# **Inorganic Chemistry**

## Synergistic Effect of Chemical Substitution and Insertion on the Thermoelectric Performance of Cu<sub>26</sub>V<sub>2</sub>Ge<sub>6</sub>S<sub>32</sub> Colusite

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interstitial Cu atoms act as phonon scatterers, thereby decreasing the lattice thermal conductivity. The combined effects increase the dimensionless thermoelectric figure of merit ZT from 0.3  $(Cu_{26}V_2Ge_6S_{32})$  to 0.8  $(Cu_{29}V_2Ge_5SbS_{32})$  at 673 K.

#### 1. INTRODUCTION

Renewable energy sources, which include sunlight, heat, and vibration, play a crucial role in realizing a sustainable society. One of the promising applications for harvesting heat to generate electricity is the thermoelectric (TE) generator, which is composed of solid-state elements.<sup>1-3</sup> The conversion from thermal to electrical energy in solids is based on the Seebeck effect. The electronic potential difference (electromotive force)  $\Delta V$  is generated in proportion to the temperature difference  $\Delta T$  ( $\Delta V = S \Delta T$ , where S is the Seebeck coefficient) between two ends of an element. The electromotive force is utilized to supply electricity to an electronic device. Therefore, highly efficient TE conversion requires an element material to have a large S. Other requisite characteristics of a TE material include low electrical resistivity  $\rho$  to reduce the internal resistance of the generator and low thermal conductivity  $\kappa$  to maintain sufficient  $\Delta T$ . By combining these parameters ( $\rho$ , S,  $\kappa$ ), the performance of a TE material can be determined using the expression:  $ZT = S^2 T \rho^{-1} \kappa^{-1}$ , where ZT is referred to as the dimensionless figure of merit, T is the absolute temperature, and  $\kappa$  is the sum of its electronic component  $\kappa_{\rm ele}$  and lattice component  $\kappa_{lat}$ . In addition to high performance (high ZT), natural abundance and nontoxic characteristics are desired for TE materials used in large-scale applications. Cu-S-based (degenerate) semiconductors have emerged as such TE materials in the recent decade,<sup>4,5</sup> for example,  $Cu_2ZnSn_{3,6}^{6}$  $CuFeS_{2,}^{7,8}$   $Cu_{1.8}S_{,}^{9}$   $Cu_{2}S_{,1}^{10}$   $Cu_{12}Sb_{4}S_{13,1}^{11-13}$   $Cu_{3}SbS_{4,1}^{14}$  $Cu_{5}FeS_{4,1}^{15-18}$   $Cu_{2}SnS_{3,1}^{19}$   $Cu_{4}Sn_{7}S_{16,2}^{20}$   $Cu_{8}Fe_{3}Sn_{2}S_{12,2}^{21}$ 

to a reduction in the electronic thermal conductivity while keeping

the thermoelectric power factor at a high value. Furthermore, the

CuFe<sub>2</sub>S<sub>31</sub><sup>22</sup> Cu<sub>22</sub>Fe<sub>8</sub>Ge<sub>4</sub>S<sub>32</sub><sup>23</sup> Cu<sub>3</sub>PS<sub>41</sub><sup>24</sup> and Cu<sub>26</sub>V<sub>2</sub>Ge<sub>6</sub>S<sub>32</sub><sup>25,26</sup> The last example is a synthetic member of the colusite family:  $Cu_{26}T_2M_6S_{32}$  (T = Ti, V, Nb, Ta, Cr, Mo, W; M = Ge, Sn, Sb).<sup>25-30</sup> Colusites have attracted increasing attention due to their high ZT value ranging from 0.5 to 1.0 at 673 K. $^{26-43}$ 

Chemical insertion + substitution

0.0

400 500 600

Temperature T / K

700

 $Cu_{26}T_2M_6S_{32}$  colusites crystallize in a cubic structure  $(P\overline{4}3n)$ , which is composed of three types of tetrahedral units: CuS<sub>4</sub>, TS<sub>4</sub>, and MS<sub>4</sub>.<sup>44,45</sup> The CuS<sub>4</sub> and MS<sub>4</sub> tetrahedra share corners to construct a three-dimensional framework structure, which is completed by the TS<sub>4</sub> tetrahedra sharing edges with  $CuS_4$  (Figure 1). The formal valence of the atoms can be represented as  $Cu_{26}^{+}T_2^{-4+}M_6^{-5+}S_{32}^{-2-}$  for T = Ti,  $Cu_{22}^{+}Cu_4^{-2+}T_2^{-5+}M_6^{-4+}S_{32}^{-2-}$  for T = V, Nb, and Ta, and  $Cu_{24}^{+}Cu_2^{-2+}T_2^{-6+}M_6^{-4+}S_{32}^{-2-}$  for T = Cr, Mo, and W, where  $M^{4+}$  and  $M^{5+}$  denote  $Ge^{4+}/Sn^{4+}$  and  $Sb^{5+}$ , respectively. The nonmagnetic and p-type degenerate semiconducting characteristics of the colusites with T = V, Cr, Mo, and W were confirmed by TE and magnetic susceptibility measurements,<sup>25</sup> Mössbauer spectroscopy,<sup>46</sup> and first-principles electronic-structure calculations.<sup>26,28,36</sup> These characteristics indicate the itinerant nature of the 3d holes of Cu<sup>2+,28,47</sup> The

