Effect of Sn Substitution on the Thermoelectric Properties of Synthetic Tetrahedrite

Sahil Tippireddy,[†] D. S. Prem Kumar,[‡] Anirudha Karati,[§] Anbalagan Ramakrishnan,[⊥] Shreya Sarkar,^{#,▽} Sebastian C. Peter,^{#,▽} P. Malar,[‡] Kuei-Hsien Chen,[⊥] B. S. Murty,^{||} and Ramesh Chandra Mallik^{*,†,§}

[†]Thermoelectric Materials and Devices Laboratory, Department of Physics, Indian Institute of Science, Bangalore 560012, India

[‡]Research Institute, Department of Physics and Nanotechnology, SRM University, Kattankulathur 603203, India

[§]Department of Chemistry and ^{||}Department of Metallurgical and Materials Engineering, Indian Institute of Technology, Chennai 600036, India

[⊥]Institute of Atomic and Molecular Sciences, Academia Sinica, No. 1, Section 4, Roosevelt Road, Taipei 10617, Taiwan

[#]New Chemistry Unit and [▽]School of Advanced Materials, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India

Supporting Information

ABSTRACT: The present study reports the effect of Sn substitution on the structural and thermoelectric properties of synthetic tetrahedrite ($\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$) system. The samples were prepared with the intended compositions of $\text{Cu}_{12}\text{Sb}_{4-x}\text{Sn}_x\text{S}_{13}$ ($x = 0.25, 0.35, 0.5, 1$) and sintered using spark plasma sintering. A detailed structural characterization of the samples revealed tetrahedrite phase as the main phase with Sn substituting at both Cu and Sb sites instead of only Sb site. The theoretical calculations using density functional theory revealed that Sn at Cu(1) 12d or Cu(2) 12e site moves the Fermi level (E_F) toward the band gap, whereas Sn at Sb 8c site introduces hybridized hole states near E_F . Consequently, a relatively high optimum power factor of 1.3 mW/mK^2 was achieved by the $x = 0.35$ sample. The Sn-substituted samples exhibited a significant decrease in the total thermal conductivity (κ_T) compared to the pristine composition ($\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$), primarily because of reduced electronic thermal conductivity. Due to an optimum power factor (1.3 mW/mK^2) and reduced thermal conductivity (0.9 W/mK), a maximum zT of 0.96 at 673 K was achieved for $x = 0.35$ sample, which is nearly 40% increment compared to that of the pristine ($\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$) sample.

KEYWORDS: tetrahedrite, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), density functional theory (DFT), thermoelectric properties

1. INTRODUCTION

Thermoelectric generators (TEGs) are important candidates for providing reliable and sustainable source of energy. The primary advantage of using TEGs to convert heat energy to electrical energy is that they do not involve carbon emissions unlike conventional engines/generators that utilize fossil fuels. But the thermoelectric materials employed in these TEGs have limited conversion efficiency, which is dependent on a quantity called thermoelectric figure of merit (zT) given by

$$zT = \frac{S^2}{\rho\kappa_T} T \quad (1)$$

where S , ρ , κ_T , and T denote the Seebeck coefficient, electrical resistivity, total thermal conductivity (consisting of lattice κ_L and electronic κ_e components), and the absolute temperature, respectively. It can be seen from eq 1 that for a high zT , S should be large while ρ and κ_T should be kept low. But since S and ρ are interdependent on each other via charge carrier concentration n , increasing/decreasing one quantity will affect

the other. One way of achieving an optimum power factor (PF) (S^2/ρ) is to introduce a dopant(s)/substituent(s) in the system, which can optimize n and result in an optimum ratio of S^2/ρ . Simultaneously, κ_L can be reduced via phonon scattering induced by the dopant/substituent atom. Consequently, zT can be enhanced via doping or substitution methods. Conventional state-of-the-art materials such as PbTe ,^{1,2} Bi_2Te_3 ,³ and SnSe ^{4,5} have shown reasonably high zT at room temperature to mid-temperature range based on various doping/substitution schemes. But unfortunately, they contain toxic, costly, or rare elements, which may not be viable for large-scale commercial use. In this context, tetrahedrites ($\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$) have received a lot of interest due to its abundant, toxic-free constituents and a relatively high thermoelectric performance in the mid-temperature range (500–700 K).^{6,7}

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Tetrahedrites with nominal composition of $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ are p-type degenerate semiconductors possessing low electrical resistivity ($0.012 \text{ m}\Omega \text{ m}$ at 673 K ⁸) and moderate Seebeck coefficient ($134 \mu\text{V/K}$ at 673 K ⁸) due to high density of states (DOS) near Fermi level (E_F). It was found that introducing divalent/trivalent substituent at Cu^{1+} 12d tetrahedral site (such as transition metals) leads to hole compensation, resulting in optimization of the power factor and electronic thermal conductivity.^{6–8} A high zT of 1 was obtained at 720 K for the composition $\text{Cu}_{11}\text{Zn}_1\text{Sb}_4\text{S}_{13}$,⁶ and 0.98 for $\text{Cu}_{11.5}\text{Co}_{0.5}\text{Sb}_4\text{S}_{13}$ (at 673 K)⁸ among transition-metal substituted tetrahedrites. A similar approach was explored by substituting Te at the Sb site, leading to a maximum zT of 0.8 at 623 K in $\text{Cu}_{12}\text{Sb}_{4-x}\text{Te}_x\text{S}_{13}$.⁹ It was also observed that double substitution at Cu, Sb or Cu, S sites can be useful in having dual control of the thermoelectric properties. A maximum zT of 0.8 was obtained for the sample $\text{Cu}_{12-x}\text{Co}_x\text{Sb}_{4-y}\text{Te}_y\text{S}_{13}$ at 673 K with $x, y = 0.82, 0.41$.¹⁰ Among the $\text{Cu}_{12-x}\text{M}_x\text{Sb}_{4-y}\text{Te}_y\text{S}_{13}$ ($\text{M} = \text{Zn}, \text{Ni}$) compositions, the highest zT of 0.7 was shown by the composition $\text{Cu}_{11.5}\text{Ni}_{0.5}\text{Sb}_{3.25}\text{Te}_{0.75}\text{S}_{13}$ at 673 K .¹¹ Further, the effect of double substitution in tetrahedrite with a divalent substituent (Zn) at Cu site and isovalent substituent (Se) at S site was explored. It was found that the combined effect of Zn and Se double substitution in tetrahedrite resulted in simultaneous optimization of power factor and thermal conductivity. Consequently, a high zT of 0.86 was achieved for the $\text{Cu}_{11}\text{Zn}_1\text{Sb}_4\text{S}_{12.75}\text{Se}_{0.25}$ sample at 673 K .¹²

