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Supporting Information for

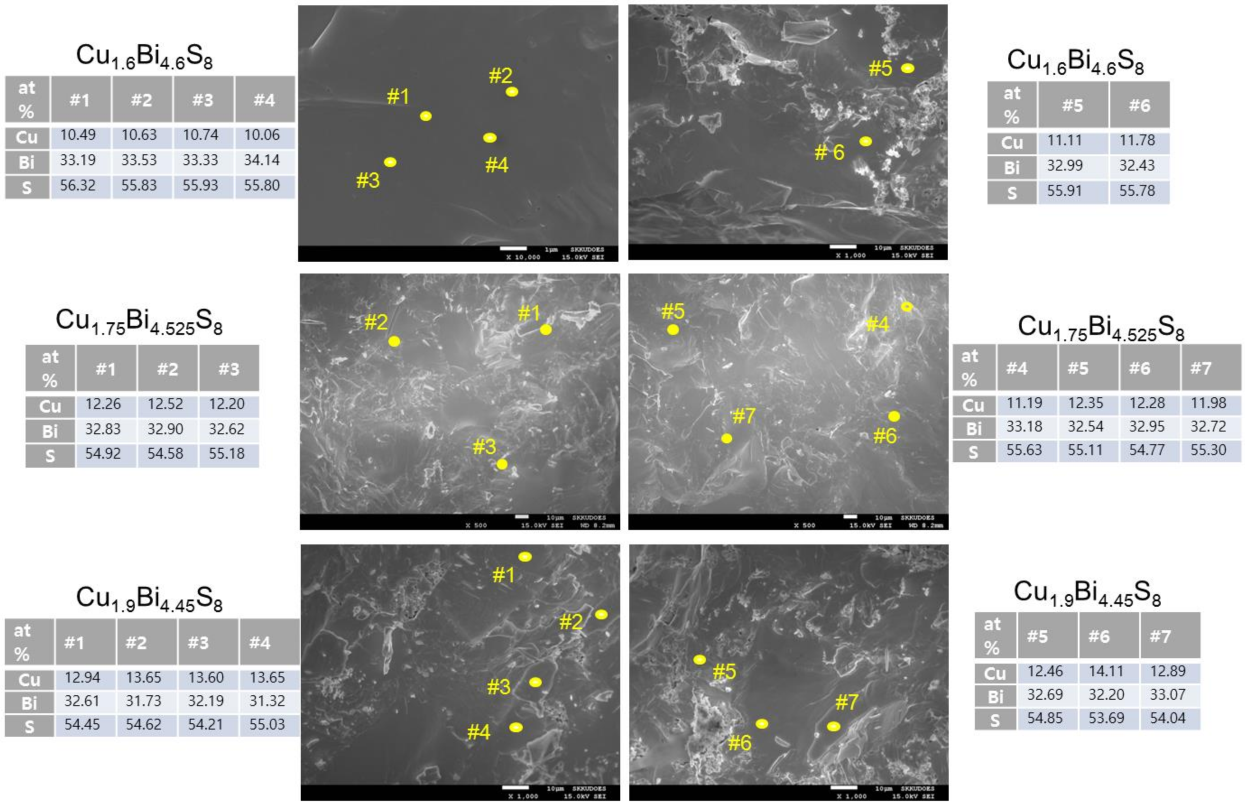
Importance of crystal chemistry with interstitial site determining thermoelectric transport properties in pavonite homologues Cu-Bi-S compound

Jun Yeon Ahn,[1,†] Jae-Yeol Hwang,[2,†] Byung Ki Ryu,[3] Min-Wook Oh,[4] Kyu Hyoung Lee,[5,*] and Sung Wng Kim[1,*]

[1]Department of Energy Science, Sungkyunkwan University, Suwon 16419, Korea
[2]Center for Integrated Nanostructure Physics (CINAP), Institute for Basic Science (IBS), Sungkyunkwan University, Suwon 16419, Korea
[3]Thermoelectric Conversion Research Center, Korea Electrotechnology Research Institute (KERI), Changwon 51543, Korea
[4]Department of Advanced Materials Engineering, Hanbat National University, Daejeon 34158, Korea
[5]Department of Nano Applied Engineering, Kangwon National University, Chuncheon 24341, Korea

*E-mail: kimsungwng@skku.edu (S. W. K.) and khlee2014@kangwon.ac.kr (K. H. L.)

