Thermoelectric properties of p-type $\text{Ag}_{1-x}(\text{Pb}_{1-y}\text{Sn}_y)_m\text{Sb}_{1-z}\text{Te}_{m+2}$

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ABSTRACT

The thermoelectric properties of $\text{Ag}_{1-x}(\text{Pb}_{1-y}\text{Sn}_y)_m\text{Sb}_{1-z}\text{Te}_{m+2}$ ($4 \leq m \leq 16$, $-0.1 \leq x \leq 0.3$, $1/3 \leq y \leq 2/3$, $0.2 \leq z \leq 0.4$; Lead Antimony Silver Tellurium Tin, LASTT- m) compositions were investigated in the temperature range of 300 to ~ 670 K. All samples crystallize in the average NaCl-type structure without any noticeable second phase and exhibit very narrow bandgaps of < 0.1 eV. We studied a range of m values, silver concentrations (x), Pb/Sn ratios (y), and antimony concentrations (z) to determine their effects on the thermoelectric properties. The samples were investigated as melt grown polycrystalline ingots. Varying the Ag contents, the Pb/Sn ratios, and the Sb contents off-stoichiometry allowed us to control the electrical conductivity, the Seebeck coefficient, and the thermal conductivity. The electrical conductivity tends to decrease with decreasing m values. The highest ZT of ~ 1.1 was achieved at ~ 660 K for $\text{Ag}_{0.9}\text{Pb}_5\text{Sn}_5\text{Sb}_{0.8}\text{Te}_{12}$ mainly due to the very low lattice thermal conductivity of ~ 0.4 W/(m·K) around 660 K. Also, samples with charge-balanced stoichiometries, $\text{Ag}(\text{Pb}_{1-y}\text{Sn}_y)_m\text{SbTe}_{m+2}$, were studied and found to exhibit a lower power factor and higher lattice thermal conductivity than the $\text{Ag}_{1-x}(\text{Pb}_{1-y}\text{Sn}_y)_m\text{Sb}_{1-z}\text{Te}_{m+2}$ compositions.

I. INTRODUCTION

The thermoelectric (TE) energy conversion of heat to electricity may have a huge impact on energy efficiency and power generation if high efficiency materials are developed.[1-10] The efficiency of thermoelectric materials is evaluated by the thermoelectric figure of merit, $ZT = (S^2 \cdot \sigma \cdot T) / \kappa$, where S , σ , T , and κ are the Seebeck coefficient (thermopower), electrical conductivity, absolute temperature, and thermal conductivity, respectively. Significant progress in raising ZT has been recently accomplished for bulk materials, especially PbTe based materials by thermal phonon engineering (nanostructuring and all-hierarchical structuring) and (or) electronic band engineering (resonance level effect and band convergence).[11-27]

Efficient thermoelectric power generation devices require both higher thermoelectric figure of merit n-type and p-type materials for practical thermoelectric modules. In 2004, we reported that n-type $\text{AgPb}_m\text{SbTe}_{m+2}$ (Lead Antimony Silver Tellurium, LAST- m) materials can achieve a high ZT and this was later confirmed and improved upon by follow-up reports from other groups.[13, 28] Polycrystalline sintered samples of $(\text{AgSbTe}_2)_x(\text{Pb}_{0.5}\text{Sn}_{0.5}\text{Te})_{1-x}$ ($x = 0.05, 0.09, 0.2$), which is a p-type analog of the LAST- m , showed the ZT of ~ 1 at 700 K.[29] Later we described similarly efficient p-type materials based on the $\text{Ag}(\text{Pb}_{1-y}\text{Sn}_y)_m\text{SbTe}_{m+2}$ (Lead Antimony Silver Tellurium Tin, LASTT- m) materials ($ZT \sim 1.45$ at 630 K).[17] The $\text{Ag}_{1-x}(\text{Pb}_{1-y}\text{Sn}_y)_m\text{Sb}_{1-z}\text{Te}_{m+2}$ compounds have been found to exhibit high performance p-type thermoelectric properties and could be considered to be a p-type PbTe-based material for practical applications.[30] Investigations by tuning primarily the m value and the Pb/Sn ratio (y value) and secondarily the Ag and Sb concentrations (x and z values) on the thermoelectric properties of p-type LASTT- m series showed that x and z are important in optimizing the properties. However, if these two parameters are varied independently of one another the resulting materials become biphasic or multi-phasic with one of the phases being Te. The latter can begin to evaporate at the temperatures of interest (~ 700 K) causing undesirable complications in the absence of encapsulation. Therefore, we reinvestigated the compositions of the present the LASTT so that no Te phase is created. For the first time we examine here in detail the effects of

varying each of these compositional parameters m , x , y , z , and δ on the thermoelectric properties of $\text{Ag}_{1-x}(\text{Pb}_{1-y}\text{Sn}_y)_m\text{Sb}_{1-z}\text{Te}_{m+2-\delta}$. We report here the thermoelectric properties of these p-type LASTT materials and the high ZT value of 1.1 achieved.

II. EXPERIMENTAL DETAILS

A. Synthesis

For the preparation of the compounds $\text{Ag}_{1-x}(\text{Pb}_{1-y}\text{Sn}_y)_m\text{Sb}_{1-z}\text{Te}_{m+2}$ ($4 \leq m \leq 16$, $-0.1 \leq x \leq 0.3$, $1/3 \leq y \leq 2/3$, $0.2 \leq z \leq 0.4$) silver (coin, 99.99%), lead and tin (Rotometals, 99.99%), antimony (Tellurex, 99.999%), and tellurium (Atlantic Metals, 99.999%) were combined in an appropriate ratio in a 8 mm diameter fused silica tube, and the tube was evacuated and sealed under the residual pressure of $\sim 1 \times 10^{-4}$ Torr. For example, Ag (0.2893 g, 2.682 mmol), Pb (3.0877 g, 14.902 mmol), Sn (1.7690 g, 14.902 mmol), Sb (0.2903 g, 2.384 mmol), and Te (4.5636 g, 35.765 mmol) were used to prepare 10 g of $\text{Ag}_{0.9}\text{Pb}_5\text{Sn}_5\text{Sb}_{0.8}\text{Te}_{12}$.

