Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

— Supplementary Information —

Thermoelectric Properties of $Bi_{1-x}Pb_xCu_{1-x}SeO$ Oxyselenides

Aleksandra Khanina,[*,†] Andrei Novitskii,[‡] Daria Pashkova,[‡] Andrei Voronin,[†] Takao Mori,[‡,¶] and Vladimir Khovaylo[*,†,§]

†*Academic Research Center for Energy Efficiency, National University of Science and Technology MISIS, Leninsky Av. 4, Moscow, 119049, Russia.*

‡*International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki, 305-0044, Japan.*

¶*Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki, 305-8573, Japan.*

§*Belgorod State University, Pobedy St. 85, Belgorod, 308015, Russia.*

E-mail: khanina.as@misis.ru; khovaylo@misis.ru

Energy-Dispersive X-ray Spectroscopy (EDS)

Nominal composition	(Bi + Pb):Cu:Se	Pb
BiCuSeO	1.04:1.00:0.96	0
$Bi_{0.98}Pb_{0.02}Cu_{0.98}SeO$	1.01:0.99:0.98	0.01
$Bi_{0.94}Pb_{0.06}Cu_{0.94}SeO$	1.06:0.94:0.95	0.06
$Bi_{0.92}Pb_{0.08}Cu_{0.92}SeO$	1.02:0.94:0.96	0.08

Table S1: Elemental ratios and Pb concentration obtained by EDS analysis for the $Bi_{1-x}Pb_xCu_{1-x}SeO$ (x = 0, 0.02, 0.06, and 0.08).

Weighted Mobility

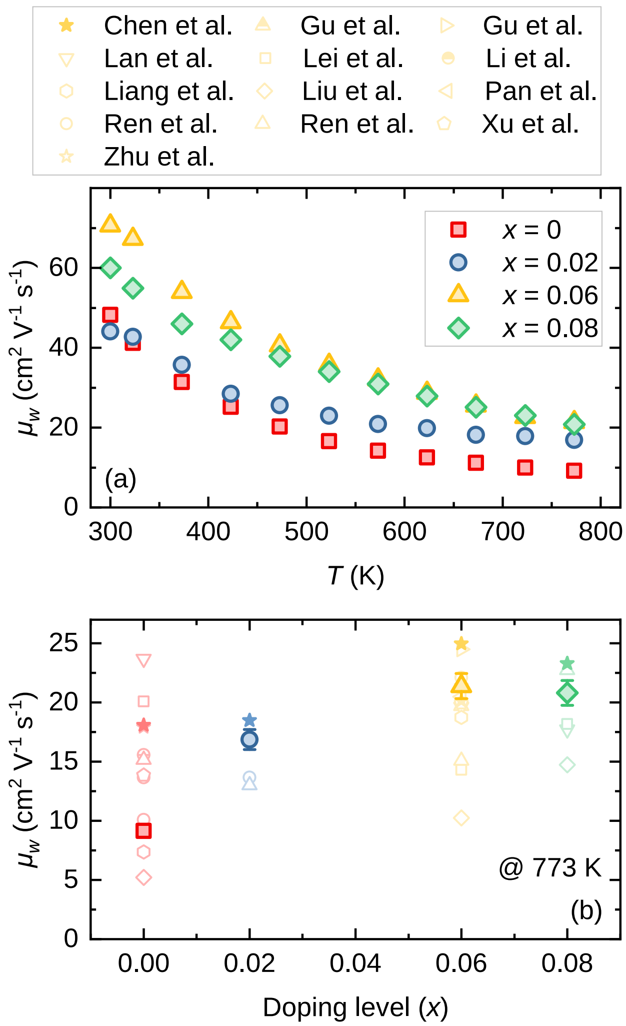

Figure S1: (a) Temperature and (b) concentration dependencies of the weighted mobility μ_w for $Bi_{1-x}Pb_xCu_{1-x}SeO$ ($x = 0$, 0.02, 0.06, and 0.08) samples. In (b), literature data for other $Bi_{1-x}Pb_xCuSeO$-based oxyselenides are also shown for comparison (Chen et al.,[1] Gu et al.,[2,3] Lan et al.,[4] Lei et al.,[5] Li et al.,[6] Liang et al.,[7] Liu et al.,[8] Pan et al.,[9] Ren et al.,[10,11] Xu et al.,[12] Zhu et al.[13]); all displayed data points correspond to values obtained at 773 K.

