Compositional fluctuations, nanostructuring and heavy hole mass in the thermoelectric material

Ag_{0.85}SnSb_{1.15}Te₃

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Supplementary Information

Experimental Section

Synthesis

AgSnSbTe_3 samples were produced by mixing appropriate stoichiometric ratios of high purity starting materials, namely Ag, Sn, Sb and Te. The initial charge was sealed in evacuated fused silica tubes, heated above the respective melting points of the constituent metals, held there for a few days and then slowly cooled to room temperature. Single crystals of AgSnSbTe_3 with suitable size for X-Ray characterization were obtained by cooling one ingot previously prepared from 700°C to 500°C at 2°C/h rate and then to room temperature in 10 h. Figure 1S shows a typical single crystal grown on the ingot and carefully removed from its surface.

Figure 1S. SEM image of one single crystal of AgSnSbTe_3

Powder X-ray Diffraction

Powder x-ray diffraction studies, performed on a Rigaku Rotaflex diffractometer operating at 45 kV and 100 mA, showed the produced specimens to be single phase. The diffractograms indicated the existence of an fcc NaCl-type cubic lattice with a lattice constant of 6.159(2) Å.

Figure 2S. Indexed powder x-ray diffractogram of $\text{Ag}_{0.85}\text{SnSb}_{1.15}\text{Te}_3$

Single crystal X-ray Diffraction

The X-ray diffraction intensities of the single crystal of AgSnSbTe_3 were recorded at room temperature on a Bruker SMART Platform CCD diffractometer using a graphite-monochromatized $\text{MoK}\alpha$ radiation under conditions shown in Table 1. Total spheres of reciprocal space (4×606 frames) were collected by using ω -scans, 20 s per frame, 0.3° oscillations for four different values of φ : 0° , 90° , 180° and 270° and with a crystal to a detector distance of 50 mm. The SMART software [1] was used for the data acquisition and SAINT [2] for data extraction and reduction. An absorption correction based on the face indexation was then applied using the program Xprep of the SHELXTL package [3]. An additional correction for absorption based on symmetry equivalent reflections was subsequently applied with the program SADABS [4]. The structure solution and refinements were performed with the SHELXTL software. The complete data collection parameters and details of the structure refinement are given in Table 1.

EDS Analysis

Quantitative microprobe analyses of the compound were performed with a JEOL JSM-35C scanning electron microscope equipped with a Tracor Northern EDS detector. Data were acquired using an accelerating voltage of 20 kV and a 40 secs accumulation time. EDS analysis on several polished pieces cut along the ingot showed chemical homogeneity and an average composition of $\text{Ag}_{0.84}\text{Sn}_{1.02}\text{Sb}_{1.16}\text{Te}_3$ which is in excellent

¹ SMART: Siemens Analytical X-Ray Systems, Inc., Madison, WI 53719 (1994).

² SAINT + version 6.02: Area-Detector Integration Software; Siemens Industrial Automation, Inc.: Madison, WI (1998).

³ G. M. Sheldrick, SHELXTL NT version 5.1, Bruker Analytical X-Ray Systems (1998).

⁴ SADABS: Area-Detector Absorption Correction; Siemens Industrial Automation, Inc.: Madison, WI, (1996).

agreement with the nominal composition. The EDS analysis of the single crystal selected for X-Ray data collection, namely $\text{Ag}_{0.81}\text{Sn}_{1.08}\text{Sb}_{1.04}\text{Te}_3$, agrees quite well with the nominal composition of the ingot. A JEOL-2200FS high resolution field emission transmission electron microscope attached to a Gatan image filter was used to structurally characterize the sample.

Details regarding the experimental apparatus used to determine the charge transport properties can be found elsewhere [⁵].

⁵ D. Y. Chung, T. P. Hogan, M. Rocci-Lane, P. Brazis, J. R. Ireland, C. R. Kannerwurf, M. Bastea, C. Uher, and M. G. Kanatzidis, J. Am. Chem. Soc. **126**, 6414 (2004).

Crystal structure refinements

The refinements were performed in $Pm\bar{3}m$ and $P4/mmm$ space groups. Both space groups implied two unique sites that could be potentially occupied by Ag, Sn and Sb atoms. The refinements were carried out by constraining the atoms occupying the same site (i.e. Ag, Sn and Sb) to have the same positional and displacement parameters. In parallel, two linear combinations of free variables were added: the first one restrained the sum of occupation factors of atoms sharing the same site to be equal to 1 (sites fully occupied) and the second one restrained the occupancies to fit the charge balance (i.e. sum of the formal charge of Ag, Sn and Sb atoms multiplied by their own site occupation factor equal to 2). Due to the weak ratio: number of weak supercell reflections to strong subcell reflections, a damping factor was introduced to help the system to converge. In the last cycles of the refinements, the damping factor was removed as well as the both linear combinations by fixing beforehand the site occupation factors of Ag, Sn and Sb atoms to the obtained values when restrained. Finally, the secondary extinction and an optimized weighting scheme were introduced leading to the final reliability factors reported in Table 1.

Both refinements are acceptable, however the tetragonal model gave better refinement results than the cubic one when considering all data. The details of the structural refinements are given in Table 1. The formula obtained after refinement was $\text{Ag}_{1.33}\text{Sn}_{1.33}\text{Sb}_{1.33}\text{Te}_4$ that corresponds to AgSnSbTe_3 ($m = 1$) in the formula scheme of $\text{AgSn}_m\text{SbTe}_{m+2}$. The refined atomic coordinates and isotropic displacement parameters are presented in Table 2.