The sealed silica tube was heated to 1323 K for 20 h in a furnace, and the furnace was rocked to homogenize a liquid phase at 1323 K for 6 h and kept at the same temperature for 24 h (or the furnace was not rocked sometimes, but the ingots from unrocked furnace showed similar thermoelectric properties to those from rocked furnace), and then the tube was slowly cooled from 1323 K to 973 K for 48 h followed by a cooling to room temperature over 12 h. Single dense ingots were obtained with a dark silvery metallic shine. The ingots are stable in water and air, were cut for electrical and thermal property measurements using a diamond saw (Buehler Isomet 1000), and were polished with water in a polishing machine (Buehler Ecomet 3000) using a silicon carbide polishing paper (Grit 400, Buehler). No additional dopants were added to these samples.

B. Powder x-ray diffraction and infrared spectroscopy

Fine powder samples of $\text{Ag}_{1-x}(\text{Pb}_{1-y}\text{Sn}_y)_m\text{Sb}_{1-z}\text{Te}_{m+2}$ were examined by the x-ray diffraction using $\text{Cu K}\alpha$ radiation and room temperature optical diffuse reflectance measurements as described previously[31].

C. Thermal conductivity

The thermal diffusivity (D) was directly measured under nitrogen atmosphere and the specific heat (C_p) was indirectly derived using a standard sample (pyroceram) as a function of temperature from room temperature to ~720 K using the flash diffusivity method in a NETZSCH LFA 457 MicroFlash instrument. In the flash diffusivity method, the front face of a disc shaped sample (~8 mm diameter and 1-2 mm thickness) is irradiated by a short laser burst, and the resulting rear face temperature rise is recorded and analyzed by an IR detector. The thermal conductivity (κ) was calculated from the equation $\kappa = D \cdot C_p \cdot \rho$, where ρ is the density of the sample, measured using sample dimensions and mass. The densities of the samples range between 7 and 7.5 g/cm³ depending on the amount of PbTe, SnTe, and AgSbTe₂ in LASTT system. The measured thermal conductivity is the sum of the electronic thermal conductivity (κ_{elec}) and the lattice thermal conductivity (κ_{latt}). The electronic thermal conductivity can be calculated from the Wiedemann-Franz law, $\kappa_{elec} = L \cdot \sigma \cdot T$, where L is the Lorenz number and T is the absolute temperature.[32] The temperature dependent Lorenz number was estimated in the single parabolic band (SPB) model from temperature dependent Seebeck coefficient.[33]

D. Electrical properties

The samples were cut into rectangular shapes of ~3 mm x 3 mm x 9 mm for electrical property measurements. The longer direction coincides with the direction in which the thermal conductivity was measured. Electrical conductivity and thermopower were measured simultaneously under a helium atmosphere (~0.1 atm) from room temperature to ~720 K using a ULVAC-RIKO-ZEM3 measurement system.

E. Hall measurements

The Hall coefficient was measured with a home-made high temperature apparatus, which provides a working range from 300 K to ~873 K. The sample was press mounted and protected with argon gas to avoid possible oxidization at high temperature. The Hall

resistance was monitored with Linear Research AC Resistance Bridge (LR-700), with constant magnetic fields of ± 1 Tesla applied by using an Oxford Superconducting Magnet.

III. RESULTS AND DISCUSSION

A. Powder x-ray diffraction and optical band gap

The powder x-ray diffraction patterns of $\text{Ag}_{0.9}(\text{Pb}_{0.5}\text{Sn}_{0.5})_m\text{Sb}_{0.8}\text{Te}_{m+2}$ samples ($m = 4, 6, 8, 10, 12, 14, 16$) reveal that they crystallize in the average cubic NaCl-type structure without any noticeable second phases, Fig 1(a). In the case of $m = 4$ and 6, however, there are small shoulders on the Bragg peaks resulting from a SnTe phase, which is indicative of bulk phase separation in low m values. Presumably, some excess tellurium should also be visible in the powder x-ray diffraction patterns, but it is obscured because the first and second highest diffraction peaks of tellurium overlap with those of the NaCl-phase or the fraction of the tellurium phase is too low to be detected. Fig. 1(b) shows the lattice parameters as a function of m for the $\text{Ag}_{0.9}(\text{Pb}_{0.5}\text{Sn}_{0.5})_m\text{Sb}_{0.8}\text{Te}_{m+2}$ samples and the lattice parameters slightly expand with increasing m . The refined lattice parameters (cross symbols) are in agreement with the calculated ones (solid line) and intermediate between the lattice parameters of AgSbTe_2 at 6.079 Å[34] and $\text{Pb}_{0.5}\text{Sn}_{0.5}\text{Te}$ at 6.385 Å[35].

Typical infrared absorption spectra from the $\text{Ag}_{0.9}(\text{Pb}_{0.5}\text{Sn}_{0.5})_m\text{Sb}_{0.8}\text{Te}_{m+2}$ samples ($m = 8, 10, 16$) are shown in Fig. 2. The band gaps are very small < 0.1 eV and seem to decrease with decreasing m value. They show similar absorption spectra to $\text{NaPb}_{18-x}\text{Sn}_x\text{MTe}_{20}$ ($M = \text{Bi}, \text{Sb}$)[36] and $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ [37]. In the case of the $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ system, the band gap decreases as the tin content increases and goes through zero.[36] The spectra are also heavily masked by the high carrier concentrations in these samples.