In a recent report, Sn-substituted tetrahedrite samples with formula $\text{Cu}_{12-x}\text{Sn}_x\text{Sb}_4\text{S}_{13}$ ($x = 0\text{--}0.6$) were prepared,¹³ where it was reported that Sn^{4+} at Cu site leads to hole compensation and optimization of the thermoelectric parameters. As a result, a maximum zT of 0.65 at 665 K was obtained for the compositions $x = 0.3\text{--}0.5$.¹³ Another recent study by Nasonova et al.¹⁴ involving high-resolution powder X-ray diffraction (XRD) and Mössbauer spectroscopy reported that Sn in $\text{Cu}_{12-x}\text{Sn}_x\text{Sb}_4\text{S}_{13}$ substitutes at Cu(1) 12d site and exhibits a +4 oxidation state.¹⁴ Previously, however, Hansen et al.¹⁵ performed a detailed study involving Sn substitution at Cu and Sb sites in tetrahedrite. It was reported that Sn can also exhibit a valence state of +2 and can be substituted at Sb site. Hence, there was further scope of studying Sn substitution in the tetrahedrite system. In the present study, our motivation, therefore, was to initially explore Sn substitution at Sb site and investigate its effect on the thermoelectric properties. But a detailed structural characterization using XRD, electron probe microanalysis (EPMA), X-ray photoelectron spectroscopy (XPS), and Mössbauer spectroscopy revealed that Sn might be substituting at both Cu(2) 12e and Sb 8c sites instead of only Sb 8c site. And thus, a kind of double substitution was observed in the substituted samples, which is explained based on characterization results, theoretical analysis, and transport property measurements.

2. EXPERIMENTAL SECTION

The starting elements: Cu, S, Sb ($\sim 5 \text{ N}$), and Sn ($\sim 4 \text{ N}$) were weighed together in stoichiometric ratio, transferred to quartz ampoules, and sealed under a dynamic vacuum of $\sim 10^{-4}$ mbar. The sealed ampoules were first heated to 973 K and soaked for 3 h. The furnace was then slowly cooled down to 823 K in 30 h. After reaching 823 K , the ampoules were cooled down to room temperature by switching off the furnace. The as-cast ingots were ground into fine powder using an agate mortar and pestle. The fine powders were then cold-pressed to form pellets and annealed in evacuated quartz tubes at 773 K for 48 h. The annealed pellets were again ground into a fine

powder and ball-milled using Fritsch Pulverisette P7 planetary mill at 300 rpm for 3 h. The milling was done in a toluene medium with a ball-to-powder mass ratio of 10:1. The ball-milled powders were then sintered using spark plasma sintering (SPS) at 753 K for 10 min under a pressure of 70 MPa. The SPS was carried out using Dr. Sinter SPS-625 system. The densities (d_s) of all of the Sn-substituted samples (obtained using Archimedes' principle) were found to be $\geq 98\%$ of the theoretical density. The sintered pellets were cut into $\sim 10 \times 2 \times 2 \text{ mm}^3$ cuboids for Seebeck coefficient and electrical resistivity measurements. For thermal diffusivity measurements, circular disks of $\sim 6 \text{ mm}$ diameter and $\sim 1 \text{ mm}$ thickness were cut from the same sintered pellets. The powder XRD of the samples was done on a Rigaku SmartLab X-ray diffractometer with $\text{Cu K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation as the X-ray source. The Rietveld refinement of the XRD patterns was performed using FullProf software¹⁶ to determine the crystal structure and phases, and evaluate the lattice parameters. A Jeol JXA-8530F electron probe microanalyzer equipped with a wavelength-dispersive spectroscope was used to perform the compositional analysis and obtain the microstructures. X-ray photoelectron spectroscopy (XPS) of the Sn-substituted samples was performed on a Prevac UHV XPS system with $\text{Al K}\alpha$ as the excitation source. The room-temperature transmission ^{119}Sn Mössbauer spectra of $\text{Cu}_{12}\text{Sb}_{4-x}\text{Sn}_x\text{S}_{13}$ ($x = 0.5$ and 1) were recorded with a Mössbauer spectrometer operating in a constant acceleration mode and equipped with $\text{Ca}^{119\text{m}}\text{SnO}_3$ (from Ritverc products) as the source of γ -rays. An amount of 10 mg of the sample was loaded in a sample holder and data collection was done over a period of 192 h. The Mössbauer data were acquired using WisoSoft CMCA-550 module in the Multichannel Scaling window. The obtained Mössbauer spectrum was fitted using Lorentzian line shapes with the WinNormos for IGOR Pro software package based on the least-squares method. All isomer shifts are referred to CaSnO_3 at 300 K . The electrical resistivity and Seebeck coefficients of the samples were measured using a Linsies LSR-3 system. The total thermal conductivity was obtained using the formula $\kappa_T = Dd_sC_p$, where D is the thermal diffusivity, d_s the sample density, and C_p the specific heat capacity. The thermal diffusivity was obtained using a Netzsch LFA 457 laser flash system and C_p was considered as 0.43 J/(g K) , which is the Dulong–Petit value of tetrahedrite. The measurement errors for electrical resistivity, Seebeck coefficient, and thermal conductivity are 10, 7, and 6%, respectively.

3. THEORETICAL CALCULATION DETAILS

The theoretical calculations using density functional theory (DFT) were done with the Quantum Espresso¹⁷ code using the generalized gradient approximation exchange–correlation functional given by Perdew, Burke, and Ernzerhof.¹⁸ An energy cutoff of 475 eV for plane-wave expansion was taken with a Monkhorst–Pack k -point grid of $7 \times 7 \times 7$. The crystal structure was considered as a body-centered cubic unit cell containing 58 atoms per unit cell with a lattice parameter of $10.33 \text{ \AA}$. The Sn atom was substituted at Cu(1) 12d site, Cu(2) 12e site, Sb 8c site, and also at both Cu(1)/Cu(2) and Sb sites. The atomic coordinates of the elements in the unit cell were relaxed in each case until the forces on the atoms were less than $0.01 \text{ eV/\AA}$. The projected density of states (PDOS) was evaluated for each case to understand the electronic structure in Sn-substituted tetrahedrite.