Jonker Plot

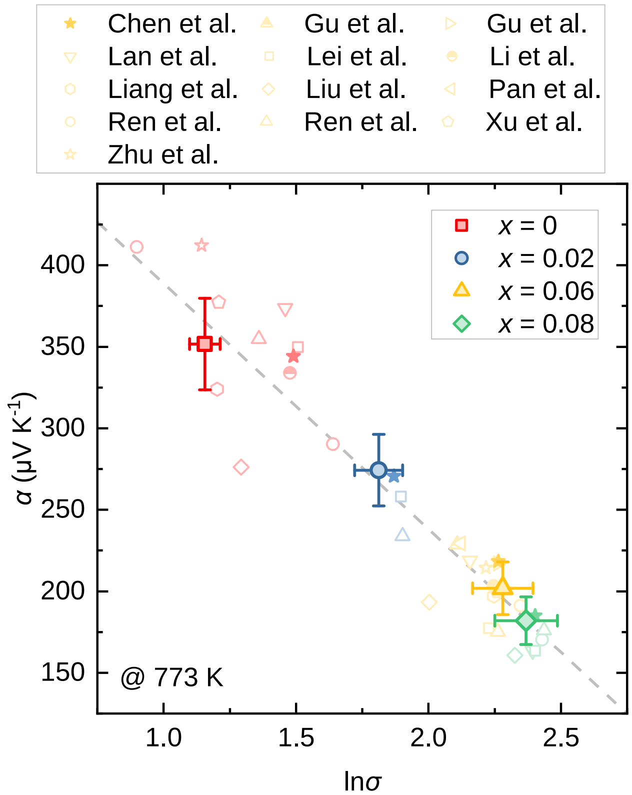

Figure S2: Seebeck coefficient as a function of lnσ for $Bi_{1-x}Pb_xCu_{1-x}SeO$ (x = 0, 0.02, 0.06, and 0.08) samples. Literature data for other $Bi_{1-x}Pb_xCuSeO$-based oxyselenides are also shown for comparison (Chen et al.,[1] Gu et al.,[2,3] Lan et al.,[4] Lei et al.,[5] Li et al.,[6] Liang et al.,[7] Liu et al.,[8] Pan et al.,[9] Ren et al.,[10,11] Xu et al.,[12] Zhu et al.[13]). All displayed data points correspond to values obtained at 773 K. The dashed line is a guide for the eyes.

