Microstructure analyses and thermoelectric properties of Ag$_{1-x}$Pb$_{18}$Sb$_{1+y}$Te$_{20}$

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1. Introduction

Given the looming shortage of natural resources, there is a growing interest in renewable energy. The feasible recovery of waste-heat energy as it is generated by industrial processes and vehicle engines has led to a strongly increasing research interest in thermoelectrics (TE) [1]. In order to obtain TE materials with high thermoelectric performance, i.e. with a large figure of merit, ZT, one needs to tune electronic and phononic properties simultaneously. In this respect, a high electrical conductivity $\sigma$ and a high thermopower $S$ are crucial as $\text{ZT} = (S^2\sigma/kT)$, where $T$ is the absolute temperature and $S^2\sigma$ is the power factor. A promising candidate for achieving high ZT values is the quaternary compound Ag$_{m}$Pb$_{18}$Sb$_{1+y}$Te$_{20}$ (Lead–Antimony–Silver–Tellurium, LAST-18) as well as of Ag$_{1-x}$Pb$_{18}$Sb$_{1+y}$Te$_{20}$, i.e. Ag-deficient and Sb-excess LAST-18 ($x \neq 0, y \neq 0$), respectively. Two different length scales are explored. The micrometer scale was evaluated by SEM to analyze the volume fraction and the number of secondary phases as well as the impact of processing parameters on the homogeneity of bulk samples. For Ag$_{m}$Pb$_{18}$Sb$_{1+y}$Te$_{20}$, site-specific FIB liftout of TEM lamellae from thermoelectrically characterized samples was accomplished to investigate the structure on the nanometer scale. High-resolution TEM and energy-filtered TEM were performed to reveal shape and size distribution of nanoprecipitates, respectively. A hypothesis concerning the structure–property relationship is set out within the framework of a gradient annealing experiment. This study is completed by results dealing with inhomogeneties on the micrometer scale of Ag$_{1-x}$Pb$_{18}$Sb$_{1+y}$Te$_{20}$ and its electronic properties.

2. Experimental

LAST-18 ingots used for TEM and TE characterization were prepared via melt synthesis as described in detail in [7].
for studying the impact of processing parameters were obtained by heating in an evacuated and sealed quartz ampoule containing high purity (99.999%) Ag, PbTe, Te, and Sb to 1000 °C within 5 h and keeping the melt for 1 h without applying a rocking furnace. The ampoule was then quenched in cold water. To study the impact of annealing treatment a gradient annealing experiment was conducted. Fig. 1 shows the synthesis route and the conditions for long-term annealing schematically.

For SEM characterization, the sample was embedded in a graphite-containing mould compound to improve mechanical stability. Microstructural examination was performed by scanning electron microscopy (SEM) using a Carl Zeiss Ultra 55 scanning electron microscope equipped with an energy-dispersive X-ray spectrometer (EDS). Standardized evaluation of EDS spectra was conducted using standardless atomic number (Z), absorption (A), and fluorescence (F) correction and a batch routine for the subtraction of bremsstrahlung background. The measurement error was estimated to be ±2%. Transmission electron microscopy (TEM) was employed to observe nanostructures in pre-selected parts of the LAST material. TEM-lamelae were obtained by focused ion beam (FIB) machining (Carl Zeiss Auriga equipped with a Cobra column and a gas injection system) using a Ga⁺-beam for cutting (30 kV) and polishing (5 kV) and were analyzed in a Hitachi H-8100 with scanning unit (beam diameter: ~5 nm) and energy-dispersive X-ray analyzer. To avoid surface artefacts introduced by Ga⁺ ions, final thinning was done by ion polishing (2.5 keV Ar⁺, 7° incident angle). High resolution TEM (HRTEM) imaging was realized in a JEOL JEM 4010 (point-to-point resolution: 0.155 nm) and a FEI CM200 FEGTEM (point-to-point resolution: 0.24 nm). In the latter, a Gatan GIF 200 was employed to perform energy-filtered imaging (EFTEM) and electron energy loss spectroscopy (EELS). A probe-corrected FEI TITAN 80-300 (operated at 300 keV, STEM resolution: 0.08 nm) and a Nion UltraSTEM 100 (SuperSTEM, operated at 100 keV, STEM resolution: 0.08 nm, energy resolution: 0.4 eV, equipped with a Gatan Enfina spectrometer) were used for high-resolution STEM imaging and analysis. The latter instrument was also used for Z-contrast imaging using the HAADF (high-angle annular dark-field) signal and for EELS.

3. Results and discussion
3.1. SEM

In order to obtain a homogeneous material on the micrometer length scale, parameters of the melt synthesis were varied (such as rocking periods in the furnace and annealing temperatures).