Figure S1. Chemical compositions of Cu-Bi-S compounds with different compositions. ($Cu_{1.6}Bi_{4.6}S_8$, $Cu_{1.75}Bi_{4.525}S_8$, $Cu_{1.9}Bi_{4.45}S_8$) by EDS analyses.



$Cu_{1.6}Bi_{4.6}S_8$

at %	#1	#2	#3	#4
Cu	10.49	10.63	10.74	10.06
Bi	33.19	33.53	33.33	34.14
S	56.32	55.83	55.93	55.80

$Cu_{1.6}Bi_{4.6}S_8$

at %	#5	#6
Cu	11.11	11.78
Bi	32.99	32.43
S	55.91	55.78

$Cu_{1.75}Bi_{4.525}S_8$

at %	#1	#2	#3
Cu	12.26	12.52	12.20
Bi	32.83	32.90	32.62
S	54.92	54.58	55.18

$Cu_{1.75}Bi_{4.525}S_8$

at %	#4	#5	#6	#7
Cu	11.19	12.35	12.28	11.98
Bi	33.18	32.54	32.95	32.72
S	55.63	55.11	54.77	55.30

$Cu_{1.9}Bi_{4.45}S_8$

at %	#1	#2	#3	#4
Cu	12.94	13.65	13.60	13.65
Bi	32.61	31.73	32.19	31.32
S	54.45	54.62	54.21	55.03

$Cu_{1.9}Bi_{4.45}S_8$

at %	#5	#6	#7
Cu	12.46	14.11	12.89
Bi	32.69	32.20	33.07
S	54.85	53.69	54.04

S1. Density Functional Theory (DFT) calculation.

We used the projector-augmented wave (PAW) pseudopotentials and the generalized gradient approximation (GGA) exchange-correlation energies parameterized by Perdew, Burke, and Ernzerhof (PBE), which are implemented in VASP (Vienna Ab initio Simulation Package) plane-wave code. The energy cutoff of 300 eV is used. The electronic band structure is examined with the inclusion of spin-orbit-interaction (SOI). We fixed the lattice parameters to be experimental cells, a = 13.217 Å, b = 4.033 Å, c = 14.076 Å, $\alpha = \gamma = 90^{o}$, and $\beta = 115.53^{o}$ for Cu-Bi-S, where 2 Cu atoms, 10 Bi atoms, and 16 S atoms are involved. We construct the (1×4×1) supercell to vary the stoichiometry of compounds.

Table S1. Refined structure parameters of Cu-Bi-S compounds.

Formula	$Cu_{1.6}Bi_{4.6}S_8$	$Cu_{1.75}Bi_{4.525}S_8$	$Cu_{1.9}Bi_{4.45}S_8$
a [Å]	13.2143(5)	13.2157(5)	13.2157(5)
b [Å]	4.02319(7)	4.0193(8)	4.01602(7)
c [Å]	14.0960(5)	14.1752(7)	14.1354(7)
α [º]	90	90	90
β [º]	115.575(2)	115.6086(3)	115.6334(5)
γ [º]	90	90	90
Volume	675.97(4)	678.99(6)	676.39(7)
Z	2	2	2
Space group	C2/m	C2/m	C2/m
R_p	8.71	8.67	8.69
R_{wp}	9.12	9.03	8.99
χ^2	4.97	4.94	4.80

Table S2. Refined atomic coordination (x, y, z) for Cu-Bi-S compounds.