B. The effect of m on TE properties of the $\text{Ag}_{0.9}(\text{Pb}_{0.5}\text{Sn}_{0.5})_m\text{Sb}_{0.8}\text{Te}_{m+2}$ samples

In this paper, we mainly focus on $\text{Ag}_{1-x}(\text{Pb}_{0.5}\text{Sn}_{0.5})_m\text{Sb}_{1-z}\text{Te}_{m+2}$ (i.e. $y = 0.5$) because the ratio of electrical conductivity to thermal conductivity was found to have a maximum at $x = 0.5$ for $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ [36]. Fig. 3(a) shows the temperature dependences of the electrical conductivity σ and the Seebeck coefficient S of the $\text{Ag}_{0.9}(\text{Pb}_{0.5}\text{Sn}_{0.5})_m\text{Sb}_{0.8}\text{Te}_{m+2}$ samples (m

= 4, 6, 8, 10, 12, 14, 16). For all compounds, the electrical conductivity decreases with increasing temperature, which is indicative of degenerate doping. The room temperature electrical conductivity tends to decrease with decreasing m value. For instance, compounds with $m = 16$, 12, and 8 exhibit room temperature electrical conductivities of ~1700, 1400, and 1100 S/cm, respectively, while they have the electrical conductivities ranging between 600 and 500 S/cm at ~660 K. Generally, the electrical conductivity of doped PbTe-based samples follows a temperature dependent power law of $\sigma \sim T^{-\lambda}$ ($\lambda \sim 2 - 3$) [38] but the power exponent value of hole mobility in p-type PbTe and SnTe decreases with increasing hole concentration.[39] In this work, the values of λ for all samples ranged between 0.9 and 1.3, which is also different from $\sigma \sim T^{-2}$ for $\text{Ag}_{0.5}\text{Pb}_6\text{Sn}_2\text{Sb}_{0.2}\text{Te}_{10}$ [17]. Such a difference in the power exponent λ results from much higher hole concentrations of our $\text{Ag}_{0.9}(\text{Pb}_{0.5}\text{Sn}_{0.5})_m\text{Sb}_{0.8}\text{Te}_{m+2}$ samples (the order of 10^{20} cm^{-3}) compared to $\text{Ag}_{0.5}\text{Pb}_6\text{Sn}_2\text{Sb}_{0.2}\text{Te}_{10}$ ($4 \times 10^{19} \text{ cm}^{-3}$).

All compounds show positive Seebeck coefficient over the entire temperature range measured indicating p-type conduction. The Seebeck coefficients at room temperature ranges between 70 and 50 $\mu\text{V/K}$ and those at ~660 K are between 180 and 170 $\mu\text{V/K}$. At room temperature, all compounds show power factors PF ($\sigma \cdot S^2$) ranging from ~8 $\mu\text{W}/(\text{cm} \cdot \text{K}^2)$ ($m = 6$) to ~4 $\mu\text{W}/(\text{cm} \cdot \text{K}^2)$ ($m = 12$) in Fig. 3(b). As the temperature increases, the power factor increases and then reaches between ~18 ($m = 10$) and ~15 $\mu\text{W}/(\text{cm} \cdot \text{K}^2)$ ($m = 4$) at ~660 K.

Figs. 3(c) and 3(d) show the temperature dependence of the total thermal conductivity κ_{tot} and lattice thermal conductivity κ_{latt} of the $\text{Ag}_{0.9}(\text{Pb}_{0.5}\text{Sn}_{0.5})_m\text{Sb}_{0.8}\text{Te}_{m+2}$ samples, respectively. For $m = 10$, the total thermal conductivity is ~1.5 $\text{W}/(\text{m} \cdot \text{K})$ at room temperature and the thermal conductivity decreases with increasing temperature, reaching ~1 $\text{W}/(\text{m} \cdot \text{K})$ at ~660 K. All compounds exhibit very low lattice thermal conductivities ($\kappa_{latt} < 1 \text{ W}/(\text{m} \cdot \text{K})$) over the entire temperature range compared to that of PbTe (dash line without symbol in Fig. 3(d)). The derived lattice thermal conductivity for $m = 10$ is ~0.5 $\text{W}/(\text{m} \cdot \text{K})$ at room temperature, only 20 % that of PbTe, and at ~660 K is ~0.4 $\text{W}/(\text{m} \cdot \text{K})$, which is ~40 % that of PbTe. Previously, we reported experimental evidence for the

nanostructured nature of these materials which results in very low lattice thermal conductivity through the strong suppression of the intermediate frequency heat-carrying phonons.[17]

Fig. 3(e) shows the thermoelectric figure of merit ZT as a function of temperature. For all compounds, the ZT s at room temperature range between 0.1 and 0.2, and those at ~ 660 K were achieved between ~ 1.1 ($m = 10$) and ~ 0.8 ($m = 4$). In this work, the highest ZT of ~ 1.1 at 660 K was obtained for $m = 10$ mainly due to a very low lattice thermal conductivity.

C. The effect of excess tellurium on TE properties of $\text{Ag}_{0.9}(\text{Pb}_{0.5}\text{Sn}_{0.5})_{10}\text{Sb}_{1-z}\text{Te}_{12-\delta}$

The highest ZT in the LASTT compounds reported is ~ 1.45 at 627 K for $\text{Ag}_{0.5}\text{Pb}_6\text{Sn}_2\text{Sb}_{0.2}\text{Te}_{10}$ [17], but this composition contains excess tellurium that can evaporate at high temperatures according to Eq. (2):