Table 1. Crystal, data collection and details of structure refinement for $\text{Ag}_{0.81}\text{Sn}_{1.08}\text{Sb}_{1.04}\text{Te}_3$

Ag _{0.81} Sn _{1.08} Sb _{1.04} Te ₃		
<i>Crystal data</i>		
Crystal symmetry	Cubic	Tetragonal
Space group	<i>Pm</i> $\bar{3}$ <i>m</i> (n°221)	<i>P4/mmm</i> (n°123)
Unit cell (Å)	a = 6.1731(5)	a = 4.3650(5) c = 6.1731(5)
Volume (Å ³)	235.24(3)	117.62(2)
Z	1	1
Calculated density (g/cm ³)	6.873	6.898
<i>Data collection</i>		
Equipment	Bruker SMART CCD-1K	
Radiation MoKα (Å)	0.71073	0.71073
Scan mode	ω - scan	ω - scan
Recording angular range 2θ (°)	6.60-56.22	6.60-56.22
Recording reciprocal space	-8 ≤ h ≤ 7	-5 ≤ h ≤ 5
	-8 ≤ k ≤ 7	-5 ≤ k ≤ 5
	-8 ≤ l ≤ 8	-8 ≤ l ≤ 7
Number of measured reflections	2625	1310
Number of independent reflections [I>2σ(I)]	86	112
R merging factor	2.85	2.31
μ (mm ⁻¹)	22.063	22.138
Crystal size (mm ³)	0.278 x 0.061 x 0.047	
Transmission factor range	0.206 – 0.442	
<i>Refinement parameters</i>		
Number of refined parameters / constraints	6 / 2	6 / 2
Goodness-of-fit on F ²	0.90	0.89
R ₁ (F) [I>2σ(I)] (%) / all data ^b	1.35 / 2.73	1.36 / 2.09
wR ₂ (F ²) [I>2σ(I)] (%) / all data ^c	2.77 / 3.82	3.03 / 3.70
w = 1 / [σ ² (Fo ²) + (A x P) ² + B x P]	A = 0.0	A = 0.0
with P = [max(Fo ² , 0) + 2 F _c ²] / 3	B = 6.0679	B = 1.9071
Isotropic secondary extinction	0.0744(9)	0.276(3)
Max / Min Δρ e/Å ³	0.52 / -0.53	0.63 / -0.67

$$^b R_1 (F) = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} \quad ^c wR_2 (F^2) = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)} \right]^{1/2}$$

Table 2. Atomic parameters and equivalent isotropic displacement parameters in $Pm\bar{3}m$ and $P4/mmm$ space groups for $\text{Ag}_{0.81}\text{Sn}_{1.08}\text{Sb}_{1.04}\text{Te}_3$. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atoms	Site	Occupancy	x	y	z	$U_{\text{eq}} (\text{\AA}^2)$
Te1	1a	1	0	0	0	0.027(1)
Te2	3c	1	1/2	1/2	0	0.027(1)
Ag1 / Sn1 / Sb1	1b	75 / 25 / 0	1/2	1/2	1/2	0.036(1)
Ag2 / Sn2 / Sb2	3d	19 / 36 / 44	1/2	0	0	0.039(1)

AgSnSbTe_3 : $a = 6.1731(5) \text{ \AA}$, $Pm\bar{3}m$ space group.

Atoms	Site	Occupancy	x	y	z	$U_{\text{eq}} (\text{\AA}^2)$
Te1	1a	1	0	0	0	0.026(1)
Te2	1d	1	1/2	1/2	1/2	0.026(1)
Ag1 / Sn1 / Sb1	1b	22 / 34 / 44	0	0	1/2	0.038(1)
Ag2 / Sn2 / Sb2	1c	44 / 33 / 23	1/2	1/2	0	0.037(1)

AgSnSbTe_3 : $a = 4.3650(5) \text{ \AA}$, $c = 6.1731(5) \text{ \AA}$, $P4/mmm$ space group.

Figure 3S. Graphical representation of the crystal structures of $\text{Ag}_{0.81}\text{Sn}_{1.08}\text{Sb}_{1.04}\text{Te}_3$ in the $Pm\bar{3}m$ and $P4/mmm$ space groups.

Thermal Conductivity and corresponding Thermoelectric Figure of Merit

Figure 4S. The total thermal conductivity data, κ_{tot} , of $\text{Ag}_{0.85}\text{SnSn}_{1.15}\text{Te}_3$.

We have extracted the electronic component of the thermal conductivity based on the Wiedemann-Franz law: $\kappa_{el} = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2 T \sigma$, where κ_{el} is the electronic contribution to the thermal conductivity. The two contributions of the thermal conductivity are plotted along with κ_{tot} (see Fig. 4S). It is readily seen that the lattice part of the thermal conductivity remains nearly constant above 100 K around 0.9 W/m·K. As expected, the electronic contribution increases with increasing temperature and at room temperature this accounts for 30% of the total. This is in agreement with the observed (see Figure 1(c)) increasing carrier concentration with increasing temperature.

The resulting dimensionless thermoelectric figure of merit, ZT , is depicted in Fig. 5S as a function of temperature. The room temperature ZT value compares well to other thermoelectric materials like PbTe ($ZT_{RT} \sim 0.3$) but still remains low presumably because of a low absolute thermopower. On the other hand, the steep monotonous increase of ZT with increasing temperature holds promise for further improvement.

Figure 5S. The dimensionless figure of merit of $\text{Ag}_{0.85}\text{SnSn}_{1.15}\text{Te}_3$.