	$Cu_{1.6}Bi_{4.6}S_8$	$Cu_{1.75}Bi_{4.525}S_8$	$Cu_{1.9}Bi_{4.45}S_8$
Bi1	(0.2102, 0.5, 0.3588)	(0.2106, 0.5, 0.3593)	(0.2106, 0.5, 0.3593)
Bi2	(0, 0, 0)	(0, 0, 0)	(0, 0, 0)
Bi3	(0.3442, 0, 0.1502)	(0.3442, 0, 0.1492)	(0.3441, 0, 0.1492)
Cu1	(0.5, 0.203, 0.5)	(0.5, 0.185, 0.5)	(0.5, 0.184, 0.5)
Cu2	(0.0491, 0.5, 0.4782)	(0.03, 0.5, 0.47)	(0.03, 0.5, 0.47)
Cu3	(0.0232, 0, 0.5436)	(0.037, 0, 0.565)	(0.037, 0, 0.565)
Cu4	(0.0519, 0, 0.0678)	(0.072, 0, 0.011)	(0.072, 0, 0.011)
Cu5	(0.3838, 0, 0.1569)	(0.423, 0, 0.1553)	(0.423, 0, 0.1552)
S1	(0.1633, 0.5, 0.0819)	(0.1648, 0.5, 0.0752)	(0.1648, 0.5, 0.0753)
S2	(0.4745, 0.5, 0.1946)	(0.4968, 0.5, 0.1967)	(0.4969, 0.5, 0.1968)
S3	(0.1184, 0, 0.4399)	(0.1282, 0, 0.4523)	(0.1282, 0, 0.4523)
S4	(0.3491, 0, 0.3557)	(0.3548, 0, 0.3432)	(0.3548, 0, 0.3432)

Table S3. Refined site occupancies for Cu-Bi-S compounds.

	$Cu_{1.6}Bi_{4.6}S_8$	$Cu_{1.75}Bi_{4.525}S_8$	$Cu_{1.9}Bi_{4.45}S_8$	Site symmetry multiplication.
Bi1	1	1	1	4
Bi2	0.8721(8)	0.7992(7)	0.7706(6)	2
Bi3	0.8639(7)	0.8637(8)	0.8473(7)	4
Cu1	0.2491(6)	0.2759(9)	0.2689(8)	4
Cu2	0.2430(4)	0.2221(10)	0.2191(9)	4
Cu3	0.2308(5)	0.2031(8)	0.1969(8)	4
Cu4	0.0182(6)	0.1024(7)	0.1735(6)	4
Cu5	0.0657(7)	0.0892(8)	0.1036(7)	4
S1	1	1	1	4
S2	1	1	1	4
S3	1	1	1	4
S4	1	1	1	4

S2. Calculation of lattice thermal conductivity (κ_{lat}) from total thermal conductivity.

We determined κ_{lat} by eliminating the electronic contribution (κ_{ele}) from κ_{tot}, where κ_{ele} is calculated by Wiedemann-Franz law, $\kappa_{\mathrm{ele}} = L_0\, T\, \sigma$. The Lorenz number, L_0 was obtained using following equation:

$$L_0 = \left(\frac{k_{\mathrm{B}}}{e}\right)^2 \left(\frac{\left(r+\frac{7}{2}\right)F_{r+\frac{5}{2}}(\eta)}{\left(r+\frac{3}{2}\right)F_{r+\frac{1}{2}}(\eta)} - \left[\frac{\left(r+\frac{5}{2}\right)F_{r+\frac{3}{2}}(\eta)}{\left(r+\frac{3}{2}\right)F_{r+\frac{1}{2}}(\eta)} \right]^2 \right) \tag{1}$$

where r is the scattering parameter, $F_n(\eta)$ is the n-th order Fermi integral, $F_n(\eta) = \int_0^\infty \frac{x^n}{1+e^{x-\eta}}\,dx$, and η is calculated from the value of S, respectively. The value of r, which was derived from the temperature dependence of μ_{H}, was ~1.5 in the Cu-Bi-S compounds, suggesting that the main scattering mechanism was mixed by the interaction between acoustic and optical phonon scatterings of the lattice atoms and/or structural defects (point defects). Calculated L_0 was nearly constant in all compounds and was in the range of $2.47 – 2.58 \times 10^{-8}\ \mathrm{V^2\ K^{-2}}$.

Table S4. Refined anisotropic atomic displacement parameters (Å^2) for $Cu_{1.6}Bi_{4.6}S_8$.

