

## Supporting information

### Remarkable Enhancement in Thermoelectric Performance of BiCuSeO by Cu deficiencies

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## Experimental details:

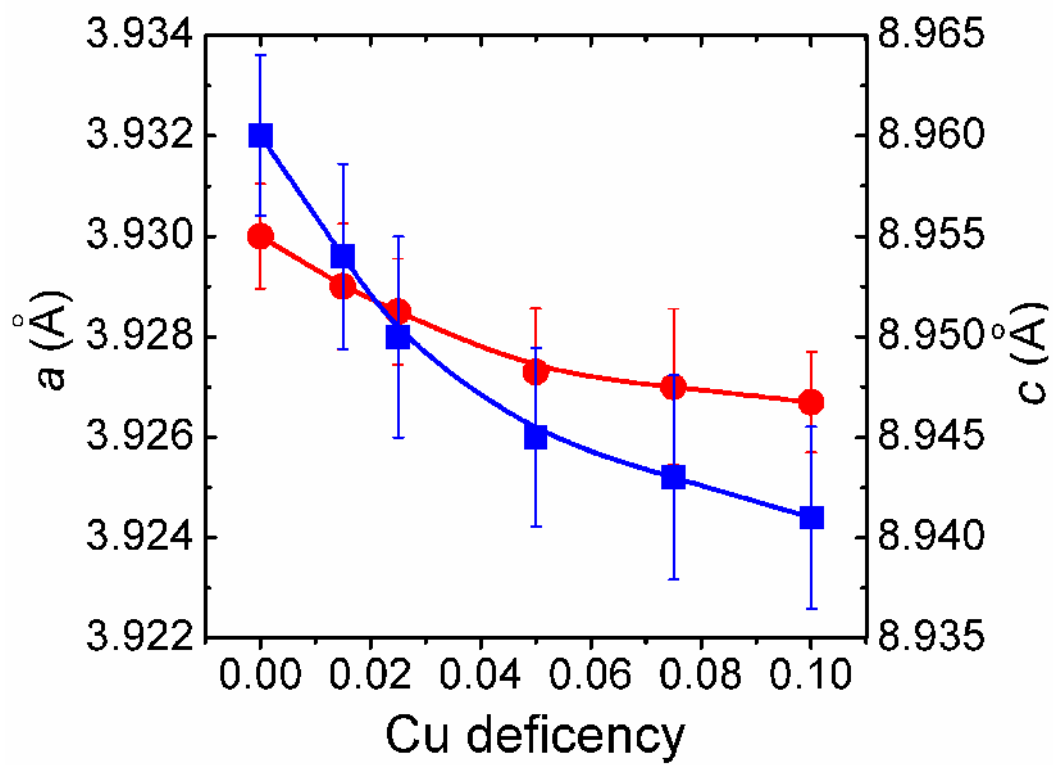
Samples with the chemical composition  $\text{BiCu}_{1-x}\text{SeO}$  ( $x = 0, 0.015, 0.025, 0.05, 0.075, \text{ and } 0.10$ ) were synthesized using a two-step solid state reaction route. Stoichiometric mixtures of  $\text{Bi}_2\text{O}_3$  (2N), Bi (4N), Cu (3N), and Se (5N) powders were thoroughly ground and heated at 300 °C for 12 h in a sealed silica tube under argon. Then, the calcined powders were ground, and heated at 700 °C for 8 h in a sealed silica tube under argon again. It is noted that the present processes required two-step heating profiles in order to avoid the presence of secondary phases such as Bi metal. The sample preparation processes including weighing raw materials and grounding powders were carried out in a pure argon-filled glove box with less than 1 ppm  $\text{O}_2$  and  $\text{H}_2\text{O}$ . All the synthesized powders were ball-milled in a planetary mill at 300 rpm for 4 h. Finally, all the bulk samples with dimensions of  $\Phi 20 \text{ mm} \times 3 \text{ mm}$  were sintered by spark plasma sintering (Sumitomo SPS1050, Japan) under 50 MPa in an argon atmosphere at 700 °C for 6 min.

The structural phases were identified using X-ray diffraction (XRD,  $\text{CuK}\alpha$ , Bruker D8, Germany). The electrical conductivity and Seebeck coefficient were measured by measurement system (ZEM-2, ULVAC-RIKO, Japan) from room temperature (RT) to 650 °C. The thermal diffusivity coefficient ( $D$ ) was measured using the laser flash method (NETZSCH, LFA457, Germany). The density ( $d$ ) of the sample was measured by the Archimedes method. The specific heat was determined by differential scanning calorimetry (NETZSCH DSC 404C Germany). The thermal conductivity ( $k$ ) was calculated from the product of thermal diffusivity, specific heat and density,  $k=D C_p d$ . Microstructure was characterized using a transmission electron microscopy (TEM, JSM-2011, Japan). The Hall coefficients,  $R_H$ , of the samples were measured at 323 K using a physical properties measurement system (PPMS-9T, Quantum Design Inc, USA), and a magnetic field of 2 T and electrical current of 30 mA were applied. The carrier concentration ( $n$ ) was calculated by  $n=1/eR_H$ , where  $e$  is the electronic charge. The carrier mobility ( $\mu$ ) was calculated by  $\mu=R_H/\rho$ , where  $\rho$  is the electrical resistivity.