Thus, we investigated the thermoelectric properties of compositions having excess tellurium and no excess. The latter are the charge-balanced $\text{Ag}_{0.9}(\text{Pb}_{0.5}\text{Sn}_{0.5})_{10}\text{Sb}_{1-z}\text{Te}_{12-\delta}$ ($z = 0.2, 0.3$ and $\delta = 0, 0.2, 0.35, 0.5$) compounds. Figs. 4(a) and 4(b) show the temperature dependences of the electrical conductivity σ and the Seebeck coefficient S of the excess tellurium and the charge-balanced compounds, respectively. The excess-Te compositions ($z = 0.2, \delta = 0$; $z = 0.3, \delta = 0.35$; $z = 0.2, \delta = 0.2$) exhibit higher electrical conductivities than the charge-balanced compounds ($z = 0.2, \delta = 0.35$; $z = 0.3, \delta = 0.5$) indicating that the excess Te acts as an electron acceptor. This is consistent with the fact that the Seebeck coefficient for the charge-balanced compounds are larger than those for the excess-Te compositions. For instance, the room temperature electrical conductivity of $\text{Ag}_{0.9}\text{Pb}_5\text{Sn}_5\text{Sb}_{0.8}\text{Te}_{12}$ and $\text{Ag}_{0.9}\text{Pb}_5\text{Sn}_5\text{Sb}_{0.8}\text{Te}_{11.65}$ are ~ 1500 and ~ 1000 S/cm, respectively, and the respective Seebeck coefficient at ~ 660 K are ~ 180 and ~ 230 $\mu\text{V/K}$. The power

factors PF ($\sim 13 - 15 \mu\text{W}/(\text{cm}\cdot\text{K}^2)$) of the charge-balanced compounds around 660 K were lower than those ($\sim 17 - 18 \mu\text{W}/(\text{cm}\cdot\text{K}^2)$) of the excess-Te compounds in Fig. 4(c).

The Hall coefficients in the temperature range of 300 – 720 K are positive indicative of p-type conduction, consistent with the positive Seebeck coefficient. Assuming a simple parabolic band and single carrier conduction in our analysis, the hole carrier concentration p_H was determined from the relationship $p_H = 1/eR_H$, where e is the electronic charge and R_H is the Hall coefficient. Fig. 4(d) shows the hole concentrations p_H as a function of temperature for $\text{Ag}_{0.9}\text{Pb}_5\text{Sn}_5\text{Sb}_{0.8}\text{Te}_{11.8}$ and $\text{Ag}_{0.9}\text{Pb}_3\text{Sn}_3\text{Sb}_{0.8}\text{Te}_{7.8}$ samples. For both samples the hole concentration was nearly constant until ~ 460 K ($\sim 4 \times 10^{20} \text{ cm}^{-3}$ for $\text{Ag}_{0.9}\text{Pb}_5\text{Sn}_5\text{Sb}_{0.8}\text{Te}_{11.8}$ and $\sim 5 \times 10^{20} \text{ cm}^{-3}$ for $\text{Ag}_{0.9}\text{Pb}_3\text{Sn}_3\text{Sb}_{0.8}\text{Te}_{7.8}$). The apparent rapid increase of hole carriers at high temperature ($1.28 \times 10^{21} \text{ cm}^{-3}$ at 723 K for $\text{Ag}_{0.9}\text{Pb}_5\text{Sn}_5\text{Sb}_{0.8}\text{Te}_{11.8}$ and $1.18 \times 10^{21} \text{ cm}^{-3}$ at 673 K for $\text{Ag}_{0.9}\text{Pb}_3\text{Sn}_3\text{Sb}_{0.8}\text{Te}_{7.8}$) is actually an artifact coming from the effect of the second so-called heavy hole valence band which begins to dominate at high temperatures.[40-42] This is an artifact that arises from the use of a single band model to extract the hole concentration in a regime where two band conduction is in effect. The hole mobility μ_p was derived from the equation $\mu_p = \sigma/(p \cdot e)$ (p =hole concentration), and the plots with temperature are shown in Fig. 5(a). The room temperature hole mobilities of $\text{Ag}_{0.9}\text{Pb}_5\text{Sn}_5\text{Sb}_{0.8}\text{Te}_{11.8}$ and $\text{Ag}_{0.9}\text{Pb}_3\text{Sn}_3\text{Sb}_{0.8}\text{Te}_{7.8}$ are ~ 20 and $\sim 14 \text{ cm}^2/(\text{V}\cdot\text{sec})$, respectively. For $\text{Ag}_{0.9}\text{Pb}_5\text{Sn}_5\text{Sb}_{0.8}\text{Te}_{11.8}$ the Seebeck coefficient rises linearly from $\sim 70 \mu\text{V/K}$ at ~ 300 K to $\sim 170 \mu\text{V/K}$ at ~ 670 K (Fig. 4(a)), which is a surprisingly large Seebeck coefficient for a heavily degenerate semiconductor with the carrier concentration of the order of $10^{20} - 10^{21} \text{ cm}^{-3}$. Androulakis *et al.*[43] reported that the large Seebeck coefficient of $\sim 160 \mu\text{V/K}$ was observed in $\text{Ag}_{1-x}\text{SnSb}_{1+x}\text{Te}_3$ with an almost metallic hole concentration of $\sim 5 \times 10^{21} \text{ cm}^{-3}$ and this arises from a high effective mass of hole carriers.

The temperature dependent lattice thermal conductivities κ_{latt} for the $\text{Ag}_{0.9}(\text{Pb}_{0.5}\text{Sn}_{0.5})_{10}\text{Sb}_{1-z}\text{Te}_{12-8}$ samples are plotted in Fig. 5(b). The lattice thermal conductivities of the excess-Te compositions are lower than those of the charge-balanced compounds, although both sample types still exhibit very low lattice thermal conductivities;

~ 0.4 W/(m·K) at ~ 660 K for $\text{Ag}_{0.9}\text{Pb}_5\text{Sn}_5\text{Sb}_{0.8}\text{Te}_{12}$ vs. ~ 0.7 W/(m·K) at ~ 660 K for $\text{Ag}_{0.9}\text{Pb}_5\text{Sn}_5\text{Sb}_{0.8}\text{Te}_{11.65}$. In Fig. 5(c) we show the lattice thermal conductivity κ_{latt} data for the $\text{Ag}_{0.9}(\text{Pb}_{0.5}\text{Sn}_{0.5})_{16}\text{Sb}_{1-z}\text{Te}_{18-\delta}$ samples to better illustrate the lower lattice thermal conductivities of the excess-Te compounds than the corresponding charge-balanced compounds. Indeed, the lower lattice thermal conductivities for the excess-Te compounds are also observed for the $\text{Ag}_{0.9}(\text{Pb}_{0.5}\text{Sn}_{0.5})_{16}\text{Sb}_{1-z}\text{Te}_{18-\delta}$ samples. The ZT s as a function of temperature are shown in Fig. 5(d). The ZT of the charge-balanced compound ($z = 0.2$, $\delta = 0.35$) is ~ 1.0 at ~ 660 K compared to the ZT of ~ 1.1 at ~ 660 K for the excess-Te compound ($z = 0.2$, $\delta = 0$).