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Figure 1. Crystal structure of  $Cu_{26}T_2M_6S_{32}$  (T = Ti, V, Nb, Ta, Cr, Mo, and W; M = Ge, Sn, and Sb) colusite.

calculations showed that the Fermi level ( $E_{\rm F}$ ) lies at the top of the valence band (VB), which primarily comprises the hybridized orbitals of Cu 3d and S 3p.<sup>26,28,36</sup> The nature of the VB indicates that the Cu–S-based tetrahedral framework governs the electronic properties. Depending on the compositions, a high power factor  $S^2 \rho^{-1}$  of 0.5–1.9 mW K<sup>-2</sup> m<sup>-1</sup> at 673 K can be achieved in colusites.<sup>26–43</sup> The tetrahedral framework also causes low  $\kappa_{\rm lat} \leq 1$  W K<sup>-1</sup> m<sup>-1</sup> due to its complexity and low-energy (~10 meV) optical phonon modes involving motions of Cu and S.<sup>28,29,36</sup> Further decrease in  $\kappa_{\rm lat}$ can be achieved by introducing various types of defects into the crystal structure: interstitial defects, antisite defects between cations, and split Cu sites.<sup>36,37,46</sup> These defects are simultaneously produced by an excessive amount of sulfur sublimation upon heating above 973 K.<sup>36,37</sup>

A good approach to introduce phonon scatterers (defects) into the colusite structure is by increasing the sintering temperature;<sup>36,37</sup> however, the difficulty in controlling sulfur loss prevents the fine-tuning of the hole carrier concentration *n*. Therefore, an alternative strategy to reduce  $\kappa_{\text{lat}}$  is required. Generally, substitutional doping of a heavier atom for a constituent atom results in a decrease in  $\kappa_{\text{lat}}$ .<sup>48</sup> Another possible way to reduce  $\kappa_{\text{lat}}$  in colusites is to introduce interstitial defects (atoms), according to the aforementioned results.<sup>37</sup> However, the peculiar effect of interstitial atoms on  $\kappa_{\text{lat}}$  has not been examined for colusites to date. Following these circumstances, this study aimed to clarify the effects of

substituting Sb for Ge and Cu insertion on  $\kappa_{lat}$  in the  $Cu_{26}V_2Ge_6S_{32}$  colusite. Hence, novel Sb-substituted  $(Cu_{26}V_2Ge_{6-x}Sb_xS_{32})$ , Cu-rich  $(Cu_{26+y}V_2Ge_6S_{32})$ , and combined Sb-substituted and Cu-rich  $(Cu_{26+y}V_2Ge_{6-x}Sb_xS_{32})$  with x = 1 series were synthesized and their TE properties were investigated. Notably, these samples were sintered at 823/873 K, which is mandatory for limiting the sublimation of sulfur.<sup>36,37,49</sup>

#### 2. EXPERIMENTAL SECTION

**2.1. Sample Synthesis.** The samples of  $Cu_{26}V_2Ge_{6-x}Sb_xS_{32}$  (x = 0-4),  $Cu_{26+y}V_2Ge_6S_{32}$  (y = 0-4), and  $Cu_{26+y}V_2Ge_{6-x}Sb_xS_{32}$  (x = 1, y = 0-3) were prepared by directly reacting the constituent elements at 1373 K, followed by heat treatment at 873 K, as reported for the samples of  $\text{Cu}_{26}\text{Nb}_2\text{Sn}_6\text{S}_{32}.^{37}$  The obtained samples were pulverized using a planetary ball mill (PULVERISETTE 7 premium line, FRITSCH) operating at room temperature at a disk rotation speed of 450 rpm for 1 h. The sample powder was put into a jar together with seven balls of 10 mm diameter in an Ar atmosphere. The jar and balls were made of tungsten carbide (WC). The pulverized sample was loaded into a WC die with an inner diameter of 10 mm. The sample was sintered at 823/873 K for 40 min in a flowing N2 atmosphere under a uniaxial pressure of 200 MPa in a hot-press sintering furnace (PLASMAN CSP-I-03121, S. S. Alloy). The relative density of the sample evaluated from its mass and dimensions was higher than 95% of the theoretical density (Table S1). The sintered sample was cut and polished into bars and disks to measure the TE properties.

