiation, operating at 40 kV and 100 mA. Scanning electron microscopy with energy dispersive X-ray (SEM-EDX) analysis was performed via a Phenom ProX Scanning Electron Microscope. The thermal expansion of the samples was tested by using a Misura 3HSML heating microscope.

2.3. Transport property measurement

TE transport properties were evaluated from 5 K to 875 K. The Seebeck coefficient and thermal conductivity below ambient were collected using longitudinal steady-state measurements in a homebuilt cryostat. Low temperature Hall effect data (2–300 K) were collected using Quantum Design Magnetic Property Measurement System (MPMS) connected to a Linear Research AC Resistance Bridge operating at 12 Hz. Both positive and negative magnetic fields of magnitude 0.5 T were used to correct for small probe misalignment. The sign of the Hall coefficient RH determines the charge carrier type, while nH = (RH e)/\mu is the carrier concentration, with e the elementary charge, calculated from a single carrier model given the linear Hall signal with respect to applied field. The charge carrier mobility is calculated by \( \mu_H = \frac{e}{\rho} \), where D is the thermal diffusivity, \( \rho \) the heat capacity and \( \rho \) the bulk density. Thermal diffusivity was measured using the LFA1000 Laser Flash apparatus from Linseis company. Specific heat was measured by differential scanning calorimetry (PT1000 Linseis company), and density was obtained from the Archimedes’ method. The typical error bar expected in the Seebeck coefficient and electrical conductivity is ±7%, while it is ±10% for thermal conductivity.

3. Results and discussion

3.1. Structural data

Fig. 1 shows the PXRD pattern obtained on (Ag2Se)1-x(nano-Cu2Se)x samples, where x = 0, 0.02 and 0.05, at 300 K. The room temperature PXRD pattern of samples confirms the main phase of Ag2Se space group P212121 [19] orthorhombic (ICCD Card #: 96-223-0973) in all compounds that is consistent with previous reports [17,27,28]. Small quantities of the Cu2Se phase were detected at 28° only in the 5 mol % nano-Cu2Se (Card # 00-088-2043) included sample.

In order to further examine the phase composition of the samples, SEM-EDX analyses were conducted on the 5 mol% nano Cu2Se included bulk Ag2Se. Fig. 2 summarizes the results.

SEM-EDX analysis of (Ag2Se)0.95(nano-Cu2Se)0.05 shows that there are two phases of Ag2Se (bright regions in Fig. 2(a)) and Cu2Se (dark regions) in the compound, as already suggested by the PXRD. However, despite observing a small trace of the Cu2Se phase in the PXRD pattern, the SEM-EDX map displays a large quantity of Cu2Se in the compound. This might be due to an agglomeration of Cu2Se likely due to inhomogeneous distribution of nano-Cu2Se in the Ag2Se matrix.

Despite attractive attributes, such as low toxicity and ease of
synthesis, the deployment of Ag$_2$Se and Cu$_2$Se into working TE devices is still problematic due to structural and chemical instability issues. In order to analyze surface deformation of the composites in this study, the thermal expansion of the samples were analyzed with heating microscopy. Obtained results are presented in Fig. 3.

Thermal expansion (%) in pure Ag$_2$Se reaches ~9% at 673 K while it is much less at 473 K and 573 K. The sudden change of shape and thermal expansion of Ag$_2$Se at 673 K might be due to decomposition (Se evaporation) above 600 K that softens the material. Contrary to bulk Ag$_2$Se, nano-Cu$_2$Se included samples show ~4% thermal expansion at 673 K, exhibiting greater thermal stability than the bulk Ag$_2$Se [37]. Increasing thermal expansion with increasing temperature for all samples is likely due to increase in the size of the unit-cell as alpha-beta transition completes [34]. The increasing thermal stability of Ag$_2$Se with nano-Cu$_2$Se inclusion might be due to partly diffusion of Cu ions into Ag$_2$Se and acting like Ag$^+$ mobility disruption center [25,35].

In order to further understand the dependence of the thermal stability of Ag$_2$Se on the amount of the nano-Cu$_2$Se, the temperature dependence of the heat capacity was examined (see Fig. 4).

