Supporting information

Manipulating the Phase Transformation Temperature to Achieve Cubic $Cu_5FeS_{4-x}Se_x$ and Enhanced Thermoelectric Performance

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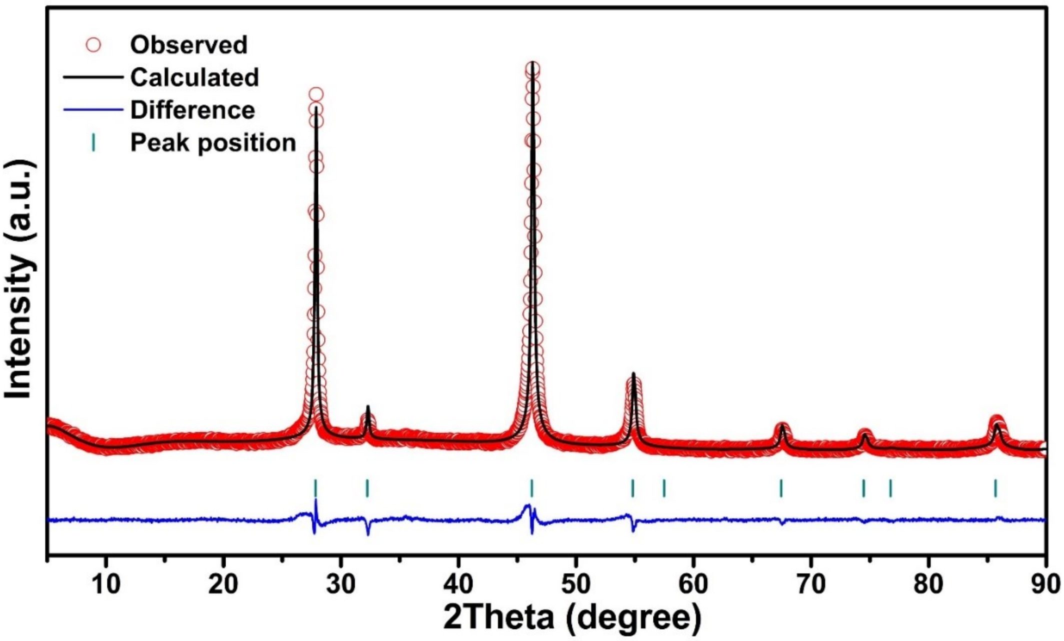

Fig. S1 Experimental XRD pattern of the $Cu_5FeS_2Se_2$ sample and the corresponding results of Rietveld refinement. The low values of R_{wp} (2.12%) and R_p (1.37%) indicate the reliability of the refinement. The XRD pattern can be indexed to the high cubic bornite phase.