Fig. 2(a) shows an SEM image of a sample which was neither applied to a rocking furnace during the melt process nor annealed. The volume fraction of secondary phases was large and amongst other phases one can see the eutectic Sb-rich phases embedded in the matrix and peritectic Ag- and Te-rich phases segregated at grain boundaries as reported by Dow et al. [3]. EDS mapping (inset Fig. 2(a)) gives a qualitative impression of the elemental distribution. As reported in [7], a gradient-temperature experiment was carried out to study the impact of annealing temperature T_{ann} on micro- and nanostructure. An SEM image of an optimized sample is shown in Fig. 2(b) and emphasizes the reduction in the size and number of the secondary phases. Together with a decrease in volume fraction of secondary phases, an increasing solubility of Sb in the matrix with increasing T_{ann} was observed, which is consistent with the PbTe–Sb phase diagram [8]. Another indication for the increased Sb solubility is the larger lattice parameter in the annealed sample in comparison with the untreated, as-quenched samples found by powder XRD [7]. However, another behavior was observed in [3], where PbTe was doped increasingly with Sb. Thermoelectric measurements revealed a favorable annealing temperature range between 450 and 550 °C, showing a ZT value of 1.05 at 425 °C for the sample annealed at T_{ann} = 505 °C. Fig. 2(b) clearly illustrates that annealing at the preferred T_{ann} reduces number and size of secondary phases in the bulk material. Fig. 3 illustrates that even a short annealing for 2 h at the preferred temperature of T_{ann} = 505 °C improves the homogeneity of the material on the micrometer length scale. Moreover, annealing the phase mixture (indicated in Fig. 3(a)) seems to form more stable stoichiometric phase compositions such as pure Sb and Ag₂Te as highlighted in Fig. 3(b). This is in accordance with our recent results [7] where...
the Ag/Sb ratio in the matrix reaches unity with increasing $T_{\text{ann}}$, simultaneously accompanied by a drop in electrical conductivity. This behavior was attributed to a coupling mechanism between Ag and Sb decreasing the charge carrier density induced by neutralizing charge effects according to Refs. [3,7].

To examine the impact of an Ag-deficient and Sb-rich matrix on electronic properties, ingots with the stoichiometry $Ag_{1-y}Pb_{18}Sb_{1+y}Te_{20}$ were synthesized with specific values for $1-x$ and $1+y$. $Ag_{0.55}Pb_{18}Sb_{0.53}Te_{20}$ was synthesized according to the data provided in supplement 20 in Ref. [5]. This composition was reported to possess especially high electron mobility and therefore seemed suitable for further investigation. $Ag_{0.45}Pb_{18}Sb_{0.53}Te_{20}$ was selected as the values correspond to four times the solubility limits of Ag and Sb in PbTe at room temperature, respectively. The melting procedure was based on a routine proposed in [5] but here the ingot was heated to 980 °C after quenching as stoichiometric LAST-18 would not melt below 900 °C according to the pseudo-binary system PbTe–Ag$_2$Te [9]. For thermoelectric measurements, the material was ground to powder and pressed to a pellet using a direct current sintering press [7]. While the gradient experiment described above showed only pure Sb and Ag$_2$Te phases on the micrometer scale, EDS measurement on Ag-deficient LAST ($Ag_{0.55}Pb_{18}Sb_{0.53}Te_{20}$) showed secondary phases such as Sb$_2$Te$_3$ and phases close to AgSbTe$_2$ (see Fig. 4(a)). This is in accordance with the phase diagram of the pseudo-binary system Ag$_2$Te–Sb$_2$Te$_3$ [10,11] where an Ag-deficient composition results in the phases $\delta$-AgSbTe$_2$ and Sb$_2$Te$_3$ as well as the mixture of the two above 400 °C. The faster cooling rate below 450 °C ($\sim$ 36 K/h) in comparison to the cooling rate between 850 °C and 450 °C (10 K/h) could have preserved these phases. Fig. 4(b) shows a SEM image of such structures which occurred only in matrix regions close to large Sb-rich secondary phases. They were also confirmed to be Sb-rich by EDS point analysis.