Heat capacity measurements are a useful, indirect yet sensitive method to detect structural changes in a material. From Fig. 4, all samples reveal a clear signature of a phase transition between 400 and 450 K, which is the well-known alpha-beta structural transition in Ag$_2$Se and Cu$_2$Se materials as described earlier [27,32]. Upon nano-Cu$_2$Se inclusion, the transition shifts by a few degrees to lower temperature. The phase transition temperature is strongly dependent on the defect structure of a
material as well as its phase composition \[36\]. Therefore, the shift of the phase transition temperature might due to increasing number of Ag vacancies in the Ag$_2$Se matrix or potentially the occurrence of the same structural transition in the Cu$_2$Se secondary phase at lower temperatures. The intensity of a phase transition peak is related to energy difference between the two phases and also reflect the chemical stability of compound \[37\]. In other words, compounds that have small peak intensity in the heat capacity are more stable thermally and chemically in comparison to compounds with higher peak intensity. As can be clearly seen in Fig. 4, the peak intensity of the phase transition in the samples of this study decreases with increasing nano-Cu$_2$Se inclusion. Therefore, both thermal expansion (Fig. 3) and heat capacity versus temperature measurements (Fig. 4) confirm the thermal stability of the compounds is enhanced with the nano inclusions.

3.2. Transport data

The temperature-dependent Hall coefficient, carrier density and mobility of nano-Cu$_2$Se included Ag$_2$Se samples are presented in Fig. 5.

Low temperature thermoelectric properties of Ag$_2$Se were studied in detail by several groups \[27,28,37–39\]. However, the different reported values of transport properties indicate that they are very sensitive to sample preparation process, excess of Ag/Se and doping. In order to determine the carrier type in the composite, the Hall coefficient measurement was performed. The negative sign of the Hall coefficient indicates that electrons are the main charge carriers in all samples. Fig. 5 (b) shows temperature dependence of the carrier density of the samples. With increasing nano-Cu$_2$Se inclusion, the electron concentration is enhanced, likely due to the diffusion of some Cu ions into the Ag$_2$Se structure that serve to donate electrons. Dependence of charge carrier density on temperature (Fig. 5(b)) is nearly flat (extrinsic conduction) for the composite with 2 mol% nano-Cu$_2$Se inclusion while with 5 mol% inclusion a thermally activated behavior is observed above 200 K that indicates some form of donor state. Carrier mobility was calculated via $\mu_H = R_H^* \sigma$. Carrier mobility (shown in Fig. 5(c)) decreases with increasing content of nano-Cu$_2$Se likely due to the increase in the carrier density (electron-electron interaction) or due to scattering of charge carrier on interfaces and grains that formed from the nano-Cu$_2$Se substitution. Fig. 5(d) displays the logarithm of the low temperature mobility plotted against log temperature with power-law exponents indicated for the samples to emphasize the particular scattering mechanism governing the $\mu_H \propto T^\alpha$ relation. The data suggest that carrier-charged defect
The electrical conductivity and Seebeck coefficient as a function of temperature for all samples are presented in Fig. 6. Because of the greater number of charge carriers, the electrical conductivity of the samples with higher nano-Cu2Se content is improved. Curiously, the room temperature electrical conductivity values of the samples (Fig. 6(a)) are quite different (1480 S/cm, 3580 S/cm, 4319 S/cm for Ag2Se, 2% nanoCu2Se and 5% nano-Cu2Se included samples respectively), whereas above the phase transition, the values are much closer (2620 S/cm, 2502 S/cm, 2981 S/cm for Ag2Se, 2% nanoCu2Se and 5% nano-Cu2Se included samples respectively). This might be due to a matching of the crystal structures of nano-Cu2Se before the phase transition and then turns into cubic structure after the phase transition [27,30]. Similarly, Ag2Se shows an orthorhombic crystal structure before the phase transition [31,32]. Similarly, the crystal structure of nano-Cu2Se is monoclinic before the phase transition and then turns into a cubic structure after the phase transition [27,30]. Therefore, both compounds have a nearly identical crystal structure above the phase transition temperature, leading to a similar environment in which the electrons move leading to similar values of \( \sigma \). As is typical for degenerate semiconductors, the Seebeck coefficient is inversely proportional with the electrical conductivity for all samples. Additionally, all materials show negative values of the Seebeck coefficient that indicates that electrons are dominant carriers in all samples, which is consistent with Hall coefficient measurements (Fig. 5(a)).

Total thermal conductivity (Fig. 7(a)) was suppressed with the inclusion of 5 mol% nano-Cu2Se, despite the increase in the electrical conductivity. The 2 mol% nano-Cu2Se included sample shows very similar values to Ag2Se.