2.2. Sample Characterization. Powder X-ray diffraction (PXRD) data were collected in the range of  $10^{\circ} \le 2\theta \le 100^{\circ}$ using an X-ray diffractometer (MiniFlex600, Rigaku) with a Cu K $\alpha$ radiation source. PXRD data were analyzed by Rietveld refinement using the FullProf and WinPLOTR software packages.<sup>50,51</sup> Zero-point shift, lattice parameter, peak shape parameters, asymmetry parameters, fractional atomic coordinates, and isotropic displacement parameters were refined after manually removing the background contribution. The density of the sample was checked by scanning electron microscopy (SEM) using a microscope (JCM-6000Plus NeoScope, JEOL). Atomic-resolution observations were performed using a transmission electron microscope (Titan Cubed G2 60-300, Thermo Fisher Scientific) equipped with a spherical aberration corrector (DCOR, CEOS) for the probe-forming lens system. The microscope was operated in the scanning transmission electron microscopy (STEM) mode at an accelerating voltage of 300 kV. The convergence semiangle of the electron probe was set to 18 mrad. The typical probe diameter was less than 0.1 nm. An annular dark-field (ADF) detector



**Figure 2.** (a) Powder X-ray diffraction patterns and (b) lattice parameters *a* for  $Cu_{26}V_2Ge_{6-x}Sb_xS_{32}$ ,  $Cu_{26+y}V_2Ge_6S_{32}$ , and  $Cu_{26+y}V_2Ge_{6-x}Sb_xS_{32}$  with x = 1 samples. In (a), the diffraction patterns for x = y = 0, x = 2, y = 0, and x = 0, y = 3 and the simulated pattern based on the colusite  $(Cu_{26}V_2Ge_6S_{32})$  structure are shown. Arrows for x = y = 0 and x = 0, y = 3 denote peaks from  $Cu_2S$ . The diffraction patterns for all samples are presented in Figures S2–S4.



**Figure 3.** Annular dark-field scanning transmission electron microscopy (ADF STEM) images for (a)  $Cu_{26}V_2Ge_6S_{32}$  (b)  $Cu_{26}V_2Ge_{6-x}Sb_xS_{32}$  (x = 2), and (c)  $Cu_{26+y}V_2Ge_6S_{32}$  (y = 3) samples along the [110] direction. Expanded views of the STEM images and the corresponding views of the colusite structure are also shown. The bright spots in the ADF STEM images show atomic columns. Along this direction, there are four types of columns labeled "4Cu", "1V", "3Cu + M"/"3Cu + Ge", and "4S" (see text). Here, the numeral denotes the number of atoms periodically contained in the columns, and M means "(4Ge + 2Sb)/6". Logarithmic intensities (levels of brightness) of columns along "lines" denoted by 1–5 in the expanded views are plotted in the graphs. The dashed lines in the graphs are eye guides for making peaks/humps clear. For (c)  $Cu_{26+y}V_2Ge_6S_{32}$  (y = 3), the intensity along a line composed of the "3Cu + 1Ge" and "4S" columns shows a hump at an interstitial position. Such a hump was hardly noticed for (a)  $Cu_{26}V_2Ge_6S_{32}$  and (b)  $Cu_{26}V_2Ge_{6-x}Sb_xS_{32}$  (x = 2).

was positioned to detect scattered electrons with an angular range from 38 to 184 mrad. Each sintered bulk sample was crushed and dispersed in ethanol under an Ar atmosphere to avoid oxidation. Thereafter, it was dropped on a carbon-supporting film and was immediately inserted in the electron microscope.