Atom	U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}
Bi1	0.0226	0.0	0.0007	0.0156	0.0	0.0267
Bi2	0.0253	0.0	0.0007	0.0156	0.0	0.0267
Bi3	0.0253	0.0	0.0089	0.0155	0.0	0.0267
Cu1	0.0405	0.001	0.036	0.2342	0.001	0.06
Cu2	0.0213	0.001	0.001	0.1591	0.001	0.06
Cu3	0.0341	0.001	0.0330	0.2320	0.001	0.06
Cu4	0.02	0.001	0.001	0.0259	0.001	0.03
Cu5	0.02	0.001	0.001	0.0259	0.001	0.03
S1	0.0241	0.0	0.0309	0.0101	0.0	0.0943
S2	0.0721	0.0	0.0068	0.0635	0.0	0.0254
S3	0.09	0.0	0.0529	0.0907	0.0	0.0465
S4	0.0268	0.0	0.0301	0.0307	0.0	0.0911

Figure S2. Thermal ellipsoid plot of $Cu_{x+y}Bi_{5-y}S_8$ visualizing atomic displacement parameters of Cu, Bi, and S.

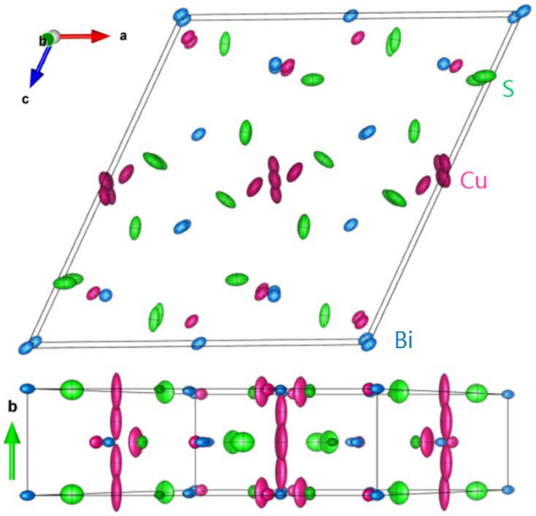


Figure S3. Powder X-ray diffraction patterns of pristine $Cu_{1.6}Bi_{4.6}S_8$ and individual site doped Cu-Bi-S compounds based on $Cu_{1.6}Bi_{4.6}S_8$ as a mother compound.

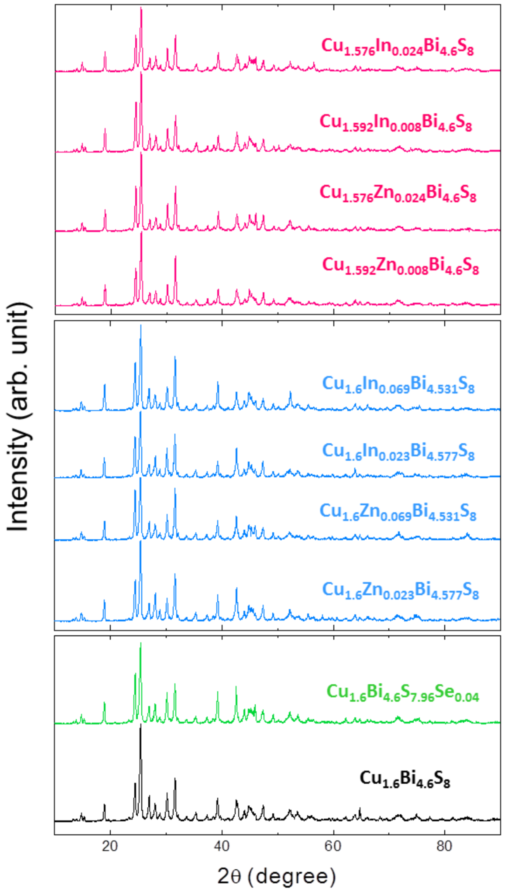
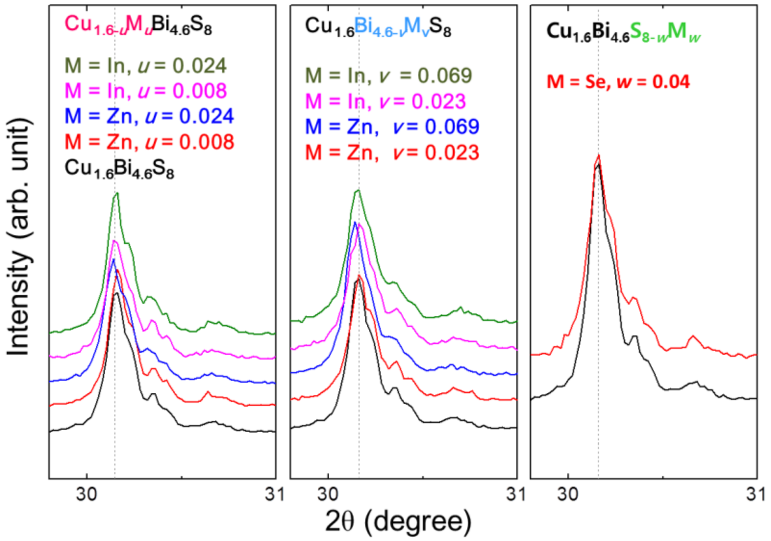