**Table S1**

**Table S1:** Carrier concentration ( $\mu$ ) and carrier density ( $n$ ) at room temperature for various BiCu<sub>1-x</sub>SeO samples

Samples	BiCuSeO	BiCu <sub>0.985</sub> SeO	BiCu <sub>0.975</sub> SeO	BiCu <sub>0.95</sub> SeO	BiCu <sub>0.925</sub> SeO	BiCu <sub>0.90</sub> SeO
$n$ (10 <sup>17</sup> /cm <sup>3</sup> )	1.07	2.67	3.86	3.97	3.71	3.60
$\mu$ (cm <sup>2</sup> /Vs)	21	60	215	139	135	2



**Figure S1: Lattice parameters ( $a$  and  $c$ ) as a function of Cu deficiencies for  $\text{BiCu}_{1-x}\text{SeO}$  samples.**

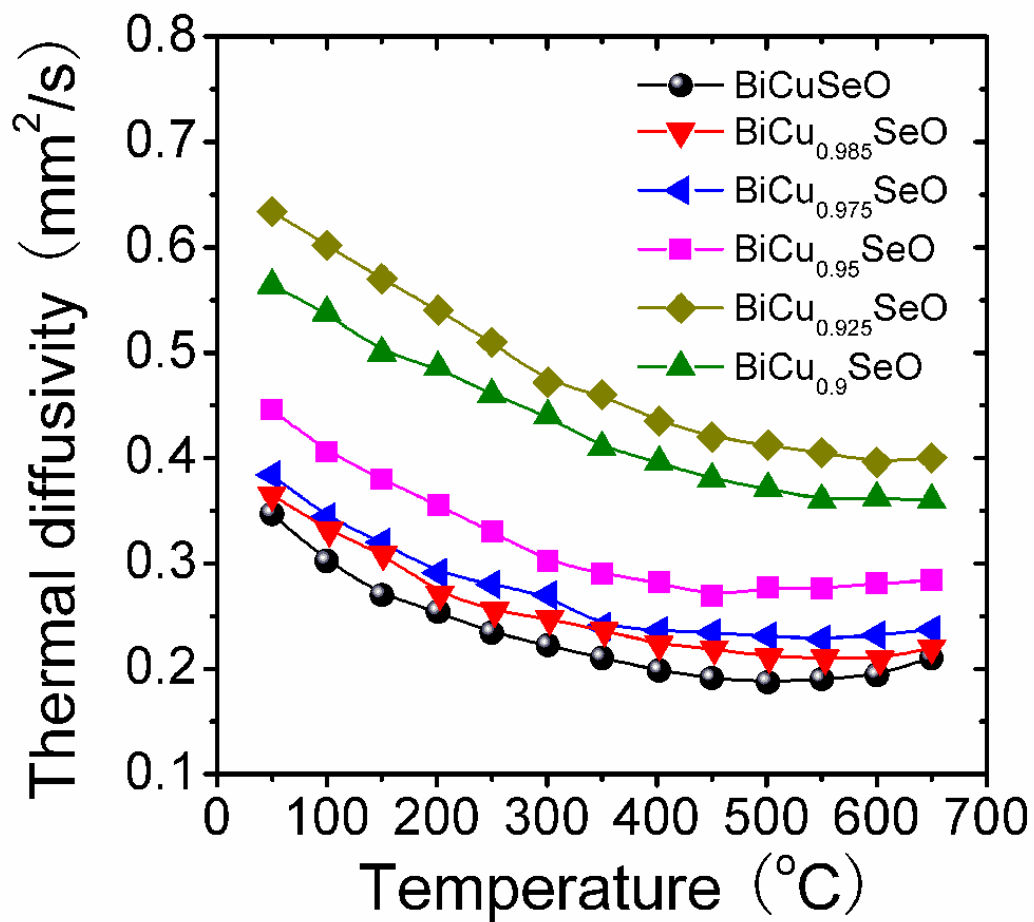


Figure S2: Temperature dependence of thermal diffusivity of BiCu<sub>1-x</sub>SeO samples.