4. RESULTS AND DISCUSSION

4.1. X-ray Diffraction (XRD). Figure 1 displays the XRD patterns of all of the substituted samples indexed with ICDD PDF # 00-024-1318 tetrahedrite phase. The XRD patterns revealed that all of the samples have tetrahedrite phase as the major phase with secondary phase peaks corresponding to Cu_3SbS_4 in all of the samples, marked in Figure 1. For $x = 1.5$ sample, peaks corresponding to Cu_4SnS_4 secondary phase were

Figure 1. XRD patterns of the samples ($x = 0.25, 0.35, 0.5, 1, 1.5$) indexed with the tetrahedrite phase.

also found. The Rietveld refinement of the XRD patterns was performed to extract the phase information and determine the lattice parameters. Interestingly, the Rietveld analysis revealed that Sn could be substituted at many possible sites, i.e., Cu(1), Cu(2), Sb, or both Cu(1)/Cu(2) and Sb simultaneously. Tables S1 and S2 of the Supporting Information show the refinement parameters of the Rietveld analysis considering all possible sites for the samples $x = 0.25$ and 1 , respectively. It was observed that the refinement parameters converged almost similarly for each case, with a slightly better convergence for the case when Sn substitutes at both Cu 12d/12e and Sb 8c sites. For instance, the R_{Bragg} for the case when Sn is substituted at both Cu(2) 12e and Sb sites is lower by 36% compared to the case when Sn substitutes at only Cu(1) 12d, and lower by 31% when Sn substitutes at only Cu(2) 12e and by about 13% when Sn is substituted at only Sb site. This implies the possibility of Sn double substitution at both Cu(1)/Cu(2) and Sb sites. It was observed that among the Cu(1) 12d and Cu(2) 12e sites, the refinement converges better for Sn substitution at Cu(2) 12e site or both Cu(2) 12e and Sb sites. Figures S1–S5 of the Supporting Information display the refined XRD patterns for all of the samples considering Sn substitution at both Cu(2) 12e and Sb 8c sites. The refined XRD pattern for $x = 0.35$ sample is also shown in Figure 2 with the inset depicting

Figure 2. Refined XRD pattern for $x = 0.35$ sample. The inset shows the variation of lattice parameter with Sn content ($x = 0.25, 0.35, 0.5, 1, 1.5$) calculated considering Sn substitution at both Cu(2) 12e and Sb 8c sites.

the lattice parameter as a function of x (calculated using Rietveld analysis for the case when Sn substitutes at both Cu(2) 12e and Sb 8c sites), where the x values (Sn content) were taken from the EPMA results. The secondary phase quantified using Rietveld analysis is given in Supporting Information, which shows Cu_3SbS_4 vol % ranging from 6 to

12% in the substituted samples. The vol % of Cu_4SnS_4 in $x = 1.5$ sample was found to be around 15% from Rietveld analysis.

From Figure 2, it was observed that the lattice parameter increased with increase in Sn concentration. This indicates successful substitution of Sn in the tetrahedrite system, with Sn^{4+} (0.69 Å) and Sn^{2+} (1.18 Å), both having larger ionic radii than $\text{Cu}^{1+}/\text{Cu}^{2+}$ (0.6/0.57 Å) and Sb^{3+} (0.76 Å).^{15,19,20} But the trend of lattice parameter versus x is not linear, which could be due to the secondary phase(s) in the samples and/or defects due to Sn substitution. Another reason for the nonlinear lattice parameter could be the partial substitution of Sn at both Cu(2) and Sb sites, as shown by Rietveld analysis. It was observed by Hansen et al. that Sn^{4+} is incorporated at the Cu site in tetrahedrite when no other divalent transition metal is present in the system.¹⁵ But it was also reported that Sn^{2+} also has a high success rate in substituting at the Sb site.¹⁵ It can therefore be concluded that a kind of double substitution might be taking place in the samples with Sn existing in mixed valence states of +4 and +2 substituting at both Cu(2) and Sb sites, respectively. This was also confirmed by X-ray photoelectron spectroscopy (XPS) and Mössbauer spectroscopy discussed in Sections 4.3 and 4.5, respectively. However, previous studies have shown that $\text{Cu}_{12-x}\text{Sn}_x\text{Sb}_4\text{S}_{13}$ series did not show Sn substitution at Sb site based on Rietveld refinements.^{13,14} The reason for this discrepancy could be the inherent Sb deficiency in the present series because our intended compositions were $\text{Cu}_{12}\text{Sb}_{4-x}\text{Sn}_x\text{S}_{13}$ with Sb added in deficiency to accommodate Sn substitution at Sb site. In conclusion, the XRD analysis reveals successful substitution of Sn in tetrahedrite with the possibility of Sn substituting at both Cu(2) 12e and Sb sites.

4.2. Electron Probe Microanalysis (EPMA). The phases of all of the samples quantified using electron probe microanalysis (EPMA) are tabulated in Table 1, and the

Table 1. Nominal and Observed Compositions from EPMA for Primary and Secondary Phases

Se content (nominal)	observed EPMA composition for main phase ^a	observed EPMA composition for secondary phase ^b
$x = 0.25$	$\text{Cu}_{11.22}\text{Sb}_{3.89}\text{Sn}_{0.25}\text{S}_{13}$	$\text{Cu}_3\text{Sb}_{0.85}\text{Sn}_{0.15}\text{S}_4$
$x = 0.35$	$\text{Cu}_{11.21}\text{Sb}_{3.84}\text{Sn}_{0.30}\text{S}_{13}$	$\text{Cu}_3\text{Sb}_{0.75}\text{Sn}_{0.25}\text{S}_4$
$x = 0.5$	$\text{Cu}_{11.17}\text{Sb}_{3.85}\text{Sn}_{0.35}\text{S}_{13}$	$\text{Cu}_3\text{Sb}_{0.63}\text{Sn}_{0.47}\text{S}_4$
$x = 1$	$\text{Cu}_{11.01}\text{Sb}_{3.82}\text{Sn}_{0.44}\text{S}_{13}$	$\text{Cu}_3\text{Sb}_{0.1}\text{Sn}_{0.95}\text{S}_4$
$x = 1.5$	$\text{Cu}_{11.06}\text{Sb}_{3.91}\text{Sn}_{0.6}\text{S}_{13}$	$\text{Cu}_3\text{Sb}_{0.03}\text{Sn}_{0.97}\text{S}_4, \text{Cu}_4\text{SnS}_4$

^aNormalized to 13 atoms of S per formula unit of tetrahedrite ($\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$). ^bNormalized to four atoms of S per formula unit of $\text{Cu}_3\text{Sb}_{1-y}\text{Sn}_y\text{S}_4$.

microstructures are shown in Figure 3a–e. All of the samples showed deficient Sn content compared to the nominal composition, with a maximum solubility of ~ 0.6 atoms p.f.u. in the tetrahedrite phase. It was found from EPMA that all of the samples contained the secondary phase of off-stoichiometric Cu_3SbS_4 , with Sn substituting partially at the Sb site, which was also confirmed from Mössbauer spectroscopy (Section 4.5). It was also found that Cu and Sb concentrations are deficient in the main phase of all of the samples, which might indicate Sn substitution at both Cu and Sb sites. It was observed that this Sb deficiency was nearly the same in all of the samples (up to $x = 1$), whereas Cu deficiency increased with increase in x . This could indicate that Sn concentration at Sb in all of the samples is similar (up to $x = 1$), but it might

Figure 3. Backscattered electron (BSE) images of (a) $x = 0.25$, (b) $x = 0.35$, (c) $x = 0.5$, (d) $x = 1$, and (e) $x = 1.5$.