D. Effect of silver content on TE properties of $\text{Ag}_{1-x}(\text{Pb}_{0.5}\text{Sn}_{0.5})_{10}\text{Sb}_{0.8}\text{Te}_{12}$

Varying x and z values as well as m and y values in $\text{Ag}_{1-x}(\text{Pb}_{1-y}\text{Sn}_y)_m\text{Sb}_{1-z}\text{Te}_{m+2}$ allows us to control the carrier concentration, Seebeck coefficient, and thermal conductivity. Fig. 6(a) shows the temperature dependences of the electrical conductivity σ and the Seebeck coefficient S for $\text{Ag}_{1-x}(\text{Pb}_{0.5}\text{Sn}_{0.5})_{10}\text{Sb}_{0.8}\text{Te}_{12}$ (where $x = -0.1, 0.1, 0.2, 0.3$). As expected, for a given temperature the electrical conductivity increases with increasing Ag concentration (x) (~ 1900 S/cm at ~ 300 K for $x = -0.1$ vs ~ 1400 S/cm at ~ 300 K for $x = 0.3$). The Seebeck coefficient increases with decreasing Ag concentration (~ 160 $\mu\text{V/K}$ at ~ 670 K for $x = -0.1$ vs ~ 180 $\mu\text{V/K}$ at ~ 670 K for $x = 0.3$). This indicates that Ag acts as an electron acceptor. The corresponding power factors PF at ~ 660 K are between ~ 19 $\mu\text{W}/(\text{cm}\cdot\text{K}^2)$ for $x = -0.1$ and ~ 16 $\mu\text{W}/(\text{cm}\cdot\text{K}^2)$ for $x = 0.2$ in Fig. 6(b). The temperature dependent total thermal conductivity κ_{tot} and lattice thermal conductivity κ_{latt} are plotted in Figs. 6(c) and 6(d), respectively. The total thermal conductivity at ~ 660 K ranges between ~ 1.5 W/(m·K) for $x = -0.1$ and ~ 1.0 W/(m·K) for $x = 0.1$. The lattice thermal conductivities at ~ 660 K for all compounds are less than 0.7 W/(m·K) and the lowest lattice thermal conductivity of ~ 0.4 W/(m·K) at ~ 660 K was achieved for $x = 0.1$. The thermoelectric figure of merit ZT as a function of temperature is shown in Fig. 6(e). At ~ 660 K, the ZT s are ~ 0.8 for $x = -0.1$, ~ 1.1 for $x = 0.1$, ~ 1.0 for $x = 0.2$, and ~ 0.9 for $x = 0.3$.

E. Effect of antimony content on TE properties of $\text{Ag}_{0.9}(\text{Pb}_{0.5}\text{Sn}_{0.5})_{16}\text{Sb}_{1-z}\text{Te}_{18}$

The electrical conductivity σ is expected to decrease with increasing the Sb concentration (z) in $\text{Ag}_{1-x}(\text{Pb}_{1-y}\text{Sn}_y)_m\text{Sb}_{1-z}\text{Te}_{m+2}$ because Sb in rock salt PbTe based materials acts as an electron donor. The temperature dependent electrical conductivity σ and Seebeck coefficient S for $\text{Ag}_{0.9}(\text{Pb}_{0.5}\text{Sn}_{0.5})_{16}\text{Sb}_{1-z}\text{Te}_{18}$ ($z = 0.2, 0.3, 0.4$) samples are shown in Fig. 7(a). Indeed the room temperature electrical conductivity decreases with increasing Sb content (~ 1900 S/cm for $z = 0.4$, ~ 1800 S/cm for $z = 0.3$, and ~ 1700 S/cm for $z = 0.2$), while the Seebeck coefficient follows the opposite trend (156 $\mu\text{V/K}$ at ~ 660 K for $z = 0.4$, 163 $\mu\text{V/K}$ for $z = 0.3$, and 172 $\mu\text{V/K}$ for $z = 0.2$). In Fig. 7(b) the corresponding power factors PF for all compounds increase with increasing temperature ranging from ~ 6 $\mu\text{W}/(\text{cm}\cdot\text{K}^2)$ at ~ 300 K to ~ 17 $\mu\text{W}/(\text{cm}\cdot\text{K}^2)$ at ~ 660 K. Figs. 7(c) and 7(d) show the total thermal conductivity κ_{tot} and the lattice thermal conductivity κ_{latt} as a function of temperature, respectively. For $z = 0.2$ the lattice thermal conductivity of ~ 0.45 W/(m·K) at ~ 660 K was achieved. The ZT s of ~ 0.9 , ~ 0.8 , and ~ 1.0 at ~ 660 K were achieved for $z = 0.4$, 0.3 , and 0.2 , respectively, Fig. 7(e).