**2.3. Electrical and Thermal Property Measurements.** S and  $\rho$ were simultaneously measured at T between 300 and 673 K in a measurement system (ZEM-3, ADVANCE RIKO) in a helium atmosphere. Thermal diffusivity  $\alpha$  and specific heat  $C_P$  at 300–673 K were measured simultaneously in a measurement system (LFA 457 MicroFlash, NETZSCH) using the laser-flash method in a flowing Ar atmosphere. In this study, the sample was coated with a thin layer of graphite. The absolute values of  $C_p$  were derived from the comparison between the measured values and  $C_p$  values measured for a standard sample (Pyroceram 9606, NETZSCH) (Figure S1). These data were used to calculate  $\kappa$  as  $\alpha C_p d_s$ , where  $d_s$  represented the sample density estimated from the dimensions and weight of the sample. Note that the obtained  $C_p$  values reasonably agreed among samples, which is comparable to the Dulong–Petit value at 300 K and higher by ≤16% at 673 K (Figure S1). The Hall effect measurements were performed using a four-probe DC method on a laboratory-built system, with a

permanent magnet generating a magnetic field of 0.62 T at 300 K. We calculated *n* as  $R_{\rm H}^{-1}e^{-1}$  and Hall mobility  $\mu_{\rm H}$  as  $R_{\rm H}\rho^{-1}$  based on the single-carrier model, where  $R_{\rm H}$  is the Hall coefficient and *e* is the elementary charge.

#### 3. RESULTS AND DISCUSSION

The PXRD patterns of the samples in different series of compositions, *i.e.*,  $Cu_{26}V_2Ge_{6-x}Sb_xS_{32}$  (x = 0-4),  $Cu_{26+y}V_2Ge_6S_{32}$  (y = 0-4), and  $Cu_{26+y}V_2Ge_{6-x}Sb_xS_{32}$  (x = 1, y = 0-3) are presented in Figures 2a and S2–S4. For all samples, the positions and relative intensities of the diffraction peaks reasonably agree with those of a simulated pattern based on the colusite structure ( $Cu_{26}V_2Ge_6S_{32}$ ,  $P\overline{43}n$ ). Note that the systematic presence of weak-intensity diffraction peaks (at 26.4 and 43.7° for x = 0) originated from Cu K $\beta$  radiation passing through a Ni filter. The diffraction patterns for x = y = 0 (pristine sample) and  $y \ge 1$  (Cu-rich samples) exhibited small peaks from a secondary phase  $Cu_2S$ , and that for x = 4 (Sb-substituted sample) showed a small peak from an unidentified

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**Figure 4.** (a) Seebeck coefficient *S*, (b) electrical resistivity  $\rho$ , (c) power factor  $S^2 \rho^{-1}$ , (d) thermal conductivity  $\kappa$ , and (e) dimensionless figure of merit *ZT* for Cu<sub>26</sub>V<sub>2</sub>Ge<sub>6-x</sub>Sb<sub>x</sub>S<sub>32</sub> samples.

phase (Figures S2–S4). For the Cu-rich series, the peak width became broader as y increased (Figures S3 and S4).

Rietveld refinement of the PXRD patterns of the Sbsubstituted series (Cu<sub>26</sub>V<sub>2</sub>Ge<sub>6-x</sub>Sb<sub>x</sub>S<sub>32</sub>) (Figures S5-S9 and Table S2), leading to low-reliability factors, confirmed the validity of the structural model of colusites, which includes seven crystallographic sites: three for Cu (6d, 8e, 12f), one for V (2a), one for Ge/Sb (6c), and two for S (8e, 24i). The lattice parameter *a* linearly increased from 10.5684(2) Å for *x* = 0 by 1.2% as x increased to 4, as shown in Figure 2b and Table S2. The lattice expansion can be attributed to the larger ionic radius of Sb<sup>5+</sup>  $(0.565 \text{ Å})^{52}$  than that of Ge<sup>4+</sup>  $(0.390 \text{ Å})^{53}$ In fact, the occupation factor of Sb at the Ge (6c) site obtained from Rietveld refinement increased with x and reached 62% (*i.e.*,  $Cu_{26}V_2Ge_{2.3}Sb_{3.7}S_{32}$ ) for x = 4 (Table S2). The increase in the Sb content was also clearly observed from the evolution of h + k + l = 2n + 1 peaks (e.g., 210, 320; see Figures 2a and S2).<sup>29</sup> It was further confirmed that this substitution increases the M(6c)–S(24i) (M = Ge, Sb) distance from 2.254 Å for x =0 to 2.383 Å for x = 4 while keeping the average Cu-S distance intact (2.291–2.300 Å) (Table S2). This indicates the limited modification of the Cu-S-based tetrahedral framework. It should be noted that the presence of Sb<sup>5+</sup> in the tetrahedral coordination of sulfides was only reported for famatinite Cu<sub>3</sub>SbS<sub>4</sub><sup>54</sup> and the colusite sister compound Cu<sub>26</sub>Ti<sub>2</sub>Sb<sub>6</sub>S<sub>32</sub>.<sup>29</sup>