have higher preference for substituting at Cu site compared to Sb site for higher concentrations of Sn. For $x = 1.5$, it was found that Sb content is almost approaching the nominal value but Cu is relatively more deficient, indicating that Sn might have substituted primarily at Cu site. This substitution behavior can be understood based on the study by Hansen et al.,¹⁵ where it was observed that solubility of Sn in tetrahedrite is higher when substituting for metal (Cu) rather than the semimetal (Sb) site. It was found that Sn at the Sb site has a higher success rate only when other divalent/trivalent atoms such as Zn/Fe were also present at the Cu site. But in the absence of such divalent/trivalent substituents, Sn can be easily incorporated at the Cu site. This is because the tetrahedrite phase is vastly stabilized when two divalent metal atoms per formula unit are added.¹⁵ Therefore, in the absence of these substituents, Sn is preferentially substituted at the Cu site, rather than Sb, which was also observed in the present study. It should be mentioned here that due to the large amount of secondary phase(s) in $x = 1.5$ sample, further characterization data and discussion has been excluded from subsequent sections in the manuscript.

4.3. X-ray Photoelectron Spectroscopy (XPS). The X-ray photoelectron spectroscopy (XPS) of the $x = 0.25$ and 1

samples (Figure 4a,b, respectively) was performed to determine the valence state of the Sn atoms in the substituted

Figure 4. XPS images of the Sn $3d_{5/2}$ lines in (a) $x = 0.25$ and (b) $x = 1$ samples.

samples. The XPS images were calibrated using the C 1s peak at a binding energy (BE) of 284.8 eV referenced from the NIST database. The individual peak assignment corresponding to Sn oxidation states with binding energy is given in Table S4. It can be seen from Figure 4a,b that peaks corresponding to both +4 and +2 oxidation states of Sn are present in the spectra. It was observed that XPS peak corresponding to Sn +4

Figure 5. Projected density of states (PDOS) when Sn is substituted at (a) Cu(1) 12d in $\text{Cu}_{11}\text{Sn}_1\text{Sb}_4\text{S}_{13}$, (b) Cu(2) 12e in $\text{Cu}_{11}\text{Sn}_1\text{Sb}_4\text{S}_{13}$, (c) Sb 8c in $\text{Cu}_{12}\text{Sb}_3\text{Sn}_1\text{S}_{13}$, (d) both Cu(2) 12e and Sb 8c in $\text{Cu}_{11.5}\text{Sn}_{0.5}\text{Sb}_{3.5}\text{Sn}_{0.5}\text{S}_{13}$, and (e) both Cu(1) 12d and Sb 8c in $\text{Cu}_{11.5}\text{Sn}_{0.5}\text{Sb}_{3.5}\text{Sn}_{0.5}\text{S}_{13}$. Sn1 and Sn2 denote Sn atom at Cu(1) 12d/Cu(2) 12e and Sb 8c sites, respectively.

was higher in intensity compared to the Sn +2 XPS peak, indicating that Sn in the tetrahedrite system exists more in the +4 oxidation state. As indicated by the XRD, EPMA, and DFT (Section 4.4) results, Sn at the Cu(2) 12e site should exhibit +4 oxidation state, whereas Sn at the Sb 8c site should be in +2 oxidation state. Therefore, in conclusion, the existence of both Sn +4 and +2 oxidation states suggests that Sn might be substituting at both Cu(2) 12e and Sb 8c sites, with a higher preference for Cu(2) 12e site (since Sn +4 XPS intensity is higher), which was also confirmed from Mössbauer spectroscopy (Section 4.5) results.

4.4. Theoretical Calculations. To have a qualitative understanding of the electronic structure in Sn-substituted tetrahedrite, DFT calculations were performed for the compositions $\text{Cu}_{11}\text{Sn}_1\text{Sb}_4\text{S}_{13}$ (Sn at either 12d site or 12e site), $\text{Cu}_{12}\text{Sb}_3\text{Sn}_1\text{S}_{13}$ (only Sb 8c site), and $\text{Cu}_{11.5}\text{Sn}_{0.5}\text{Sb}_{3.5}\text{Sn}_{0.5}\text{S}_{13}$ (both Cu 12d/12e and Sb 8c sites). Figure 5a–e shows the PDOS of the substituted tetrahedrite systems with Sn at the aforementioned Wyckoff positions. It was observed that Sn at either Cu 12d or 12e site (Figure 5a,b, respectively) moves the Fermi level toward the band gap with

negligible states near E_F . This is consistent with the picture of Sn^{4+} substitution at $\text{Cu}^{1+}/\text{Cu}^{2+}$ resulting in effective compensation of holes. On the other hand, Sn at Sb site (Figure 5c) creates hybridized hole states near E_F that could indicate Sn^{2+} substitution at Sb^{3+} site, which will supply holes to the system. In the case of double-substituted composition $\text{Cu}_{11.5}\text{Sn}_{0.5}\text{Sb}_{3.5}\text{Sn}_{0.5}\text{S}_{13}$ (Figure 5d,e), it was observed that a combined effect takes place with E_F moving toward band gap as well as creation of hole states near E_F . Consequently, there is a trade-off between the two effects that will ultimately determine the transport properties. In the present series, the XRD, EPMA, and Mössbauer spectroscopy (Section 4.5) results revealed that Sn may possibly be substituting at both Cu(2) 12e and Sb sites with a higher preference for Cu(2) 12e site. The reason for this higher preference could be the fact that Sn^{4+} at the Cu site has a filled $4d^{10}$ orbital, which is relatively more stable, compared to Sn^{2+} at Sb site, which has a valence electronic configuration of $4d^{10}5s^2$. Because of the Sn double substitution, it is expected that the effective charge carrier compensation in the present series will be relatively more subtle compared to the scenario when Sn was

substituting at only Cu site. This is indeed reflected in the transport properties as explained in subsequent sections.