Power Factor

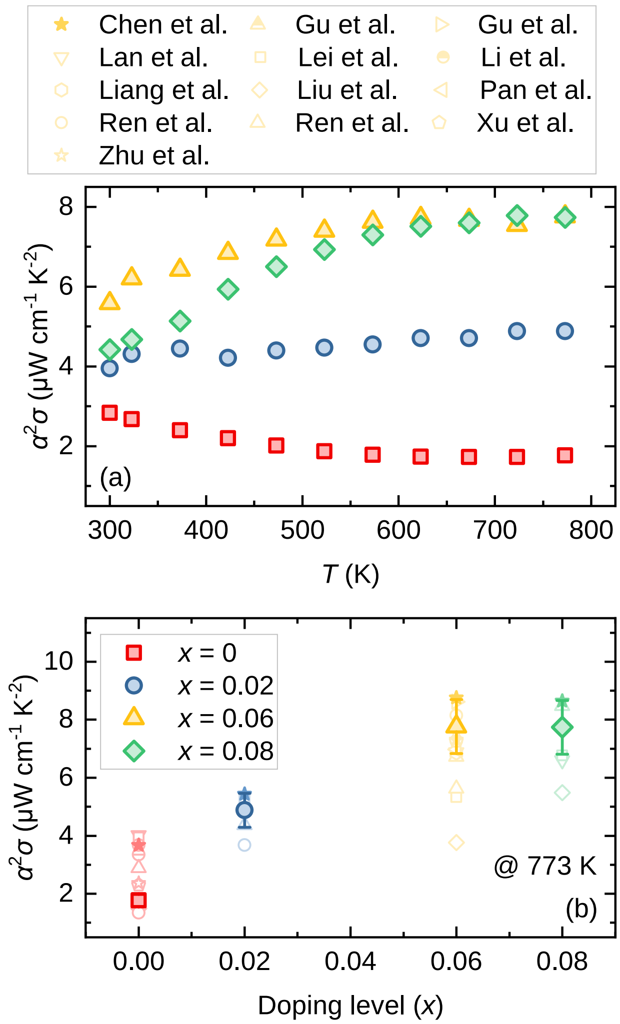

Figure S3: (a) Temperature and (b) concentration dependencies of the power factor $\alpha^2\sigma$ for $Bi_{1-x}Pb_xCu_{1-x}SeO$ ($x = 0$, 0.02, 0.06, and 0.08) samples. In (b), literature data for other $Bi_{1-x}Pb_xCuSeO$-based oxyselenides are also shown for comparison (Chen et al.,[1] Gu et al.,[2,3] Lan et al.,[4] Lei et al.,[5] Li et al.,[6] Liang et al.,[7] Liu et al.,[8] Pan et al.,[9] Ren et al.,[10,11] Xu et al.,[12] Zhu et al.[13]); all displayed data points correspond to values obtained at 773 K.

Thermal Conductivity

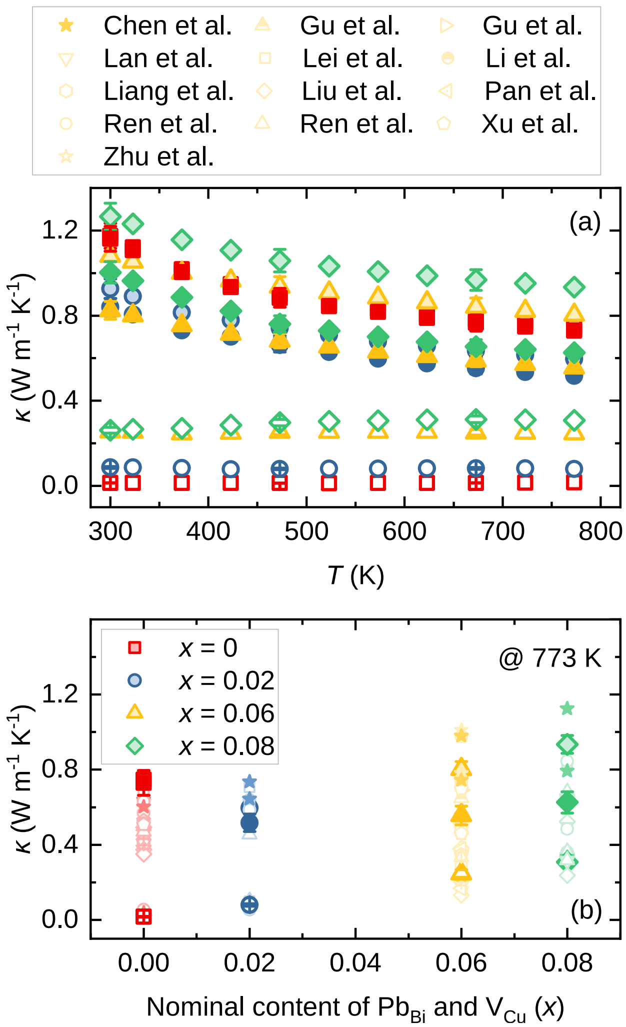

Figure S4: (a) Temperature and (b) concentration dependencies of the total κ_{tot}, lattice κ_{lat} (solid symbols), and electronic κ_{el} (empty symbols) thermal conductivity for $Bi_{1-x}Pb_xCu_{1-x}SeO$ ($x = 0$, 0.02, 0.06, and 0.08) samples. In (b), literature data for other $Bi_{1-x}Pb_xCuSeO$-based oxyselenides are also shown for comparison (Chen et al.,[1] Gu et al.,[2,3] Lan et al.,[4] Lei et al.,[5] Li et al.,[6] Liang et al.,[7] Liu et al.,[8] Pan et al.,[9] Ren et al.,[10,11] Xu et al.,[12] Zhu et al.[13]); all displayed data points correspond to values obtained at 773 K.