For the Cu-rich series  $(Cu_{26+y}V_2Ge_6S_{32})$  and  $Cu_{26+y}V_2Ge_{6-x}Sb_xS_{32}$  with x = 1, Rietveld refinement of the PXRD patterns confirmed a lattice expansion attributed to Cu insertion (Figure 2b). More specifically, *a* increased slightly for y = 1 and increased by 0.44 and 0.47% for y = 3 in  $Cu_{26+y}V_2Ge_6S_{32}$  and  $Cu_{26+y}V_2Ge_{6-x}Sb_xS_{32}$  with x = 1,

respectively. Saturation of the *a* value for y = 4 (Cu<sub>30</sub>V<sub>2</sub>Ge<sub>6</sub>S<sub>32</sub>) suggests a lower (actual) Cu content, which is consistent with the increase in the amount of the Cu-rich secondary phase (Cu<sub>2</sub>S) for y = 4 (wt % of Cu<sub>2</sub>S for Cu<sub>26+y</sub>V<sub>2</sub>Ge<sub>6</sub>S<sub>32</sub> samples: y = 0, ~1%; 1–3, ~2–3%; 4, ~7%) and reflects a limit of Cu insertion into the VGe-colusite structure. A possible mechanism of the lattice expansion for the Cu-rich series deals with the introduction of Cu atoms into interstitial sites, as previously reported for the Cu<sub>26</sub>Nb<sub>2</sub>Sn<sub>6</sub>S<sub>32–δ</sub> colusite.<sup>37</sup> The fact that Cu insertion leads to electron doping (decrease in *n*), as shown below, strongly supports this mechanism.

To confirm the existence of interstitial Cu ions, STEM analysis was performed for pristine, Sb-substituted, and Curich samples, as shown in Figures 3 and S10-S13. The ADF STEM images for  $Cu_{26}V_2Ge_6S_{32}$ ,  $Cu_{26}V_2Ge_{6-x}Sb_xS_{32}$  with x =2, and  $Cu_{26+y}V_2Ge_6S_{32}$  with y = 3 showed well-aligned atom columns with intensities (levels of brightness in the image) that are mostly consistent with those expected from the pristine colusite  $(Cu_{26}V_2Ge_6S_{32})$  structure. Along the [110] direction (Figure 3), there were four types of columns: pure copper columns labeled "4Cu", pure vanadium columns labeled "1V", pure sulfur columns labeled "4S", and mixed columns containing, besides copper, either mixtures of Ge and Sb labeled "3Cu + 1M" or only Ge labeled as "3Cu + 1Ge". Here, the numeral denotes the number of atoms periodically contained in the columns and M means "(4Ge + 2Sb)/6". Bearing in mind that the intensity of the spots corresponding to the columns is approximately proportional to the square of the atomic number  $\overline{Z}$  (29 for Cu, 32 for Ge, 51 for Sb, 23 for V, and 16 for S), one can expect a decrease in their relative intensity from "3Cu + 1M" to "3Cu + 1Ge" to "4Cu" to "4S"

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**Figure 5.** (a) Seebeck coefficient *S*, (b) electrical resistivity  $\rho$ , (c) power factor  $S^2 \rho^{-1}$ , (d) thermal conductivity  $\kappa$ , and (e) dimensionless figure of merit *ZT* for Cu<sub>26+y</sub>V<sub>2</sub>Ge<sub>6</sub>S<sub>32</sub> samples.

to "1V" columns and that the intensities of the "3Cu + 1Ge" and "4Cu" columns are comparable. As a result, the "3Cu + 1M"/"3Cu + 1Ge", "4Cu", and "4S" columns are clearly identified in the STEM images. As shown in the line profiles of the intensity (Figure 3), the relative intensities of the "3Cu + 1M" column were higher than those of the "3Cu + 1Ge" column, which is consistent with the substitution of Sb for Ge determined from PXRD analyses. The line profile also allows us to see the "1V" columns, whose position agrees with that of the colusite structure.

Remarkably, for the Cu-rich sample  $(Cu_{26+v}V_2Ge_6S_{32})$  with y = 3), the logarithmic intensity along the line composed of "3Cu + 1Ge" and "4S" columns showed a hump at an interstitial position for the colusite structure (Figure 3c). Such a hump was hardly noticed in the pristine and Sb-substituted samples,  $Cu_{26}V_2Ge_6S_{32}$  and  $Cu_{26}V_2Ge_{6-x}Sb_xS_{32}$  with x = 2(Figure 3a,b). These results strongly indicate the existence of atoms at interstitial sites in the Cu-rich sample. This position may be consistent with the presence of Cu at an interstitial 24i site (0.255, 0.215, 0.032), as determined by the powder synchrotron X-ray diffraction for Cu<sub>26</sub>Nb<sub>2</sub>Sn<sub>6</sub>S<sub>32-δ</sub>.<sup>37</sup> However, signals from interstitial atoms were observed at a part of the "columns" of the interstitial sites. This suggests a nonuniform arrangement (or aggregation) of interstitial atoms, which might result in the broadening of diffraction peaks (Figures 2a and S3). Signals from interstitial ions in the STEM images along the [100] and [111] directions (Figures S10-S13) could not be extracted. These results reflect a preferential direction, [110], for the aggregation of interstitial atoms and/or might be due to a very weak contribution to the intensity from the interstitial atoms compared with the other ones.