4.5. Mössbauer Spectroscopy. ^{119}Sn Mössbauer spectra were recorded for $x = 0.5$ and 1 compounds. According to Rietveld refinement, although there was a considerable amount of secondary phase in both samples, they were chosen for Mössbauer measurements to obtain high-intensity and good-quality data (since Sn content is relatively high in these samples). The main aim was to find the oxidation state of Sn, understand the site of Sn substitution in the major phase, and verify the presence of Sn in the impurity phase. The Mössbauer spectra of the compounds $\text{Cu}_{11.17}\text{Sb}_{3.85}\text{Sn}_{0.35}\text{S}_{13}$ and $\text{Cu}_{11.01}\text{Sb}_{3.82}\text{Sn}_{0.44}\text{S}_{13}$ are shown in Figure 6, and the hyperfine

Figure 6. ^{119}Sn Mössbauer spectrum of (a) $\text{Cu}_{11.17}\text{Sb}_{3.85}\text{Sn}_{0.35}\text{S}_{13}$ ($x = 0.5$) and (b) $\text{Cu}_{11.01}\text{Sb}_{3.82}\text{Sn}_{0.44}\text{S}_{13}$ ($x = 1$) measured at room temperature.

parameters are tabulated in Table 2. The main component in both the Mössbauer spectra reflects tin in $x = 0.5$ and 1 samples. The isomer shift, $\delta = 0.55\text{--}0.58$ mm/s, corresponding to the main component refers to +4 oxidation state of Sn. The quadrupole splitting is high, $\Delta E_Q = 0.98\text{--}1$ mm/s, reflecting low symmetry of Sn(IV) coordination. This could indicate Sn^{4+} to substitute at the Cu(2) 12e site, which feels an anharmonic potential due to the lone pair of Sb atoms situated on top and bottom of the trigonal plane. As a result, there is asymmetrical charge distribution around Sn at the Cu(2) 12e site leading to a high quadrupole splitting. Apart from the main component corresponding to Sn^{4+} , the presence of Sn^{2+} is also evident in both the samples. The values of the hyperfine

parameters are $\delta = 1.3\text{--}1.4$ mm/s and $\Delta E_Q = 0.02\text{--}0.04$ mm/s. The low quadrupole splitting values commensurate relatively higher-symmetry coordination environment around Sn and validate the assumption that Sn^{2+} substitutes at the Sb site, which occupies the 8c Wyckoff position. Hence, the Mössbauer spectra confirm Sn to substitute at two different crystallographic sites (Cu(2) 12e and Sb 8c) exhibiting two different oxidation states (+4 and +2, respectively), consistent with XRD, EPMA, and XPS. It was also found that among the two Cu sites (12d and 12e), Sn may have a higher preference for Cu(2) 12e site when there is a double-substitution scenario in the tetrahedrite system. We hypothesize a possible reason for this higher preference of Sn^{4+} to substitute at the Cu(2) 12e site in the following way: As explained in Section 4.2, the tetrahedrite system has been observed to be stable with compositions having a filled valence band. The DFT calculations (Section 4.4) revealed that Sn at Sb 8c site introduces hole states, whereas Sn at Cu 12d/12e compensates these hole states. It was observed that Sn substituting at both Cu(2) 12e and Sb 8c (Figure 5d) leads to more effective hole compensation (and hence a more filled valence band) compared to Sn substituting at Cu(1) 12d and Sb 8c (Figure 5e). Therefore, Sn in doubly substituted tetrahedrite occupies Cu(2) 12e and Sb 8c with +4 and +2 oxidation states, respectively.

In addition to the above-mentioned components, the Mössbauer spectra of both $\text{Cu}_{11.17}\text{Sb}_{3.85}\text{Sn}_{0.35}\text{S}_{13}$ and $\text{Cu}_{11.01}\text{Sb}_{3.82}\text{Sn}_{0.44}\text{S}_{13}$ also contain a second component with $\delta = 0.62\text{--}0.63$ mm/s and $\Delta E_Q = -(1.5\text{--}1.6)$ mm/s. The values of hyperfine parameters well correspond to Sn^{4+} , and the higher quadrupole splitting value compared to the main component indicates more distorted Sn in this second component. As evident from Rietveld refinement, this second component corresponds to an impurity phase of $\text{Cu}_3\text{Sb}_{0.63}\text{Sn}_{0.47}\text{S}_4$ and $\text{Cu}_3\text{Sb}_{0.1}\text{Sn}_{0.95}\text{S}_4$ in $\text{Cu}_{11.17}\text{Sb}_{3.85}\text{Sn}_{0.35}\text{S}_{13}$ and $\text{Cu}_{11.01}\text{Sb}_{3.82}\text{Sn}_{0.44}\text{S}_{13}$, respectively. The relative percentages of these two impurity phases were found to be 10.57 and 11.94%, respectively, which is well validated by Rietveld refinement.

4.6. Transport Properties. **4.6.1. Electrical Resistivity (ρ).** The electrical resistivities (ρ) of the Sn-substituted samples ($x = 0.25, 0.35, 0.5$, and 1) as a function of temperature are shown in Figure 7. The transport properties of $x = 1.5$ samples are not shown due to a significant amount of secondary phases and inferior thermoelectric properties. It was observed that the electrical resistivity increased with increasing temperature, indicating degenerate semiconductor behavior. It was found that the substituted samples exhibited higher ρ values across the measured temperature range compared to that of $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$,⁸ indicating effective compensation of holes in

Table 2. Values of the Mössbauer Hyperfine Parameters^a

x	phase	δ (mm/s)	ΔE_Q (mm/s)	W (mm/s)	RA (%)	assignment
0.5	$\text{Cu}_{11.17}\text{Sb}_{3.85}\text{Sn}_{0.35}\text{S}_{13}$	0.571	0.9835	1.0694	63.97	Sn^{4+}
		1.405	0.0408	0.9945	25.4	Sn^{2+}
	$\text{Cu}_3\text{Sb}_{0.63}\text{Sn}_{0.47}\text{S}_4$	0.630	-1.642	0.9613	10.57	Sn^{4+}
1	$\text{Cu}_{11.01}\text{Sb}_{3.82}\text{Sn}_{0.44}\text{S}_{13}$	0.569	1.001	1.0869	61.9	Sn^{4+}
		1.388	0.0206	0.9761	26.07	Sn^{2+}
	$\text{Cu}_3\text{Sb}_{0.1}\text{Sn}_{0.95}\text{S}_4$	0.621	-1.583	0.8764	11.94	Sn^{4+}

^aDerived from the fitting of the recorded room-temperature ^{119}Sn Mössbauer spectrum of the $\text{Cu}_{12}\text{Sb}_{4-x}\text{Sn}_x\text{S}_{13}$ ($x = 0.5, 1$), where δ is the isomer shift, ΔE_Q is the quadrupole splitting, W is the full width at half-maximum, and RA is the relative spectral area of individual spectral components.

Figure 7. Electrical resistivity as a function of temperature for the samples $x = 0.25, 0.35, 0.5$, and 1 .

the Sn-substituted samples because of Sn^{4+} substitution at $\text{Cu}(1)^{1+}$ 12e site. It was observed that ρ increased slightly with increasing x , but the increase is quite subtle, which could be due to Sn double substitution at both $\text{Cu}(2)$ 12e and Sb 8c sites. Since Sn at Sb site may possess +2 oxidation state (as verified by XPS, DFT, and Mössbauer spectroscopy), it could supply holes to the system, and the combined effect may increase ρ slightly, as elaborated in the theoretical Section 4.4. Another factor that can increase ρ in $x = 1$ sample is the enhanced charge carrier scattering from the interfaces of the secondary phase, leading to decrease in the charge carrier mobility and hence increase in ρ . To determine the charge carrier concentration and verify the above analysis, Hall measurements were performed for the samples. But unfortunately, a very low and inconsistent Hall voltage was observed in the samples, leading to inconclusive results.