F. Effect of Pb/Sn ratio on TE properties of $\text{Ag}_{0.9}(\text{Pb}_{1-y}\text{Sn}_y)_6\text{Sb}_{0.8}\text{Te}_8$

Fig. 8(a) shows the electrical conductivity σ and the Seebeck coefficient S as a function of temperature for $\text{Ag}_{0.9}(\text{Pb}_{1-y}\text{Sn}_y)_6\text{Sb}_{0.8}\text{Te}_8$ ($y = 2/3, 1/2, 1/3$). The room temperature electrical conductivity decreases with increasing the Pb/Sn ratio (~ 2300 S/cm for $y = 2/3$, ~ 1300 S/cm for $y = 1/2$, and ~ 600 S/cm for $y = 1/3$), while the Seebeck coefficient increases with increasing the Pb/Sn ratio (~ 120 $\mu\text{V/K}$ at ~ 670 K for $y = 2/3$, ~ 170 $\mu\text{V/K}$ for $y = 1/2$, and ~ 220 $\mu\text{V/K}$ for $y = 1/3$). It is well known that the Sn sites are prone to forming a large number of vacancies in SnTe giving rise to high hole concentrations ($>10^{20}$ cm^{-3}). [44-46] By contrast the Pb in PbTe shows no such tendency. The decreasing fraction Sn in the NaCl structure of $\text{Ag}_{1-x}(\text{Pb}_{1-y}\text{Sn}_y)_m\text{Sb}_{1-z}\text{Te}_{m+2}$ reduces the number of vacancies and thus decreases the hole concentrations. The power factors PF of ~ 16 , ~ 17 , and ~ 11 $\mu\text{W}/(\text{cm}\cdot\text{K}^2)$ at ~ 670 K were obtained for $y = 2/3, 1/2$, and $1/3$, respectively, Fig. 8(b). The total thermal conductivity κ_{tot} and lattice thermal conductivity

κ_{latt} as a function of temperature are plotted in Figs. 8(c) and 8(d), respectively. The lowest lattice thermal conductivity of ~ 0.5 W/(m·K) at ~ 670 K was achieved for $y = 1/2$. The ZT s of ~ 0.5 , ~ 1.0 , ~ 0.7 at ~ 670 K were obtained for $y = 2/3$, $1/2$, and $1/3$, respectively, Fig. 8(e).

IV. CONCLUSIONS

The $\text{Ag}_{1-x}(\text{Pb}_{1-y}\text{Sn}_y)_m\text{Sb}_{1-z}\text{Te}_{m+2}$ system can be prepared by a melt-solidification method and adopt an average NaCl-type phase. Several types of compositions were investigated, those with off-stoichiometric ratios, those with Te excess and those which gave valence precise charge balanced stoichiometries. For the $\text{Ag}_{0.9}(\text{Pb}_{0.5}\text{Sn}_{0.5})_m\text{Sb}_{0.8}\text{Te}_{m+2}$ class of compounds with excess Te, different m values ($m = 16, 14, 12, 10, 8, 6, 4$) were studied and the highest ZT of ~ 1.1 was obtained at ~ 660 K for $m = 10$ mainly due to very low lattice thermal conductivity (~ 0.4 W/(m·K) at 660 K). The electrical conductivity can be tuned with the Ag concentrations, the Sb concentrations, and the Pb/Sn ratios because in LASTT the Ag and Sb atoms play the role of electron acceptor and electron donor, respectively. Interestingly, for $m = 10$ the ZT s of the charge-balanced compounds are similar to those of the excess-Te compounds. The lattice thermal conductivities of ~ 0.7 W/(m·K) at ~ 660 K were achieved for the charge-balanced $\text{Ag}_{0.9}\text{Pb}_5\text{Sn}_5\text{Sb}_{0.8}\text{Te}_{11.65}$ and $\text{Ag}_{0.9}\text{Pb}_5\text{Sn}_5\text{Sb}_{0.7}\text{Te}_{11.5}$ compounds. Clearly the $\text{Ag}_{1-x}(\text{Pb}_{1-y}\text{Sn}_y)_m\text{Sb}_{1-z}\text{Te}_{m+2}$ system is complex but flexible and comprises a tunable thermoelectric class of materials which warrant further investigations. If a deeper understanding of their electronic, microstructural and phase stability properties is achieved a strong increase in their thermoelectric performance is expected.

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FIGURE CAPTIONS

FIG. 1. (Color online) (a) Powder x-ray diffraction patterns of samples of $\text{Ag}_{0.9}(\text{Pb}_{0.5}\text{Sn}_{0.5})_m\text{Sb}_{0.8}\text{Te}_{m+2}$ ($m = 4, 6, 8, 10, 12, 14, 16$) and (b) variation of the lattice parameters as a function of m for $\text{Ag}_{0.9}(\text{Pb}_{0.5}\text{Sn}_{0.5})_m\text{Sb}_{0.8}\text{Te}_{m+2}$ (cross symbols). The solid line indicates the calculated lattice parameter from Eq. (1). The lattice parameters were refined by using a full profile Rietveld refinement technique.[47]

FIG. 2. (Color online) Infrared absorption spectra and estimated energy band gaps of samples of $\text{Ag}_{0.9}(\text{Pb}_{0.5}\text{Sn}_{0.5})_m\text{Sb}_{0.8}\text{Te}_{m+2}$ ($m = 8, 10, 16$).

FIG. 3. (Color online) (a) Temperature dependence of the electrical conductivity σ and Seebeck coefficient S , (b) power factor PF , (c) total thermal conductivity κ_{tot} , (d) lattice thermal conductivity κ_{latt} , and (e) thermoelectric figure of merit ZT of samples of $\text{Ag}_{0.9}(\text{Pb}_{0.5}\text{Sn}_{0.5})_m\text{Sb}_{0.8}\text{Te}_{m+2}$ ($m = 4, 6, 8, 10, 12, 14, 16$).

FIG 4. (Color online) (a) Temperature dependence of the electrical conductivity σ and the Seebeck coefficient S of the excess-Te compounds, (b) temperature dependence of the electrical conductivity σ and the Seebeck coefficient S of the charge-balanced compounds, (c) temperature dependence of the power factor PF , and (d) temperature dependence of the hole concentration p_H of samples of $\text{Ag}_{0.9}(\text{Pb}_{0.5}\text{Sn}_{0.5})_{10}\text{Sb}_{1-z}\text{Te}_{12-\delta}$.