The existence of interstitial atoms was further confirmed by Rietveld refinement of the PXRD pattern for  $Cu_{26+y}V_2Ge_6S_{32}$ with y = 3 (Figure S14). Refinement based on the colusite structure showed a residual electron density at an interstitial 24i site (0.236, 0.235, 0.007). Thereafter, refinement based on a colusite structure with interstitial Cu atoms at the 24i site (atomic coordinates being fixed) was performed, which significantly improved the reliability factors (Table S3). The refined occupation factor at the 24i site was 0.042(1), which corresponds to an extra 1.0 Cu atom per formula unit, *i.e.*,  $Cu_{27}V_2Ge_6S_{32}$ . Although the quality of the PXRD pattern was not sufficient for quantitative analysis (*e.g.*, broadened peaks), the refinement confirmed partial occupation of a 24i site (~0.24, ~0.24, ~0.01) by extra atoms.

Next, the TE properties for the three series of samples were discussed (except for x = 4 and y = 4). All samples had relative densities higher than 95%, which is consistent with a highly dense character seen in SEM images (Figure S15). For the Sbsubstituted series (Cu<sub>26</sub>V<sub>2</sub>Ge<sub>6-x</sub>Sb<sub>x</sub>S<sub>32</sub>), all samples exhibited the p-type metallic behavior of degenerated semiconductors. The pristine sample (x = 0) had low *S* (18  $\mu$ V K<sup>-1</sup>) and  $\rho$  (1.7  $\mu\Omega$  m) values at 300 K (Figure 4a,b), which is in agreement with previous studies.<sup>25,28</sup> The values of S and  $\rho$  increased with x and reached 116  $\mu$ V K<sup>-1</sup> and 17  $\mu$ \Omega m, respectively, for x = 3. The increase in S and  $\rho$  results from a decrease in *n* from 6.8  $\times 10^{21}$  cm<sup>-3</sup> for x = 0 to  $1.9 \times 10^{21}$  cm<sup>-3</sup> for x = 3 (*i.e.*, electron doping) (Table S4), which can be attributed to the larger valence of Sb<sup>5+</sup> compared to Ge<sup>4+</sup>. As a result, the power factor  $S^2 \rho^{-1}$  increased from 1.2 mW K<sup>-2</sup> m<sup>-1</sup> for x = 0 to 1.4 mW K<sup>-2</sup> m<sup>-1</sup> for x = 1 and 2 and then decreased to 1.0 mW  $K^{-2}$  m<sup>-1</sup> for x = 3 at 673 K (Figure 4c). The increase in  $\rho$  led

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**Figure 6.** (a) Seebeck coefficient *S*, (b) electrical resistivity  $\rho$ , (c) power factor  $S^2 \rho^{-1}$ , (d) thermal conductivity  $\kappa$ , and (e) dimensionless figure of merit *ZT* for Cu<sub>26+y</sub>V<sub>2</sub>Ge<sub>6-x</sub>Sb<sub>x</sub>S<sub>32</sub> with x = 1 samples.

to a strong reduction in  $\kappa_{ele}$ , which manifested itself in the form of a drastic decrease in  $\kappa$  (Figure 4d). Consequently, the combination of enhanced  $S^2 \rho^{-1}$  and reduced  $\kappa$  resulted in the enhancement of *ZT* from 0.3 (x = 0) to 0.7 (x = 3) at 673 K for the Sb-substituted samples (Figure 4e).