4.6.2. Seebeck Coefficient (S). Figure 8 shows the Seebeck coefficient of the substituted samples ($x = 0.25, 0.35, 0.5$, and

Figure 8. Seebeck coefficient as a function of temperature for the samples $x = 0.25, 0.35, 0.5$, and 1 . The inset shows Seebeck coefficient as a function of Sn content at 673 K.

1) as a function of temperature. The positive Seebeck coefficient throughout the temperature range of all of the samples indicates holes as the majority charge carriers. Comparing the Seebeck coefficient of the substituted samples with that of $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$,⁸ the substituted samples exhibited higher S values due to effective hole compensation caused by Sn substitution. But the trend of S with x is not in accordance with the electrical resistivity results. The behavior of Seebeck coefficient in the substituted samples can be understood from Mott's formula given as

$$S = \frac{\pi^2}{3} k_B^2 T \left[\frac{1}{n} \frac{dn}{dE} + \frac{1}{\mu} \frac{d\mu}{dE} \right]_{E=E_F} \quad (2)$$

where k_B , n , μ , T , and E_F denote the Boltzmann constant, charge carrier concentration, charge carrier mobility, absolute temperature, and Fermi energy, respectively.

As can be seen from eq 2, the Seebeck coefficient depends on two factors: the first term has the factor $1/n$ and a decrease in charge carrier concentration (n) will increase the first term. But it also contains dn/dE , which is directly proportional to DOS near E_F , and an increase in DOS (near E_F) relates to an increase in dn/dE . It was observed from DFT calculations (Section 4.4) that Sn substituting at Cu compensates holes, resulting in an increase of the $1/n$ factor. The Fermi level moves toward the band gap, and the DOS near E_F decreases as seen in Figure 5a,b for Sn substituting at Cu, which should lead to a decrease in dn/dE . However, it was observed from Figure 5d,e that for Sn double substitution at Cu and Sb, a finite DOS near E_F can arise due to hybridized hole states that can retain the dn/dE term. And, it was established from the XRD and Mössbauer spectroscopy analysis that Sn may have substituted at both $\text{Cu}(2)$ 12e and Sb sites. Therefore, the weightage of the first term in eq 2 depends on the relative concentration of Sn substitution at $\text{Cu}(2)$ 12e and Sb sites. In the case of the second term (in eq 2), the $1/\mu$ factor should increase when charge carrier mobility (μ) is low. Another contributing factor to the second term in eq 2 is $d\mu/dE$, which signifies the mobility dependence on energy. In other words, $d\mu/dE$ is affected when a scattering mechanism depends strongly on the energy of the charge carriers and thus may show a slight variation with Sn substitution. Hence, the second term in eq 2 is a combined effect of the charge carrier mobility and its energy dependence in the substituted samples.

The Seebeck coefficient of the Sn-substituted samples is therefore a complex function of the above-mentioned parameters. Consequently, the Seebeck coefficient of the substituted samples is higher than that of $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ ⁸ because both the first and second terms of eq 2 are higher. The inset of Figure 7 shows a plot of Seebeck coefficient versus x at 673 K. It can be observed that the Seebeck coefficient (at 673 K) first rises, achieves a maximum value for $x = 0.35$, and then decreases for $x > 0.35$. Assuming that $d\mu/dE$ is similar in these samples, the variation of Seebeck coefficient with x should arise from the slight variation in charge carrier mobility (μ) and the difference in the relative weightages of the $1/n$ and dn/dE (DOS near E_F) factors of the first term in eq 2. In other words, if we consider the simplified Mott formula

$$S = \frac{8\pi^2 k_B^2 T}{3qh^2} m_d^* \left(\frac{\pi}{3n} \right)^{2/3} \quad (3)$$

where n is the charge carrier concentration and m_d^* is the DOS effective mass, the Seebeck coefficient scales as $1/n^{2/3}$, whereas it is directly proportional to m_d^* (which is proportional to DOS near E_F and in turn depends on the relative occupancy of Sn substitution at $\text{Cu}(2)$ 12e and Sb sites). Hence, the numerator (m_d^*) carries higher weightage in influencing the Seebeck coefficient compared to the denominator ($n^{2/3}$). For $x \geq 0.5$ samples, although the effective charge carrier concentration (denominator of eq 3) decreases, it is offset by the numerator (m_d^*), which also decreases as Sn substitutes more at the $\text{Cu}(2)$ 12e site (rather than Sb) compared to samples with $x < 0.5$, effectively resulting in a lower value of $m_d^*/n^{2/3}$ ratio and hence

lower Seebeck coefficient. The reason for Sn to prefer the Cu(2) site (at higher concentrations of x) can be inferred from the DFT results where it was explained that Sn^{4+} having a $4d^{10}$ valence electronic configuration is relatively more stable at the Cu(2) 12e site rather than Sn^{2+} having $4d^{10}5s^2$ configuration at Sb site. Moreover, as mentioned previously, the tetrahedrite system has been observed to be stable with compositions having a substituent that compensates holes and fills the valence band,¹⁵ such as Sn at Cu(2) 12e site in the present case. In addition, the effect of secondary phase should also be considered. It has been reported that the Seebeck coefficient of $\text{Cu}_3\text{Sb}_{1-y}\text{Sn}_y\text{S}_4$ (secondary phase in the present series) decreases with increasing Sn content.²¹ For $x = 0.5$ sample, there is relatively more Sn content (6 atom %) in a total of 10 vol % of $\text{Cu}_3\text{Sb}_{0.85}\text{Sn}_{0.15}\text{S}_4$ secondary phase, whereas for $x = 0.25$ and 0.35 , Sn content is around 1.8 and 3 atom % in a total of 6 and 7 vol % of secondary phase, respectively. Hence, for $x = 0.5$ sample, the Seebeck coefficient of the secondary phase may also play a role in affecting the overall Seebeck coefficient. This factor combined with the lower $m_d^*/n^{2/3}$ ratio leads to Seebeck coefficient values of $x = 0.5$ sample, intermediate to that of $x = 0.25$ and 0.35 . The same argument also applies for $x = 1$ sample. But for $x = 1$ sample, Sn substitutes at Cu(2) site even more (compared to $x < 1$ samples), and the $m_d^*/n^{2/3}$ ratio reduces even further. Combined with the fact that Sn content in the secondary phase is even higher (12 atom %), the overall Seebeck coefficient of $x = 1$ sample is lower than other samples. Another reason that can affect the variation of the S versus x trend could be differences in selective scattering of charge carriers due to differences in distribution and size of grain boundaries.