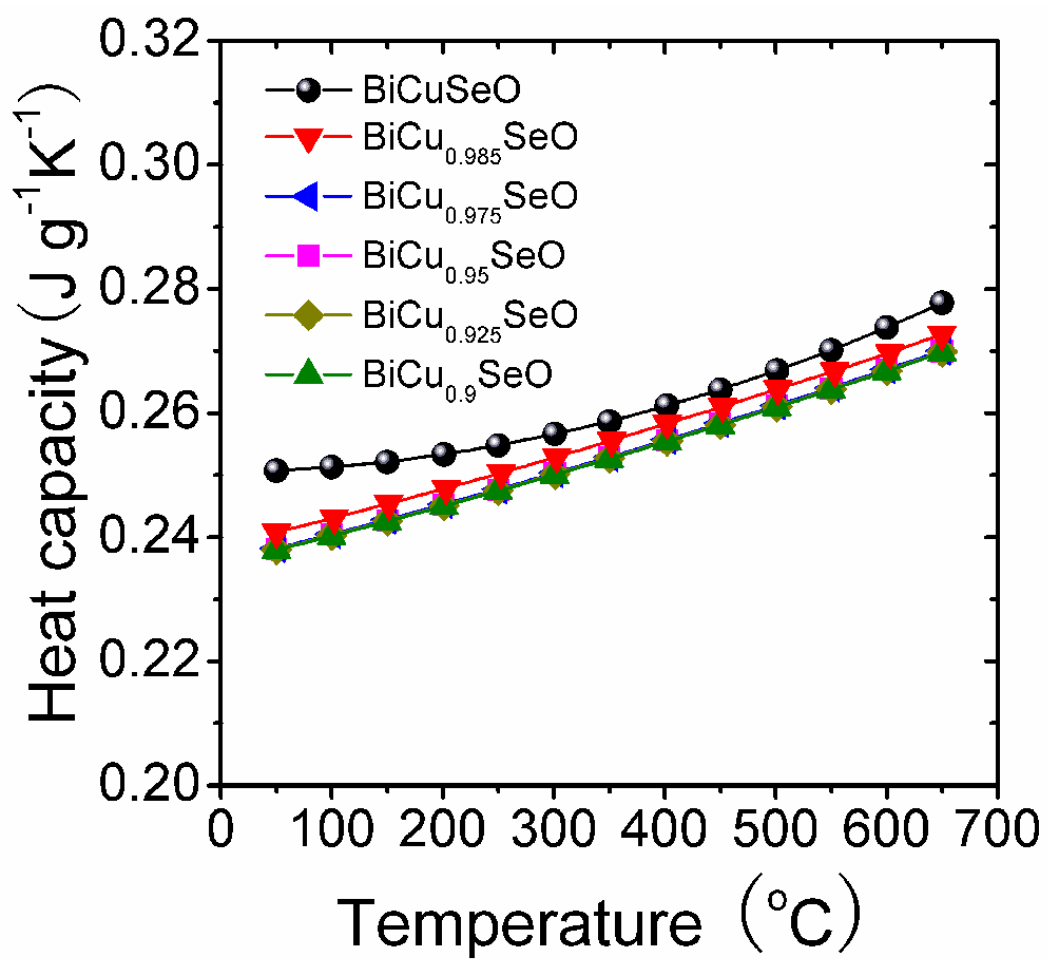
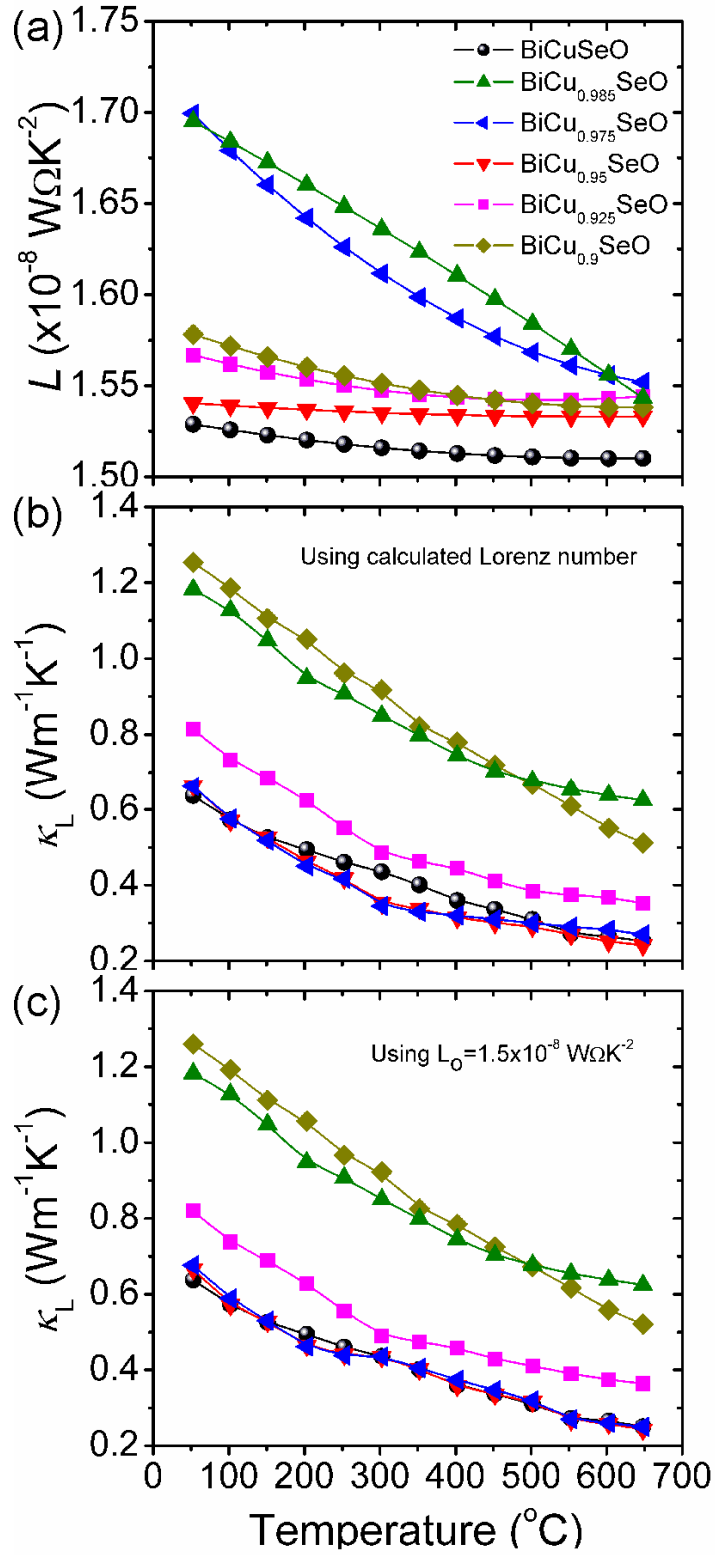