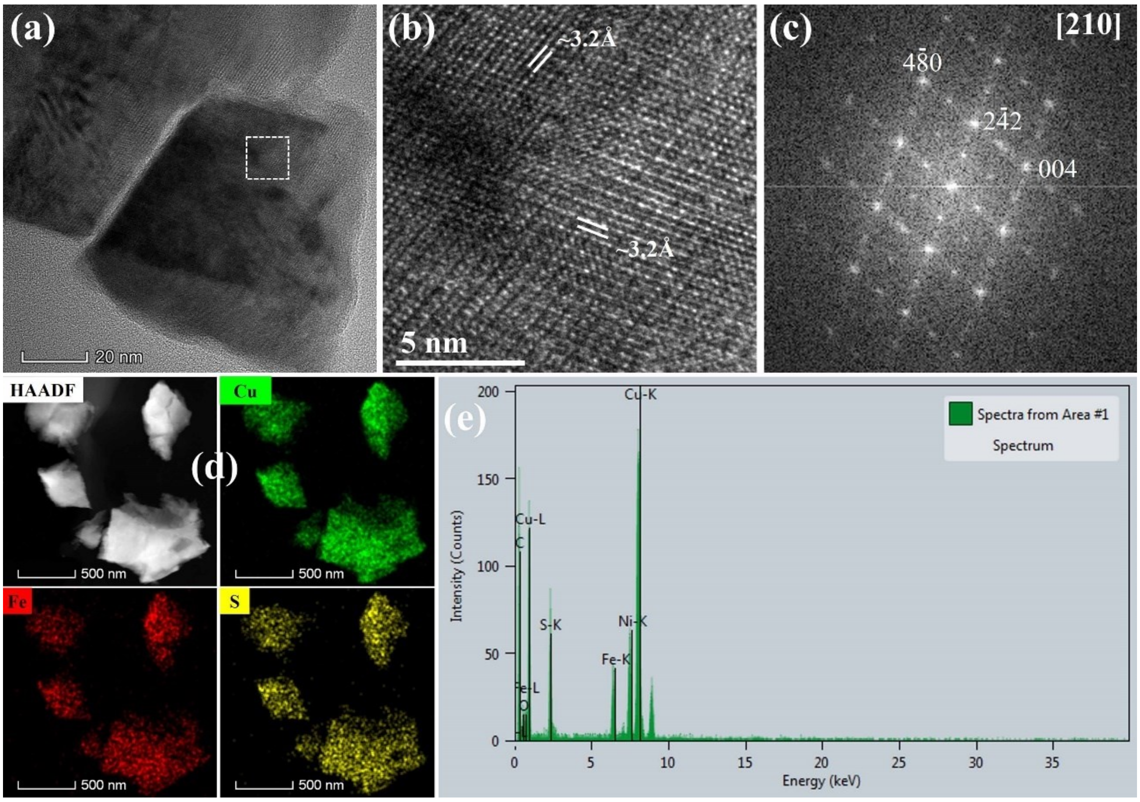

Fig. S2 Electron microscopy characterization of Cu_5FeS_4: (a) TEM image, (b) HRTEM image of the marked region in (b) and (c) the corresponding FFT pattern, (d) HAADF image and EDS elemental mapping of Cu, Fe and S, (e) EDS spectrum.

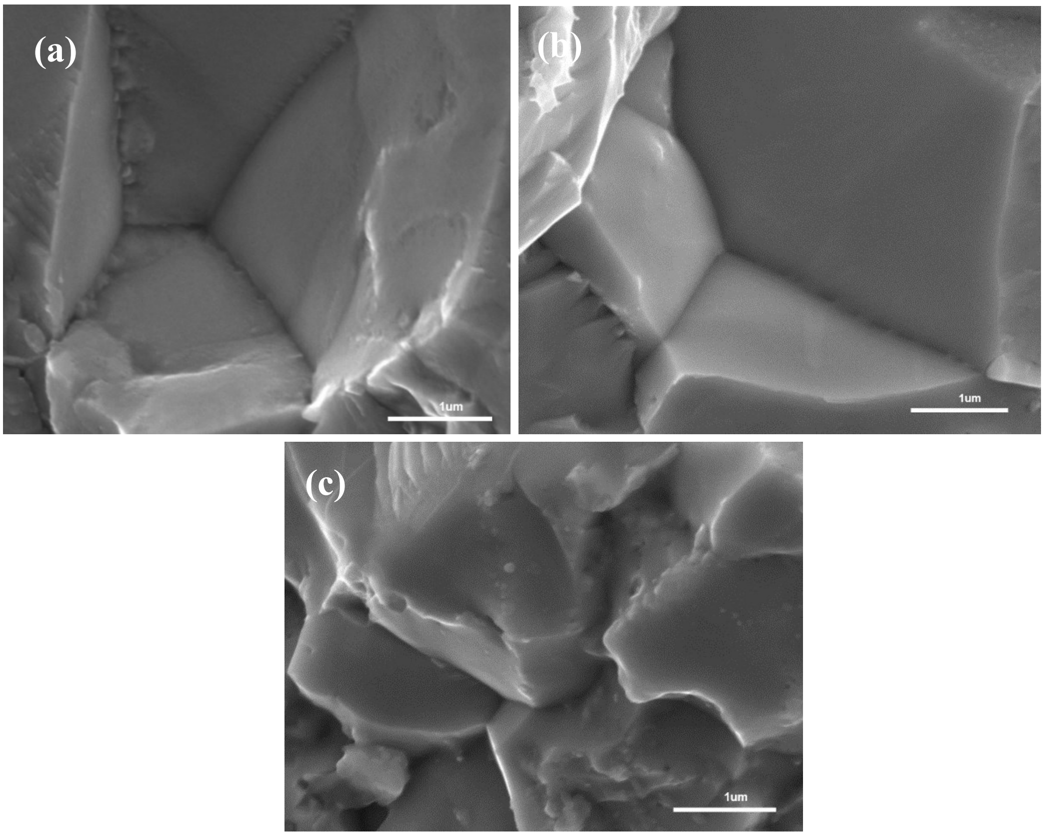

Fig. S3 SEM images of sintered $Cu_5FeS_{4-x}S_x$: (a) $x = 0$, (b) $x = 0.4$, (c) $x= 2.0$. The sintered samples are composed of micrometer-sized particles.

Fig. S4 (a) UV-vis absorption spectra, (b) $(\alpha h\nu)^2$ *vs* photon energy plots for $Cu_5FeS_{4-x}Se_x$ (x = 0, 0.4, 0.8, 1.5, 2.0) at room temperature.