4.6.3. Power Factor (S^2/ρ). Figure 9 displays the power factor (PF) of all of the samples ($x = 0.25, 0.35, 0.5$, and 1) as

Figure 9. Power factor as a function of temperature for the samples $x = 0.25, 0.35, 0.5$, and 1 .

a function of temperature. Among the substituted samples, the maximum PF $\sim 1.3 \text{ mW/mK}^2$ at 673 K was shown by $x = 0.35$ sample due to relatively high Seebeck coefficient ($124\text{--}182 \mu\text{V/K}$) and low electrical resistivity ($0.021\text{--}0.026 \text{ m}\Omega \text{ m}$) across the measured temperature range. This PF value is comparable to or higher than values obtained in the literature^{6,7,10–12,22,23} for single substitutions (for instance, $\sim 1.2 \text{ mW/mK}^2$ for $\text{Cu}_{11.5}\text{Zn}_{0.5}\text{Sb}_4\text{S}_{13}$ ⁶ and $\text{Cu}_{11.5}\text{Mn}_{0.5}\text{Sb}_4\text{S}_{13}$ at 673 K,²³ $\sim 1.1 \text{ mW/mK}^2$ for $\text{Cu}_{11.75}\text{Pb}_{0.25}\text{Sb}_4\text{S}_{13}$ at 723 K²⁸) and double substitutions ($\sim 0.5 \text{ mW/mK}^2$ for $\text{Cu}_{11.5}\text{Ni}_{0.5}\text{Sb}_{3.25}\text{Te}_{0.75}\text{S}_{13}$ at 723 K¹¹ and $\sim 1 \text{ mW/mK}^2$ for $\text{Cu}_{11}\text{Zn}_1\text{Sb}_4\text{S}_{12.5}\text{Se}_{0.5}$ at 673 K¹²) in tetrahedrite, including the recently reported Sn-substituted series $\text{Cu}_{12-x}\text{Sn}_x\text{Sb}_4\text{S}_{13}$ ¹³

($\sim 1.1 \text{ mW/mK}^2$ at 665 K). On the other hand, the minimum PF was obtained for $x = 1$ sample due to relatively large electrical resistivity across the measured temperature range. It can be concluded that Sn double substitution in low concentrations ($x \leq 0.5$) at the two Wyckoff positions of Cu(2) 12e and Sb 8c sites in tetrahedrite can be beneficial for enhancement of the power factor. This is due to the fact that Sn^{4+} at Cu(2) 12e and Sn^{2+} at Sb sites effectively lead to only a slight increase in electrical resistivity with x but also retain a relatively moderate Seebeck coefficient. As a result, a reasonably high power factor could be achieved in $x \leq 0.5$ samples.

4.6.4. Thermal Conductivity (κ). Figure 10 shows the temperature-dependent total thermal conductivity (κ_T) of all of

Figure 10. Total thermal conductivity as a function of temperature for the samples $x = 0.25, 0.35, 0.5$, and 1 .

the samples ($x = 0.25, 0.35, 0.5$, and 1). The total thermal conductivity consists of electronic (κ_e) and lattice (κ_l) components. The electronic component of the thermal conductivity (κ_e) was evaluated from the Wiedemann–Franz relation given by

$$\kappa_e = \frac{LT}{\rho} \quad (4)$$

where L represents the temperature-dependent Lorenz number, T is the temperature, and ρ denotes the electrical resistivity. The Lorenz number L can be written as

$$L = \left(\frac{k_B}{e} \right)^2 \left(\frac{\left(r + \frac{7}{2} \right) F_{r+5/2}(\eta)}{\left(r + \frac{3}{2} \right) F_{r+1/2}(\eta)} - \left[\frac{\left(r + \frac{5}{2} \right) F_{r+3/2}(\eta)}{\left(r + \frac{3}{2} \right) F_{r+1/2}(\eta)} \right]^2 \right) \quad (5)$$

where $\eta = E_F/k_B T$ denotes the reduced Fermi energy and was calculated from Seebeck coefficient values via the equation

$$S = \pm \frac{k_B}{e} \left(\frac{\left(r + \frac{5}{2} \right) F_{r+3/2}(\eta)}{\left(r + \frac{3}{2} \right) F_{r+1/2}(\eta)} - \eta \right) \quad (6)$$

$F(\eta)$ denotes the reduced Fermi integral evaluated as

$$F_n(\eta) = \int_0^\infty \frac{x^n}{1 + e^{x-\eta}} dx \quad (7)$$

Considering that the major scattering mechanism in the samples is acoustic phonon scattering, r was considered as $-1/2$. From the known Seebeck coefficient values, η was deduced from eq 6. Finally, the temperature-dependent Lorenz number

(L) was evaluated at each temperature by substituting r and η in eq 5. The electronic thermal conductivity, κ_e was then obtained by substituting L in eq 4. The lattice thermal conductivity (κ_L) was calculated by subtracting κ_e from κ_T according to the equation $\kappa_T = \kappa_e + \kappa_L$. Figures 11 and 12 show the plots of κ_e and κ_L as a function of temperature, respectively.

Figure 11. Carrier thermal conductivity as a function of temperature for the samples $x = 0.25, 0.35, 0.5$, and 1 .

Figure 12. Lattice thermal conductivity as a function of temperature for the samples $x = 0.25, 0.35, 0.5$, and 1 .

The total thermal conductivity of the Sn-substituted samples was found to be lower than that of $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$.⁸ This is due to the effective charge carrier compensation (causing reduction in κ_e) and higher phonon scattering (because of Sn–Cu and Sn–Sb mass difference) in the substituted samples compared to $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$. It was found that κ_e decreased with increase in Sn content, due to effective compensation of holes in the Sn-substituted samples because of Sn^{4+} substitution at Cu(2) 12e site, as explained in the electrical resistivity Section 4.6.1. The decrease in κ_e with x thus follows inversely with the electrical resistivity trend according to eq 4. However, it was observed that the total thermal conductivity increased with x primarily due to increase in the lattice thermal conductivity of the substituted samples with x as seen from Figure 12. The intrinsically low values of lattice thermal conductivity in tetrahedrite arise due to the large anharmonic out-of-plane oscillations of the Cu(2) atoms, caused by the lone pair electrons on Sb situated on either side of the Cu(2) atoms. This results in a localized low-energy mode perpendicular to the CuS_3 triangle plane. Consequently, this localized mode scatters the high-velocity acoustic phonons (the main carriers of heat) and hybridizes with the acoustic dispersions leading to a reduction in thermal conductivity due to reduced group

velocities.²⁴ But it was shown by May et al.²⁵ that with a divalent substituent such as Zn in $\text{Cu}_{11}\text{Zn}_2\text{Sb}_4\text{S}_{13}$, the charge carrier concentration decreases (due to compensation of holes by Zn^{2+} at Cu^{1+} site), leading to suppression of electronic screening of the atomic displacements. As a result, the localized low-energy mode perpendicular to the CuS_3 plane stiffens and the structure is stabilized. Similarly, in the present case, the increase in κ_L with x could be due to the suppression of out-of-plane anharmonic vibration of the Cu(2) atoms because of Sn substitution at the Cu(2) 12e and Sb sites. As the Sn content (x) increases, this effect becomes more pronounced, thereby leading to increase in lattice thermal conductivity. Another factor could be a stronger covalent overlap of the Sn orbitals with the host atoms that can relatively mediate a higher phonon movement. A similar behavior was also observed in Zn and Se double-substituted samples, where a higher Se bond covalency resulted in an increase in the lattice component of thermal conductivity.¹² The other factors for a high κ_L in $x = 1$ sample could be the influence of secondary phase in the sample with a high Sn content ($\text{Cu}_3\text{Sb}_{0.1}\text{Sn}_{0.95}\text{S}_4$), which possesses a relatively higher thermal conductivity²¹ compared to the main tetrahedrite phase.