We used the Wiedemann-Franz law to calculate the lattice contribution to the thermal conductivity of (Ag2Se)\(_{1-x}\)(Cu2Se)\(_x\) samples by subtracting the electronic term \( (k_e = L_0 T \text{ where } L, \sigma \text{ and } T \text{ are the Lorenz number, electrical conductivity and absolute temperature, respectively}) \) from the total thermal conductivity. The Lorenz number for all compounds was calculated by using the following equations;

\[
L = \left( \frac{k_B^2}{\sigma T} \right)^2 \frac{\left( r + \frac{5}{2} \right) F_{r+3/2}(\xi)}{\left( r + \frac{3}{2} \right) F_{r+1/2}(\xi)} - \left( \frac{r + \frac{5}{2}}{r + \frac{3}{2}} \right)^2 \right]
\]

where \( r \) is the scattering parameter, \( k_B \) the Boltzmann constant, \( e \) is the electron charge, and \( F_\ell(\xi) \) is the Fermi integral given by

\[
F_\ell(\xi) = \int_0^\infty \frac{x^\ell e^{-x}}{1 + e^{-x}} dx
\]

Here \( \xi \) is the reduced Fermi energy that can be calculated from the Seebeck coefficient \( S \) and the scattering parameter \( r \) according to

\[
S = \frac{k_B}{e} \frac{(r + \frac{5}{2}) F_{r+3/2}(\xi)}{(r + \frac{3}{2}) F_{r+1/2}(\xi)} - \xi
\]

We assumed the system to be highly degenerate and scattering dominated by acoustic phonons [32]. The calculated Lorenz numbers for Ag2Se, (Ag2Se)\(_{0.98}\)(Cu2Se)\(_{0.02}\), and (Ag2Se)\(_{0.95}\)(Cu2Se)\(_{0.05}\) samples, are 1.87 \times 10^{-8} \text{ V}^2/\text{K}^2, 2.01 \times 10^{-8} \text{ V}^2/\text{K}^2, and 2.05 \times 10^{-8} \text{ V}^2/\text{K}^2 respectively. The calculated lattice thermal conductivities \( (\kappa_L) \) are shown in Fig. 7(b). Unrealistic negative values of the lattice thermal conductivity in 5% mol nano Cu2Se resulted from our calculations so they are not shown here. Although one reason for the drastically reduced lattice
thermal conductivity is the scattering of heat carrying phonons on the interface and grain boundary that form via nano phases, the negative values might be due to softening lattice vibration in this compound as Olvera et al. indicated in their work [25]. Another possible reason for observing negative values is that the laser flash technique may not be entirely accurate with materials that are somewhat thermally unstable, causing an underestimation of the total thermal conductivity.

The combination of high Seebeck coefficient and high electrical conductivity leads to a maximum power factor of 24 μW/(K²-cm) at room temperature for the sample with 2 mol% nano-Cu2Se inclusion. The dimensionless TE figure of merit, ZT, reaches ~0.25 at 300 K for bulk Ag2Se and ~0.45 at 875 K for the 5 mol% nano-Cu2Se included compound, due to lower thermal conductivity and a relatively high power factor (Fig. 8).

4. Conclusion

(Ag2Se)1-x(Cu2Se)x solid solutions, where x = 0, 0.02 and 0.05, were prepared by a two-step process in which the bulk Ag2Se was melted and annealed, while the nano-grained Cu2Se powders were derived from a microwave assisted synthetic procedure. The two compounds were mixed via ball milling then densified with the spark plasma sintering method. PXRD and SEM-EDX patterns indicate that there are two phases in microstructure, which are Ag2Se and Cu2Se. Thermal expansion and thermodynamic stability of samples were tested with Heating microscopy and heat capacity measurement. Both analyses revealed that nano-Cu2Se increases the thermal stability of compounds. The Hall effect measurement and electrical conductivity demonstrated a positive trend in the electrical conductivity with increasing nano inclusion due to higher resultant carrier density. Total thermal conductivity decreases and ZT values increase with nano-Cu2Se inclusion. It is concluded that all transport and structural data indicate that nano Cu2Se inclusions improve TE properties and thermal stability of Ag2Se. Synthesizing nano sized powder of Ag2Se and its effect on transport properties of Cu2Se will be a part of our future work.

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