### 3.2. TEM

As described in Section 3.1, several LAST-18 samples (sliced disks from the cylindrical bar) associated with a specific $T_{\text{ann}}$ have been examined by SEM and revealed only Sb and Ag$_2$Te as secondary phases. To obtain a better insight into the morphology of material at the nanometer length scale, TEM samples taken from the matrix were prepared by site-specific FIB machining. TEM images revealed a wide range of different features. One form were “bulky” Ag$_2$Te precipitates (confirmed by EDS point measurement) for lower $T_{\text{ann}}$, see Fig. 5(a) and (b). In Fig. 5(a), the domain-like structure characteristic of monoclinic Ag$_2$Te [12] is evident, whereas Fig. 5(b) shows that these features possess a faceted shape which suggests a semi-coherent growth mechanism [13]. Nucleation of semi-coherent precipitates usually requires dislocations providing diffusion pipes for the Ag atoms in the case of Ag$_2$Te. Dislocation loops appearing in the Z-contrast images (Fig. 5(c)) strengthen this assumption. The strainfield surrounding such dislocations could already have been present in the PbTe host lattice providing the location for precipitate formation [14].

Other Ag-rich precipitates, perhaps originating from dislocation cores, were rather rod-shaped causing strainfields in their vicinity, possibly contributing to a further reduction of thermal lattice conductivity (Fig. 6(a)). Certainly dislocations originally introduced for strain relaxation in the matrix during the sintering process would offer additional volume interstitial space for excessive Ag and Sb atoms along dislocation lines. To minimize their free energy, Ag- and Sb-rich nuclei should grow parallel to these lines gaining a needle-like shape [13]. High resolution TEM analysis showed various orientation domains in the same precipitate, see Fig. 6(b), but the spots in the power spectra (fast Fourier transformation of a TEM image with atomic resolution) of these features could not be correlated to any stoichiometric Ag–Te-composition. Another prominent feature were ca. 5 nm sized Moiré patterns (Fig. 7(a) and (b)), apparent in samples for nearly all $T_{\text{ann}}$. Similar features were observed by Zhou et al. [15] who related them to compositional fluctuations of Ag, Sb, and Pb in LAST. However, these features were also recognized in polycrystalline PbTe, although very marginally (see Fig. 7(c)) and therefore indicate a different mechanism for their formation. Subsequent EELS line scans across these features in the LAST...
material were not able to reveal any measurable change in composition, suggesting only a very slight compositional change or that the features are an intrinsic part (fluctuations in Pb levels) of the PbTe matrix itself. The Moiré patterns were only seen when the beam was incident along a low-index orientation of the matrix which is clearly an indication for coherent growth. However, in the sample correlated to \( T_{\text{ann}} = 505 \, ^{\circ}\text{C} \), these Moiré fringes were not observed but instead stacking fault-like features were evident (white arrows in Fig. 7(d)), which have already been observed and investigated in [5,16,17].

3.3. Thermoelectric properties

As reported in [7], thermoelectric measurements were performed on samples from the long-term gradient experiment correlated to a specific \( T_{\text{ann}} \) in order to obtain the lattice thermal conductivity \( k_L \).

Fig. 8 shows that \( k_L \) first decreases with increasing \( T_{\text{ann}} \) and then increases again for very high \( T_{\text{ann}} \). One needs to link \( k_L \) with the size, shape, and occurrence of the potential phonon scatterers mentioned in Section 3.2. For example, for \( T_{\text{ann}} = 580 \, ^{\circ}\text{C} \), neither the large, bulky features nor the rod-shaped features were observed. On the other hand, for \( T_{\text{ann}} = 238 \, ^{\circ}\text{C} \), both of these features were observed but perhaps there was insufficient Sb dissolved in the matrix to form the desired amount of atomic-scale inhomogeneities. That is to say, for both low and very high \( T_{\text{ann}} \), the bulk samples seem to lack the required variation in features and in their size distribution to decrease \( k_L \) significantly. As stated in [18] there are two strategies to reduce \( k_L \). Besides its general dependence on temperature, for an isotropic material \( k_L \) is dependent on the specific heat \( C_s \), the group...
velocity \nu and the phonon mean free path \Lp of the material. One strategy is to lower the \Cv - \nu term by altering the bulk phonon dispersion, that is to flatten the dispersion relation by phonon confinement effects as one would expect in idealized superlattices or nanowires. With regards to non-idealized bulk materials, a second strategy, in relation to classical size effects, is to lower \Lp by random scattering at boundaries and interfaces. Here the effective mean free path can be approximated by the Matthiessen rule, which takes the mean free paths of the bulk scattering mechanisms, i.e. impurity scattering, phonon–phonon Umklapp scattering and boundary/interface scattering \Lbdy into account. The scattering strength of \Lbdy is highly anisotropic and depends on roughness and the acoustic impedance mismatch of an interface as well as on phonon wavelengths. The scattering ability, however, is primarily determined by the size of the nanostructures, whereas a detailed analysis provides a by far wider size range on suitable \Lbdy as widely believed. Thus a wide size range of nanostructures comes into consideration. These facts could support the positive impact of rather large and semi-coherent precipitates on lowering \kL. On the other hand, these nanoscale secondary phases cannot be the only contribution. However, the source of the Moiré pattern features can also not be considered to be the sole determining criterion as these were observed for a wide range of \Tann. Further investigation should deal with the density distribution of these latter features. If they are connected to atomic levels of Sb, Ag and Pb fluctuations one should be able to link them to \Tann.