FIG. 5. (Color online) (a) Temperature dependence of hole mobility μ_p of samples of $\text{Ag}_{0.9}\text{Pb}_5\text{Sn}_5\text{Sb}_{0.8}\text{Te}_{11.8}$ and $\text{Ag}_{0.9}\text{Pb}_3\text{Sn}_3\text{Sb}_{0.8}\text{Te}_{7.8}$, (b) lattice thermal conductivity κ_{latt} of samples of $\text{Ag}_{0.9}(\text{Pb}_{0.5}\text{Sn}_{0.5})_{10}\text{Sb}_{1-z}\text{Te}_{12-\delta}$ and (c) lattice thermal conductivity κ_{latt} of samples of $\text{Ag}_{0.9}(\text{Pb}_{0.5}\text{Sn}_{0.5})_{16}\text{Sb}_{1-z}\text{Te}_{18-\delta}$, and (d) thermoelectric figure of merit ZT of samples of $\text{Ag}_{0.9}(\text{Pb}_{0.5}\text{Sn}_{0.5})_{10}\text{Sb}_{1-z}\text{Te}_{12-\delta}$.

FIG. 6. (Color online) (a) Temperature dependence of the electrical conductivity σ and Seebeck coefficient S , (b) power factor PF , (c) total thermal conductivity κ_{tot} , (d) lattice thermal conductivity κ_{latt} , and (e) thermoelectric figure of merit ZT of samples of $\text{Ag}_{1-x}(\text{Pb}_{0.5}\text{Sn}_{0.5})_{10}\text{Sb}_{0.8}\text{Te}_{12}$ ($x = -0.1, 0.1, 0.2, 0.3$).

FIG. 7. (Color online) (a) Temperature dependence of the electrical conductivity σ and the Seebeck coefficient S , (b) power factor PF , (c) total thermal conductivity κ_{tot} , (d) lattice thermal conductivity κ_{latt} , and (e) thermoelectric figure of merit ZT of samples of $\text{Ag}_{0.9}(\text{Pb}_{0.5}\text{Sn}_{0.5})_{16}\text{Sb}_{1-z}\text{Te}_{18}$ ($z = 0.2, 0.3, 0.4$).

FIG. 8. (Color online) (a) Temperature dependence of the electrical conductivity σ and the Seebeck coefficient S , (b) power factor PF , (c) total thermal conductivity κ_{tot} , (d) lattice thermal conductivity κ_{latt} , and (e) thermoelectric figure of merit ZT of samples of $\text{Ag}_{0.9}(\text{Pb}_{1-y}\text{Sn}_y)_6\text{Sb}_{0.8}\text{Te}_8$ ($y = 2/3, 1/2, 1/3$).

FIG. 1.

FIG. 2.

FIG. 3.

FIG. 4.

FIG. 5.

FIG. 6.

FIG. 7.

FIG. 8.

REFERENCES

- [1] C. Wood, Reports on Progress in Physics 51 (1988) 459.
- [2] G. Mahan, B. Sales, J. Sharp, Physics Today 50 (1997) 42-47.
- [3] F.J. DiSalvo, Science 285 (1999) 703-706.
- [4] M.S. Dresselhaus, G. Chen, M.Y. Tang, R.G. Yang, H. Lee, D.Z. Wang, Z.F. Ren, J.P. Fleurial, P. Gogna, Advanced Materials 19 (2007) 1043-1053.
- [5] G.J. Snyder, E.S. Toberer, Nat Mater 7 (2008) 105-114.
- [6] L.E. Bell, Science 321 (2008) 1457-1461.
- [7] J.R. Sootsman, D.Y. Chung, M.G. Kanatzidis, Angewandte Chemie International Edition 48 (2009) 8616-8639.
- [8] C.J. Vineis, A. Shakouri, A. Majumdar, M.G. Kanatzidis, Advanced Materials 22 (2010) 3970-3980.
- [9] M.G. Kanatzidis, Chemistry of Materials 22 (2010) 648-659.
- [10] J.P. Heremans, B. Wiendlocha, A.M. Chamoire, Energy & Environmental Science 5 (2012) 5510-5530.
- [11] B.C. Sales, D. Mandrus, R.K. Williams, Science 272 (1996) 1325-1328.
- [12] C. Uher, in Thermoelectric Handbook, Macro to Nano, in: D.M. Rowe (Ed.) CRC Taylor & Francis, Boca Raton, 2006.
- [13] K.F. Hsu, S. Loo, F. Guo, W. Chen, J.S. Dyck, C. Uher, T. Hogan, E.K. Polychroniadis, M.G. Kanatzidis, Science 303 (2004) 818-821.
- [14] K. Biswas, J. He, Q. Zhang, G. Wang, C. Uher, V.P. Dravid, M.G. Kanatzidis, Nat Chem 3 (2011) 160-166.
- [15] K. Biswas, J. He, I.D. Blum, C.-I. Wu, T.P. Hogan, D.N. Seidman, V.P. Dravid, M.G. Kanatzidis, Nature 489 (2012) 414-418.
- [16] P.F.P. Poudeu, J. D'Angelo, A.D. Downey, J.L. Short, T.P. Hogan, M.G. Kanatzidis, Angewandte Chemie International Edition 45 (2006) 3835-3839.
- [17] J. Androulakis, K.F. Hsu, R. Pcionek, H. Kong, C. Uher, J.J. D'Angelo, A. Downey, T. Hogan, M.G. Kanatzidis, Advanced Materials 18 (2006) 1170-1173.
- [18] J. Androulakis, C.-H. Lin, H.-J. Kong, C. Uher, C.-I. Wu, T. Hogan, B.A. Cook, T. Caillat, K.M. Paraskevopoulos, M.G. Kanatzidis, Journal of the American Chemical Society 129 (2007) 9780-9788.
- [19] J.P. Heremans, V. Jovovic, E.S. Toberer, A. Saramat, K. Kurosaki, A. Charoenphakdee, S. Yamanaka, G.J. Snyder, Science 321 (2008) 554-557.
- [20] Y. Pei, X. Shi, A. LaLonde, H. Wang, L. Chen, G.J. Snyder, Nature 473 (2011) 66-69.
- [21] J.R. Sootsman, H. Kong, C. Uher, J.J. D'Angelo, C.-I. Wu, T.P. Hogan, T. Caillat, M.G. Kanatzidis, Angewandte Chemie International Edition 47 (2008) 8618-8622.
- [22] K. Ahn, C. Li, C. Uher, M.G. Kanatzidis, Chemistry of Materials 21 (2009) 1361-1367.
- [23] K. Ahn, M.-K. Han, J. He, J. Androulakis, S. Ballikaya, C. Uher, V.P. Dravid, M.G. Kanatzidis, Journal of the American Chemical Society 132 (2010) 5227-5235.
- [24] Q. Zhang, F. Cao, W. Liu, K. Lukas, B. Yu, S. Chen, C. Opeil, D. Broido, G. Chen, Z. Ren, Journal of the American Chemical Society 134 (2012) 10031-10038.