For the Cu-rich series  $(Cu_{26+y}V_2Ge_6S_{32})$ , the values of S and  $\rho$  increased with y (Figure 5a,b), and it is consistent with a decrease in *n* from  $6.8 \times 10^{21}$  cm<sup>-3</sup> for y = 0 to  $4.1 \times 10^{21}$  cm<sup>-3</sup> for y = 3 at 300 K (Table S4). The decrease in *n* originates from that the insertion of Cu<sup>+</sup> doped an electron into the VB. As a result,  $S^2 \rho^{-1}$  remains at a high level (1.2–1.4 mW K<sup>-2</sup>  $m^{-1}$ ) at 673 K (Figure 5c). The value of  $\kappa$  decreases with y due to the reduction in  $\kappa_{ele}$  (Figure 5d). Consequently, ZT value increases from 0.3 (y = 0) to 0.6 (y = 3) at 673 K (Figure 5e). For the combined Sb-substituted and Cu-rich series  $(Cu_{26+y}V_2Ge_{6-x}Sb_xS_{32}$  with x = 1), the increase in S and  $\rho$ (Figure 6a,b) with increasing y is consistent with the aforementioned results for  $Cu_{26+y}V_2Ge_6S_{32}$  (Figure 5a,b). Remarkably, an increase in  $\rho$  was observed at temperatures below 400 K for  $Cu_{26+y}V_2Ge_{6-x}Sb_xS_{32}$  (x = 1, y = 3) (Figure 6b), unlike the metallic behavior observed in  $\rho$  for  $Cu_{26}V_2Ge_{6-x}Sb_xS_{32}$  (x = 3) (Figure 4b). Because the samples of x = 1, y = 3, and x = 3 have a similar *n* at 300 K (*i.e.*, 1.7 ×  $10^{21}$  cm<sup>-3</sup> for x = 1, y = 3;  $1.9 \times 10^{21}$  cm<sup>-3</sup> for x = 3), the enlargement of  $\rho$  for x = 1, y = 3 can be attributed to a decrease in the electron mobility  $\mu_{\rm H}$  from 1.9 to 1.0 cm<sup>2</sup> V<sup>-1</sup>  $s^{-1}$  (Table S4). Also, because the electronic properties of colusite are governed by the Cu-S tetrahedral framework,<sup>39</sup> the presence of interstitial atoms probably affects  $\mu_{\rm H}$  in the conductive network. A similar upturn in  $\rho$  was observed in cation-rich  $[Cu_{26}Cr_2Ge_6]_{1+\delta}S_{32}$  colusites.<sup>40</sup> As a result of the

aforementioned variation of *y* for  $Cu_{26+y}V_2Ge_{6-x}Sb_xS_{32}$  with x = 1, the value of  $S^2\rho^{-1}$  at 300 K remains unchanged, whereas it increases at 673 K for y = 1 and decreases for  $y \ge 2$  (Figure 6c). The sample produced at x = 1, y = 1 showed the highest  $S^2\rho^{-1}$  value of 1.5 mW K<sup>-2</sup> m<sup>-1</sup> at 673 K compared to the other samples in this study. The value of  $\kappa$  (and  $\kappa_{ele}$ ) decreased as *y* increased (Figure 6d). As a result, the reduction in  $\kappa$  boosts *ZT* at 673 K from 0.4 (x = 1, y = 0) to 0.8 (x = 1, y = 3) (Figure 6e). The *ZT* value of the samples produced at x = 1, y = 3 in the  $Cu_{26+y}V_2Ge_{6-x}Sb_xS_{32}$  series was higher than that of x = 3 in the  $Cu_{26+y}V_2Ge_{6-x}Sb_xS_{32}$  series (Figure 4e) despite similar values of *S* and  $\rho$  at 673 K (Figures 4 and 6). This comparison indicates that the reduction in  $\kappa_{lat}$  via Cu insertion contributes to the enhancement of *ZT*.

To determine the effects of Sb substitution and Cu insertion on  $\kappa_{lat}$  the value of  $\kappa_{lat}$  was estimated by subtracting  $\kappa_{ele}$  =  $LT\rho^{-1}$  from  $\kappa$ , where  $L = 1.5 + \exp(-|S|/116)$ .<sup>55</sup> The equation regarding L is based on the acoustic phonon scattering of electrons, which is consistent with the metallic increase in  $\rho(T)$ at temperatures between 400 and 673 K for all of the samples (Figures 4b, 5b, and 6b). Conversely, a single parabolic band assumed for the equation may be too simple to describe the VB of colusites. As shown in Figure S16, the obtained  $\kappa_{lat}$  for Cu<sub>26</sub>V<sub>2</sub>Ge<sub>6-x</sub>Sb<sub>x</sub>S<sub>32</sub>, Cu<sub>26+y</sub>V<sub>2</sub>Ge<sub>6</sub>S<sub>32</sub>, and Cu<sub>26+y</sub>V<sub>2</sub>Ge<sub>6-x</sub>Sb<sub>x</sub>S<sub>32</sub> with x = 1 exhibited complicated variations with different x and y values. More specifically,  $\kappa_{lat}$  for  $Cu_{26}V_2Ge_{6-x}Sb_xS_{32}$  increased for x = 2 and decreased for x = 3. For the  $Cu_{26+y}V_2Ge_6S_{32}$ series,  $\kappa_{\text{lat}}$  slightly increased for  $y \ge 1$ , whereas for the  $Cu_{26+y}V_2Ge_{6-x}Sb_xS_{32}$  with x = 1 series,  $\kappa_{lat}$  decreased for  $y \ge 1$ . These opposite trends for the Cu-rich series imply that the variation of  $\kappa_{lat}$  is not influenced by the existence of Cu<sub>2</sub>S