Figure S3: Temperature dependence of heat capacity of BiCu<sub>1-x</sub>SeO samples.



**Figure S4:** Temperature dependence of (a) Calculated Lorenz number, (b) lattice thermal conductivity using calculated Lorenz number, and (c) lattice thermal conductivity using  $L_0$ . (\*with Lorenz number calculation in details)

\* Lorenz number calculation in details:

The total thermal conductivity ( $\kappa_{\text{tot}}$ ) includes a sum of the electronic ( $\kappa_e$ ) and lattice thermal conductivity ( $\kappa_L$ ). The electronic part  $\kappa_e$  is directly proportional to the electrical conductivity  $\sigma$  through the Wiedemann-Franz relation,  $\kappa_e = L\sigma T$ , where  $L$  is the Lorenz number. Generally, the lattice thermal conductivity  $\kappa_L$  can be estimated by directly subtracting  $\kappa_e$  from  $\kappa_{\text{tot}}$  with using  $L_0$  ( $1.5 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$ ) for a nondegenerate semiconductor and  $L_0$  ( $2.45 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$ ) for a degenerate semiconductor. For most thermoelectric materials, the true Lorenz number is in fact lower than  $L_0$  ( $2.45 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$ ) especially at high temperature. The Lorenz number depends on the scattering parameter  $r$  and will decrease as the reduced Fermi energy  $\eta$  decreases with increasing temperature. The Lorenz number can be given as:<sup>34</sup>

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

For the Lorenz number calculation, we should get reduced Fermi energy  $\eta$  firstly; the calculation of  $\eta$  can be derived from the measured Seebeck coefficients by using the following relationship:

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

where  $F_n(\eta)$  is the  $n$ -th order Fermi integral,

$$F_n(\eta) = \int_0^{\infty} \frac{x^n}{1+e^{x-\eta}} dx \quad (3)$$

In the above equations,  $k_B$  is the Boltzman constant and  $e$  the electron. Meanwhile, acoustic phonon scattering has been assumed as the main carrier scattering mechanism, so,  $r = -1/2$ . The Lorenz number can be obtained by applying the calculated reduced Fermi energy  $\eta$  and scattering parameter  $r$  into Eq. (1). Based on the above calculation for Lorenz number, the  $\kappa_L$  can be estimated by subtracting  $\kappa_e$  from  $\kappa_{\text{tot}}$  if no bipolar diffusion exists. If bipolar diffusion takes place the electronic thermal conductivity  $\kappa_e$  will be overestimated when both holes and electrons are present at high temperature, and an extra term (bipolar thermal conductivity,  $k_{\text{bipolar}}$ )



then needs to be added to the total thermal conductivity. Here, no upturn at high temperature was observed for any of the Cu deficiencies samples, indicating that bipolar diffusion is negligible at these doping levels and temperatures.