Lattice Thermal Conductivity

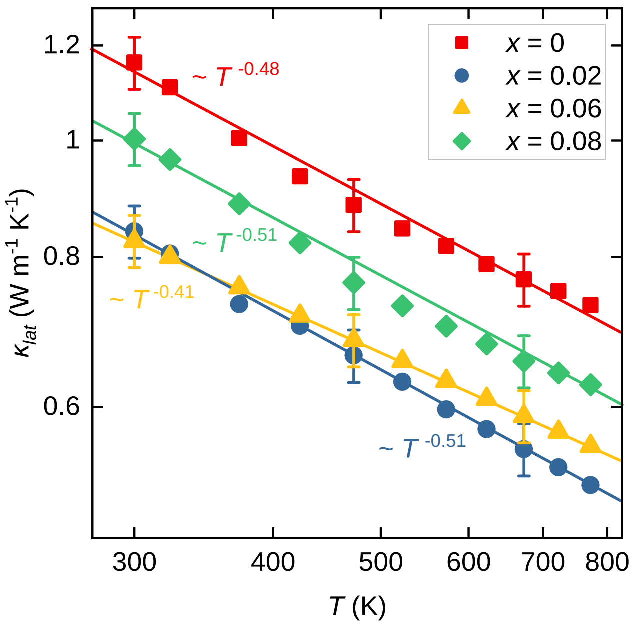

Figure S5: Temperature dependence of the lattice thermal conductivity κ_{lat} in a log–log scale for $Bi_{1-x}Pb_xCu_{1-x}SeO$ ($x = 0$, 0.02, 0.06, and 0.08) samples.

Lattice Thermal Conductivity and Figure-of-Merit

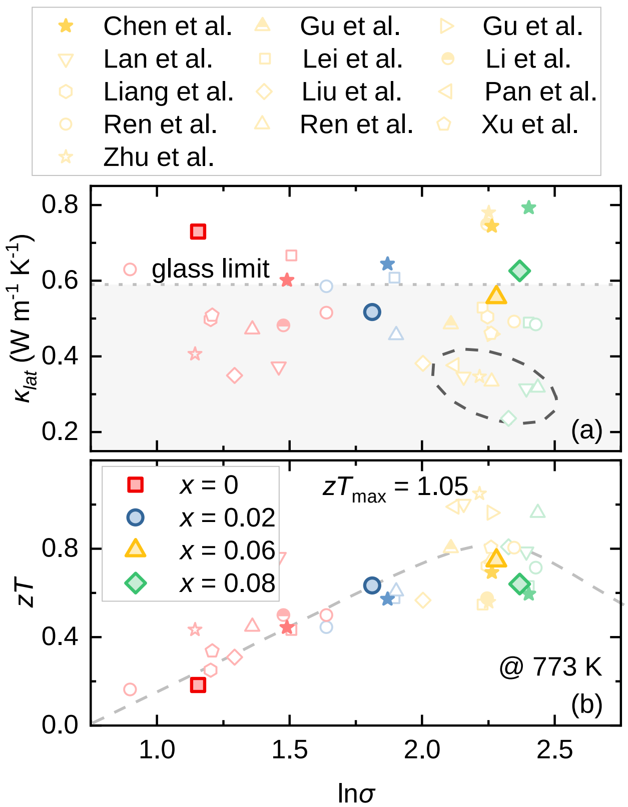

Figure S6: (a) Lattice thermal conductivity κ_{lat} and (b) figure-of-metir zT as functions of lnσ for $Bi_{1-x}Pb_xCu_{1-x}SeO$ ($x = 0$, 0.02, 0.06, and 0.08) samples. In (b), literature data for other $Bi_{1-x}Pb_xCuSeO$-based oxyselenides are also shown for comparison (Chen et al.,[1] Gu et al.,[2,3] Lan et al.,[4] Lei et al.,[5] Li et al.,[6] Liang et al.,[7] Liu et al.,[8] Pan et al.,[9] Ren et al.,[10,11] Xu et al.,[12] Zhu et al.[13]); all displayed data points correspond to values obtained at 773 K.

References

(1) Chen, Y.-X.; Shi, K.-D.; Li, F.; Xu, X.; Ge, Z.-H.; He, J. Highly enhanced thermoelectric performance in BiCuSeO ceramics realized by Pb doping and introducing Cu deficiencies. *Journal of the American Ceramic Society* **2019**, *102*, 5989–5996.