Fig. S5 Calculated Seebeck-Normalized conductivity ($|S|$-σ/σ_{E0}) relation assuming (a) acoustic phonon scattering, and (b) ionization scattering dominant charge carrier transport. The σ_{E0} could be extracted from a pair of experimentally measured S and σ at the same temperature.

Table S1. A summary of thermoelectric properties of Cu_5FeS_4 based materials

Materials	$T^{a)}$ [K]	$zT^{b)}$	$S^2\sigma^{b)}$ [mW m^{-1} K^{-2}]	Synthesis method	References
Cu_5FeS_4	735	0.49	0.31	Melting + annealing + SPS	This work
$Cu_5FeS_{3.6}Se_{0.4}$	735	0.60	0.39	Melting + annealing + SPS	This work
$Cu_5FeS_{3.2}Se_{0.8}$	735	0.57	0.42	Melting + annealing + SPS	This work
$Cu_5FeS_{2.5}Se_{1.5}$	735	0.56	0.56	Melting + annealing + SPS	This work
$Cu_5FeS_{2.0}Se_{2.0}$	735	0.54	0.56	Melting + annealing + SPS	This work
Cu_5FeS_4	700	~0.38	~0.25	Melting + annealing + SPS	1
$Cu_{5.04}Fe_{0.96}S_4$	700	0.52	~0.35	Melting + annealing + SPS	1
Cu_5FeS_4	710	0.62	0.39	Colloidal synthesis + SPS	2
Cu_5FeS_4	690	0.56	0.4	Colloidal synthesis + SPS	3
$Cu_5Fe_{0.95}Mn_{0.05}S_4$	543	0.55	0.34	Ball milling + hot pressing	4
$Cu_5FeS_{3.8}Se_{0.2}$	540	0.5	0.43	Ball milling + SPS	5
$Cu_5FeS_{3.8}Se_{0.2}$	670	~0.59	~0.41	Ball milling + SPS	5
$Cu_5FeS_{3.6}Se_{0.4}$	670	~0.66	~0.52	Ball milling + SPS	5
$Cu_{4.972}Fe_{0.968}S_4$	550	0.79	~0.44	Ball milling + hot pressing	6
$Cu_{4.96}Co_{0.04}FeS_4$	590	~0.5	~0.30	Ball milling + hot pressing	7
Cu_5FeS_4	593	0.28	0.24	Ball milling + sintering	8
$Cu_{4.96}Co_{0.04}Fe_{0.96}Zn_{0.04}S_4$	590	0.6	0.37	Ball milling + hot pressing	9
Cu_5FeS_4 nanocomposite	663	0.55	~0.56	Chemical synthesis + particle blending + pulse electric current sintering	10

a) The temperature at which maximum zT was achieved; b) zT and $S^2\sigma$ at T.

References:

1. P. F. Qiu, T. S. Zhang, Y. T. Qiu, X. Shi and L. D. Chen, *Energy Environ. Sci.*, 2014, **7**, 4000-4006.
2. A. J. Zhang, B. Zhang, W. Lu, D. D. Xie, H. X. Ou, X. D. Han, J. Y. Dai, X. Lu, G. Han, G. Y. Wang and X. Y. Zhou, *Adv. Funct. Mater.*, 2018, **28**, 1705117.
3. A. J. Zhang, X. C. Shen, Z. Zhang, X. Lu, W. Yao, J. Y. Dai, D. D. Xie, L. J. Guo, G. Y. Wang and X. Y. Zhou, *J. Mater. Chem. C*, 2017, **5**, 301-308.
4. G. Guelou, A. V. Powell and P. Vaqueiro, *J. Mater. Chem. C*, 2015, **3**, 10624-10629.
5. V. P. Kumar, T. Barbier, P. Lemoine, B. Raveau, V. Nassif and E. Guilmeau, *Dalton Trans.*, 2017, **46**, 2174-2183.
6. S. O. J. Long, A. V. Powell, P. Vaqueiro and S. Hull, *Chem. Mater.*, 2018, **30**, 456-464.
7. A. O. Moghaddam, A. Shokuhfar and A. Cabot, *J. Alloy. Compd.*, 2018, **750**, 1-7.
8. A. O. Moghaddam, A. Shokuhfar, A. Cabot and A. Zolriasatein, *Powder Technol.*, 2018, **333**, 160-166.
9. A. O. Moghaddam, A. Shokuhfar, P. Guardia, Y. Zhang and A. Cabot, *J. Alloy. Compd.*, 2019, **773**, 1064-1074.
10. M. Singh, P. Dwivedi, D. Mott, K. Higashimine, M. Ohta, H. Miwa, T. Akatsuka and S. Maenosono, *Ind. Eng. Chem. Res.*, 2019, **58**, 3688-3697.