Article



**Figure 7.** (a) Seebeck coefficient *S*, (b) electrical resistivity  $\rho$ , and (c) lattice thermal conductivity  $\kappa_{\text{lat}}$  for the selected Cu<sub>26+y</sub>V<sub>2</sub>Ge<sub>6-x</sub>Sb<sub>x</sub>S<sub>32</sub> samples (see text).

(secondary phase), whose amount increased with y in both series. The variations of  $\kappa_{lat}$  can originate from different effects/ mechanisms: (i) the substitutional doping of Sb for Ge, (ii) the interstitial doping of Cu, (iii) uncertainty in the estimation of L due to the complexity of the actual electronic structure,<sup>28</sup> and (iv) phonon scattering by electrons.<sup>56</sup> Hence, we chose three pairs of samples in the  $Cu_{26+y}V_2Ge_{6-x}Sb_xS_{32}$  series with similar S and  $\rho$  values (equivalent *n* and  $E_{\rm F}$ ) to minimize the influence of (iii) and (iv) on  $\kappa$ . Each pair includes Sb-substituted/non-Cu-rich and Cu-rich samples (*i.e.*, x = 1, y = 0 ( $n = 5.5 \times 10^{21}$ cm<sup>-3</sup> at 300 K) vs x = 0, y = 2 (5.1 × 10<sup>21</sup> cm<sup>-3</sup>); x = 2, y = 0 $\begin{array}{l} (4.0 \times 10^{21} \, \mathrm{cm}^{-3}) \, vs \, x = 0, \, y = 3 \, (4.1 \times 10^{21} \, \mathrm{cm}^{-3}); \, x = 3, \, y = \\ 0 \, (1.9 \times 10^{21} \, \mathrm{cm}^{-3}) \, vs \, x = 1, \, y = 3 \, (1.7 \times 10^{21} \, \mathrm{cm}^{-3})). \ \mathrm{As} \end{array}$ shown in Figure 7, although the substitution of Sb for Ge has a negligible effect on  $\kappa_{lat}$  all Cu-rich samples showed lower  $\kappa_{lat}$ compared with the non-Cu-rich samples. This result demonstrates that the interstitial Cu ions act as phonon scatterers in the crystal structure, leading to the reduction of  $\kappa_{lat}$ . Furthermore, the decrease in  $\kappa_{lat}$  at approximately 300 K was more pronounced in the samples showing a larger upturn in  $\rho(T)$  (Figure 7). This means that the insertion of Cu has a significant impact on both enhanced phonon scattering and reduced  $\mu_{\rm H}$  (Table S4). Further investigations (e.g., Mössbauer spectroscopy, extended X-ray absorption fine structure spectroscopy) are required to investigate the local structural modification of the colusite structure.

#### 4. CONCLUSIONS

In this work, we performed the substitution of Sb for Ge and the insertion of Cu into the crystal structure of the  $Cu_{26+y}V_2Ge_{6-x}Sb_xS_{32}$  colusite. Both chemical approaches led to a decrease in *n* and  $\kappa_{ele}$ , while maintaining  $S^2\rho^{-1} \ge 0.9$  mW  $K^{-2}$  m<sup>-1</sup> (at  $x \le 3$ ,  $y \le 3$ ). Furthermore, the interstitial Cu atoms act as phonon scatterers, leading to the suppression of  $\kappa_{lat}$ . These combined effects boost *ZT*, which reaches a value of 0.8 at 673 K for the x = 1, y = 3 sample. Thus, the Cu insertion into the corner-sharing three-dimensional tetrahedral framework structures of Cu–S-based materials is a powerful chemical approach for improving TE performance *via* tuning of *n* and reducing of  $\kappa_{lat}$ .

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c01321.

Sample density; specific heat; PXRD patterns; Rietveld refinement results of PXRD patterns; STEM results; SEM images; hole carrier concentration; and lattice thermal conductivity (PDF)

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The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

#### Notes

The authors declare no competing financial interest.

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