- [25] K. Ahn, K. Biswas, J. He, I. Chung, V. Dravid, M.G. Kanatzidis, *Energy & Environmental Science* 6 (2013) 1529-1537.
- [26] R.J. Korkosz, T.C. Chasapis, S.-h. Lo, J.W. Doak, Y.J. Kim, C.-I. Wu, E. Hatzikraniotis, T.P. Hogan, D.N. Seidman, C. Wolverton, V.P. Dravid, M.G. Kanatzidis, *Journal of the American Chemical Society* 136 (2014) 3225-3237.
- [27] H. Wang, J. Hwang, M.L. Snedaker, I.-h. Kim, C. Kang, J. Kim, G.D. Stucky, J. Bowers, W. Kim, *Chemistry of Materials* 27 (2015) 944-949.
- [28] M. Zhou, J.-F. Li, T. Kita, *Journal of the American Chemical Society* 130 (2008) 4527-4532.
- [29] A. Kosuga, K. Kurosaki, H. Muta, S. Yamanaka, *Journal of Alloys and Compounds* 416 (2006) 218-221.
- [30] T. Hogan, A. Downey, J. Short, J. D'Angelo, C.-I. Wu, E. Quarez, J. Androulakis, P.F.P. Poudeu, J. Sootsman, D.-Y. Chung, M.G. Kanatzidis, S.D. Mahanti, E. Timm, H. Schock, F. Ren, J. Johnson, E. Case, *Journal of Electronic Materials* 36 (2007) 704-710.
- [31] M.-K. Han, K. Hoang, H. Kong, R. Pcionek, C. Uher, K.M. Paraskevopoulos, S.D. Mahanti, M.G. Kanatzidis, *Chemistry of Materials* 20 (2008) 3512-3520.
- [32] C. Kittel, *Introduction to Solid State Physics*, John Wiley, 1996.
- [33] A.F. May, E.S. Toberer, A. Saramat, G.J. Snyder, *Physical Review B* 80 (2009) 125205.
- [34] E. Quarez, K.-F. Hsu, R. Pcionek, N. Frangis, E.K. Polychroniadis, M.G. Kanatzidis, *Journal of the American Chemical Society* 127 (2005) 9177-9190.
- [35] S. Miotkowska, E. Dynowska, I. Miotkowski, A. Szczerbakow, B. Witkowska, J. Kachniarz, W. Paszkowicz, *Journal of Crystal Growth* 200 (1999) 483-489.
- [36] A. Guéguen, P.F.P. Poudeu, C.-P. Li, S. Moses, C. Uher, J. He, V. Dravid, K.M. Paraskevopoulos, M.G. Kanatzidis, *Chemistry of Materials* 21 (2009) 1683-1694.
- [37] M. Orihashi, Y. Noda, L. Chen, T. Hirai, *Mater. Trans. JIM* 41 (2000).
- [38] R.S. Allgaier, W.W. Scanlon, *Physical Review* 111 (1958) 1029-1037.
- [39] Y.I. Ravich, B.A. Efimova, I.A. Smirnov, *Semiconducting Lead Chalcogenides*, Plenum Press, New York-London, 1970.
- [40] K. Biswas, J. He, G. Wang, S.-H. Lo, C. Uher, V.P. Dravid, M.G. Kanatzidis, *Energy & Environmental Science* 4 (2011) 4675-4684.
- [41] J. Androulakis, I. Todorov, D.-Y. Chung, S. Ballikaya, G. Wang, C. Uher, M. Kanatzidis, *Physical Review B* 82 (2010) 115209.
- [42] C.M. Jaworski, M.D. Nielsen, H. Wang, S.N. Girard, W. Cai, W.D. Porter, M.G. Kanatzidis, J.P. Heremans, *Physical Review B* 87 (2013) 045203.
- [43] J. Androulakis, R. Pcionek, E. Quarez, J.-H. Do, H. Kong, O. Palchik, C. Uher, J.J. D'Angelo, J. Short, T. Hogan, M.G. Kanatzidis, *Chemistry of Materials* 18 (2006) 4719-4721.
- [44] G. Tan, F. Shi, S. Hao, H. Chi, T.P. Bailey, L.-D. Zhao, C. Uher, C. Wolverton, V.P. Dravid, M.G. Kanatzidis, *Journal of the American Chemical Society* 137 (2015) 11507-11516.
- [45] G. Tan, L.-D. Zhao, F. Shi, J.W. Doak, S.-H. Lo, H. Sun, C. Wolverton, V.P. Dravid, C. Uher, M.G. Kanatzidis, *Journal of the American Chemical Society* 136 (2014) 7006-7017.

- [46] G. Tan, F. Shi, S. Hao, H. Chi, L.-D. Zhao, C. Uher, C. Wolverton, V.P. Dravid, M.G. Kanatzidis, *Journal of the American Chemical Society* 137 (2015) 5100-5112.
- [47] B.A. Hunter, Rietica-A visual Rietveld program, International Union of Crystallography Commission on Powder Diffraction, Newsletter No. 20, <http://www.rietica.org>, Summer, 1998.

Graphical Abstract Legend

The $\text{Ag}_{1-x}(\text{Pb}_{1-y}\text{Sn}_y)_m\text{Sb}_{1-z}\text{Te}_{m+2}$ system defines a complex and flexible class of tunable thermoelectric class of materials with high performance.

Graphical Abstract