Besides enhancing ZT by decreasing \kappa, it is also possible to improve electrical properties and therefore increase the power-factor. For this reason \Ag_{0.55}\Pb_{18}\Sb_{1.533}\Te_{20} was produced with the amount and ratio of Ag and Sb being varied. Electrical conductivity and Hall measurements revealed a remarkable increase in both \sigma and charge carrier density \nd for \Ag_{0.46}\Pb_{18}\Sb_{1.533}\Te_{20} in comparison with \Ag\Pb_{18}\Sb_{1.533}\Te_{20} whereas \kappa did not change considerably, see Table 1. Like \Ag\Pb_{18}\Sb_{1.533}\Te_{20} the material shows a behavior, in which \sigma is decreasing with increasing operating temperature (Fig. 9). In view of the considerations mentioned above, the Ag/Sb ratio in the matrix should also play a crucial role in atomic-scale disordering. Therefore our hypothesis states that precipitation of Ag- and Sb-rich structures are not exclusively responsible for lowering \kappaL but that a more extensive approach is required to include the phenomena described above. Ag-deficient \Ag_{0.55}\Pb_{18}\Sb_{1.533}\Te_{20} exhibited decreased values of \nd and \sigma. Although one avoids charge neutralization effects when Ag/Sb \neq 1 there seems to be a certain amount of Ag and Sb required to have a positive effect on \nd and \sigma. The results are in accordance with our SEM results where this material exhibited various Sb–Te secondary phases which could prevent the Sb contributing to \nd. The corresponding plot in Fig. 9 shows a more complex behavior for the Ag-deficient material.

4. Conclusions

SEM results showed that an improved homogeneity on the micrometer scale can be reached by applying distinct repeatable melting and annealing parameters. For the gradient experiment described in [7], an attempt was made to categorize the character of detected nanoscale features. More work is necessary to study the relationship between their shape as well as size and their phonon scattering ability. Relevant phonon scattering mechanisms are likely to be related to the nanoscale precipitates within the matrix. Their occurrence is clearly connected to \Tann as well as to the available amount of Ag and Sb in the matrix outside these secondary phases. A further approach dealt with LAST material with Ag/Sb ratio below 1 and showed evidence for the formation of new phases.

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**Table 1**

\( n \) and \( \sigma \) at room temperature for different \( \Ag_{1-x}\Pb_{18}\Sb_{1+y}\Te_{20} \) compositions. Measurements were done on sintered samples.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Charge carrier density ( n ) (cm(^{-3}))</th>
<th>Electrical conductivity ( \sigma ) (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>\Ag_{0.15}\Pb_{18}\Sb\Te_{20}</td>
<td>( 9.9 \times 10^{17} )</td>
<td>90.5</td>
</tr>
<tr>
<td>\Ag\Pb_{18}\Sb\Te_{20}</td>
<td>( 1.6 \times 10^{18} )</td>
<td>221.0</td>
</tr>
<tr>
<td>\Ag_{0.46}\Pb_{18}\Sb_{1.533}\Te_{20}</td>
<td>( 3.0 \times 10^{19} )</td>
<td>676.0</td>
</tr>
</tbody>
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**Fig. 8.** Thermal conductivity \( \kappaL \) plotted as a function of temperature. All annealed LAST samples exhibit lower \( \kappaL \) values than n-PbTe. For the annealed samples, \( \kappaL \) first decreases with increasing \( \Tann \) and then increases again for high \( \Tann \). The lattice part of thermal conductivity can be evaluated from the equation, \( \kappaL = \kappaE + \kappaL \), where \( \kappaE \) is the measured total thermal conductivity and \( \kappaL \) is the electronic contribution—derived from the Wiedemann–Franz law. Adapted from [7].

**Fig. 9.** Electrical conductivity \( \sigma \) plotted as a function of temperature. \( \Ag\Pb_{18}\Sb\Te_{20} \) and \( \Ag_{0.46}\Pb_{18}\Sb_{1.533}\Te_{20} \) show a monotonically decreasing behavior whereas \( \Ag_{0.15}\Pb_{18}\Sb\Te_{20} \) acts like a lightly doped conductor due to the small fractions of Ag and Sb.
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References