(2) Gu, Y.; Shi, X.-L.; Pan, L.; Liu, W.-D.; Sun, Q.; Tang, X.; Kou, L.-Z.; Liu, Q.-F.; Wang, Y.-F.; Chen, Z.-G. Rational electronic and structural designs advance BiCuSeO thermoelectrics. *Advanced Functional Materials* **2021**, *31*, 2101289.

(3) Gu, Y.; Ai, W.; Pan, L.; Hu, X.; Zong, P.; Chen, C.; Lu, C.; Xu, Z.; Wang, Y. High thermoelectric performance of BiCuSeO via minimizing the electronegativity difference in Bi–O layer. *Materials Today Physics* **2022**, *24*, 100688.

(4) Lan, J.-L.; Liu, Y.-C.; Zhan, B.; Lin, Y.-H.; Zhang, B.; Yuan, X.; Zhang, W.; Xu, W.; Nan, C.-W. Enhanced thermoelectric properties of Pb-doped BiCuSeO ceramics. *Advanced Materials* **2013**, *25*, 5086–5090.

(5) Lei, Y.; Zheng, R.; Yang, H.; Li, Y.; Yong, C.; Jiang, X.; Liu, R.; Wan, R. Microwave synthesis combined with SPS sintering to fabricate Pb doped p-type BiCuSeO oxyselenides thermoelectric bulks in a few minutes. *Scripta Materialia* **2021**, *199*, 113885.

(6) Li, F.; Zheng, Z.; Chang, Y.; Ruan, M.; Ge, Z.; Chen, Y.; Fan, P. Synergetic tuning of the electrical and thermal transport properties via Pb/Ag dual doping in BiCuSeO. *ACS applied materials & interfaces* **2019**, *11*, 45737–45745.

(7) Liang, X.; Xu, R.; Kong, M.; Wan, H.; Bai, W.; Dong, D.; Li, Q.; Xu, H.; Li, Z.; Ge, B.; others Raising the thermoelectric performance in Pb/In-codoped BiCuSeO by alleviating the contradiction between carrier mobility and lattice thermal conductivity. *Materials Today Physics* **2023**, *34*, 101084.

(8) Liu, Y.-c.; Lan, J.-L.; Zhan, B.; Ding, J.; Liu, Y.; Lin, Y.-H.; Zhang, B.; Nan, C.-w. Thermoelectric Properties of Pb-Doped BiCuSeO Ceramics. *Journal of the American Ceramic Society* **2013**, *96*, 2710–2713.

(9) Pan, L.; Lang, Y.; Zhao, L.; Berardan, D.; Amzallag, E.; Xu, C.; Gu, Y.; Chen, C.; Zhao, L.-D.; Shen, X.; others Realization of n-type and enhanced thermoelectric performance of p-type BiCuSeO by controlled iron incorporation. *Journal of Materials Chemistry A* **2018**, *6*, 13340–13349.

(10) Ren, G.-K.; Butt, S.; Ventura, K. J.; Lin, Y.-H.; Nan, C.-W.; others Enhanced thermoelectric properties in Pb-doped BiCuSeO oxyselenides prepared by ultrafast synthesis. *RSC advances* **2015**, *5*, 69878–69885.

(11) Ren, G.-K.; Wang, S.; Zhou, Z.; Li, X.; Yang, J.; Zhang, W.; Lin, Y.-H.; Yang, J.; Nan, C.-W. Complex electronic structure and compositing effect in high performance thermoelectric BiCuSeO. *Nature communications* **2019**, *10*, 2814.

(12) Xu, R.; Chen, Z.; Li, Q.; Yang, X.; Wan, H.; Kong, M.; Bai, W.; Zhu, N.; Wang, R.; Song, J.; others Realizing Plain Optimization of the Thermoelectric Properties in BiCuSeO Oxide via Self-Substitution-Induced Lattice Dislocations. *Research* **2023**, *6*, 0123.

(13) Zhu, H.; Li, Z.; Zhao, C.; Li, X.; Yang, J.; Xiao, C.; Xie, Y. Efficient interlayer charge release for high-performance layered thermoelectrics. *National Science Review* **2021**, *8*, nwaa085.