4.6.5. Thermoelectric Figure of Merit (zT). The dimensionless thermoelectric figure of merit of all of the substituted samples as a function of temperature is shown in Figure 13.

Figure 13. Thermoelectric figure of merit as a function of temperature for the samples $x = 0.25, 0.35, 0.5$, and 1 .

Although Sn substitution caused an increase in electrical resistivity and could not improve the power factor compared to $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ (1.45 mW/mK^2 at 673 K),⁸ a significant reduction of thermal conductivity was obtained in the present series. As a result, the maximum zT of 0.96 at 673 K was shown by the $x = 0.35$ sample primarily due to suppressed total thermal conductivity (0.88 W/mK at 673 K). This zT value is comparable to or higher than values in the literature^{6–12,26–28} for single substitutions (e.g., 0.7 for $\text{Cu}_{10.5}\text{Ni}_{1.5}\text{Sb}_4\text{S}_{13}$ at 665 K ⁷ and 0.8 at 623 K for $\text{Cu}_{12}\text{Sb}_{4-x}\text{Te}_x\text{S}_{13}$ ⁹) and double substitutions (0.8 obtained for $\text{Cu}_{11.18}\text{Co}_{0.82}\text{Sb}_{3.59}\text{Te}_{0.41}\text{S}_{13}$ at 673 K ¹⁰ and 0.7 for $\text{Cu}_{11.5}\text{Ni}_{0.5}\text{Sb}_{3.25}\text{Te}_{0.75}\text{S}_{13}$ at 673 K ¹¹) in tetrahedrite. The current zT value is also higher than that obtained for Sn-substituted $\text{Cu}_{12-x}\text{Sn}_x\text{Sb}_4\text{S}_{13}$ series investigated by Kosaka et al., where the highest zT of 0.65 was achieved at 665 K for $x = 0.3–0.5$.¹³ Therefore, it was noted that a significant enhancement of zT can be attained in tetrahedrite with small Sn concentrations ($x < 0.5$ per formula unit) doubly occupying the Cu(2) 12e and Sb sites.

4.6.6. Compatibility Factor (s). Apart from having a reasonably high zT , the compatibility factor of the material is

also important in determining the overall efficiency of a segmented thermoelectric device or generator. Since different materials exhibit maximum zT s at different operating temperatures, the efficiency of a practical device over a large temperature range can be maximized using segmented legs of different materials, which should have compatibility factor within a factor of 2. The compatibility factor (s) of the Sn-substituted samples ($x = 0.25, 0.35, 0.5$, and 1) as a function of

Figure 14. Compatibility factor as a function of temperature for the Sn-substituted samples ($x = 0.25, 0.35, 0.5$, and 1).

temperature is shown in Figure 14, calculated using the following equation²⁹

$$s = \frac{\sqrt{1 + zT} - 1}{ST} \quad (8)$$

where z is the thermoelectric figure of merit, S is the Seebeck coefficient, and T is the temperature. It was observed from Figure 13 that all of the samples exhibit an almost unchanged s with temperature, which is beneficial for a segmented assembly in a thermoelectric device. The $x = 0.35$ sample exhibiting the highest zT among the Sn-substituted samples has s values between 3.8 and 3.2 V^{-1} across the measured temperature range. These values are within a factor of 2 compared to other high-performing p-type materials such as $Yb_{14}MnSb_{12}$, TAGS, $CeFe_4Sb_{12}$,³⁰ and $PbTe_{0.7}S_{0.3}$.³¹ In conclusion, the near invariance of compatibility factor with temperature coupled with its similar magnitude compared to other materials makes Sn-substituted samples potential candidates for device applications.

5. CONCLUSIONS

In summary, a detailed investigation was performed in the present study to understand the effect of Sn substitution in tetrahedrite. It was found from a combined analysis of XRD, XPS, DFT, and Mössbauer spectroscopy that Sn exists in mixed valency of +4 and +2 and substituting at both Cu(2) 12e and Sb 8c sites. The DFT analysis revealed that Sn at Cu(2) 12e site compensates holes and moves the Fermi level toward the band gap, whereas Sn at Sb 8c site introduces hole states near E_F . Therefore, a trade-off between these two effects determined the overall transport properties. Based on characterization and electrical resistivity results, it was found that Sn has a higher preference for Cu(2) 12e site but also substituted at Sb site in small concentrations. Effectively, the charge carrier compensation increased with x only slightly leading to a slight increment in the electrical resistivity. But a relatively moderate DOS near E_F was retained, resulting in a

significant increase in the Seebeck coefficient in the substituted samples (compared to $Cu_{12}Sb_4S_{13}$). The thermal conductivity of the substituted samples could be reduced primarily due to reduced electronic thermal conductivity. As a result, a maximum zT of 0.96 at 673 K was achieved for $x = 0.35$ sample. It can be concluded that Sn has the interesting property of exhibiting dual oxidation states and therefore could substitute at two different Wyckoff positions in the crystal unit cell of tetrahedrite. As a result, a double-substitution scenario could be achieved using only one kind of substituent, which also facilitates cost-effectiveness in material preparation. Coupled with a favorable compatibility factor over the measured temperature range, the Sn-substituted samples ($x < 0.5$ p.f.u.) can be suitable for device applications. The present work also opens up the possibility of performing similar studies in other ternary chalcogenides with group 14 element substitution.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b02956.

Refinement parameters with Sn substituted at various Wyckoff positions for $x = 0.25$ and 1 samples (Tables S1 and S2); lattice parameter with Sn (x) content (Table S3); XPS peak assignment of Sn 3d_{5/2} in $x = 0.25$ and 1 samples (Table S4); refined XRD patterns of all of the Sn-substituted samples ($x = 0.25, 0.35, 0.5, 1, 1.5$) (Figures S1–S5) (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: rcmallik@iisc.ac.in.

ORCID

Ramesh Chandra Mallik: 0000-0002-8383-7812

Notes

The authors declare no competing financial interest.

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