Figure S4. Enlarged XRD peaks of pristine $Cu_{1.6}Bi_{4.6}S_8$ and individual site doped Cu-Bi-S compounds.



S3. Lattice thermal conductivity (κ_{lat}) calculation.

According to the Debye-Callaway model,[1] κ_{lat} can be written as following equation:

$$\kappa_{\mathrm{lat}} = \frac{k_{\mathrm{B}}}{2\,\pi^2\,v_g}\left(\frac{k_{\mathrm{B}}\,T}{\hbar}\right)^3 \int_0^{\theta_{\mathrm{D}}/T} \frac{\tau_c\,x^4\,e^x}{(e^x-1)^2}\,dx, \tag{1}$$

where $x = \hbar\omega/k_{\mathrm{B}}T$ is dimensionless factor, ω is the phonon frequency, $\hbar$ is the Planck constant, θ_{D} is the Debye temperature, v_g is an average phonon-group velocity, and τ_c is the combined relaxation time, respectively. The τ_c can be determined by various scattering processes:

$$\tau_c{}^{-1} = \tau_U{}^{-1} + \tau_I{}^{-1} + \tau_B{}^{-1} \tag{2}$$

where τ_U, τ_B, and τ_I are the relaxation times for Umklapp processes, boundary scattering, and point defect scattering, respectively. Umklapp processes are characterized by a relaxation rate proposed by Slack and Galginaitis:[2-5]

$$\tau_U{}^{-1} = U\,\omega^2\,T\,exp\left(-\frac{\theta_{\mathrm{D}}}{3T}\right) \qquad U = \frac{\hbar\,\gamma^2}{M\,v_g{}^2\,\theta_{\mathrm{D}}} \tag{3}$$

where γ is the Gruneisen anharmonicity parameter, M is the average mass of an atom in the crystal. On the other hand, phonon relaxation mechanism is strongly affected by the mass-difference scattering, which results in the change in v_g. Relaxation rate for point defect scattering generated by interaction with atoms of different masses[6] is given by

$$\tau_I{}^{-1} = PD\,\omega^4 \qquad PD = \frac{V_0}{4\,\pi\,v_g^3}\sum_i f_i\left[1-\left(\frac{M_i}{M}\right)\right]^2 \tag{4}$$

where V_0 is the volume per atom, M_i is the mass of an atom, and f_i is the fractional content of atoms with mass M_i which is different from M. The boundary scattering rate is

$$\tau_B{}^{-1} = B \qquad B = \frac{v_g}{L}, \tag{5}$$

where L is the grain size of sample. In case of small amount of doping, there is little difference in grain size and structure by doping, thus the only point defect scattering prefactor (*PD*) could be significantly changed among three fitting parameters (Umklapp (*U*), boundary (*B*), and point defect (*PD*) scattering prefactors). We tried to include normal scattering[7,8] and electron-phonon interaction,[9-10] but these did not improve the overall fit significantly. Therefore, we consider only the three contributors in our calculations.

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