Supplementary information for "Thermoelectric properties of n-type $Bi_4O_4SeX_2$ (X = Cl, Br)"

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I. HALL RESISTIVITY

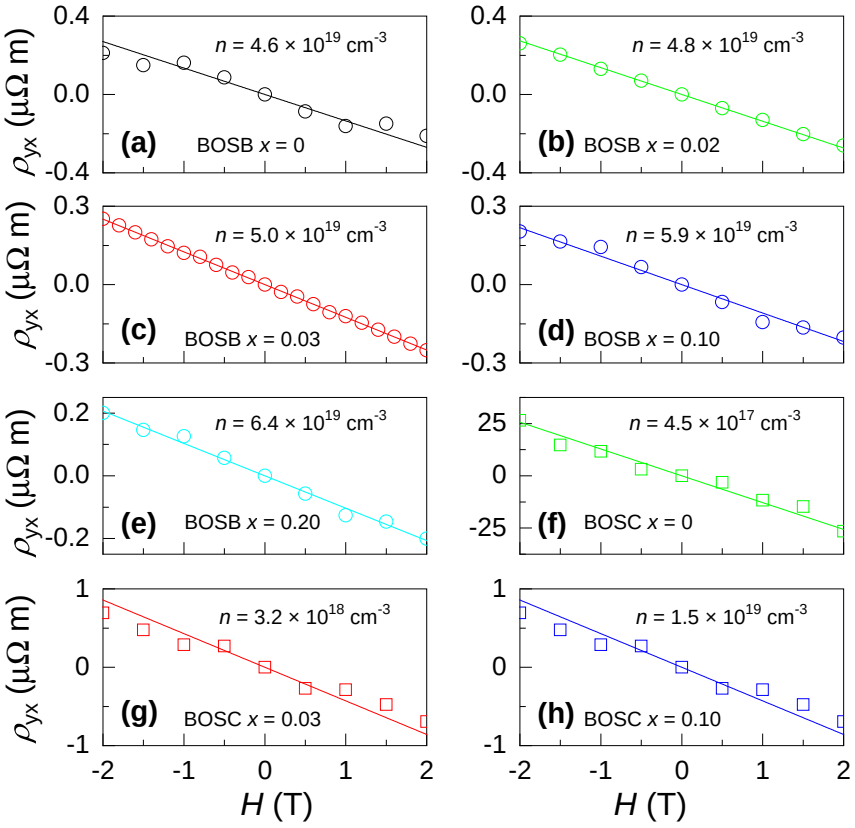

Figure S1. Hall resistivity at 300 K for BOSB and BOSB (x = 0, 0.02, 0.03, 0.10, 0.20).

Fig. S1 presents the Hall resistivity (ρ_{yx}) for all samples at room-temperature. The negative slope (ρ_{yx}/B) demonstrates that electrons dominate the electrical transport. The carrier concentration (n) is estimated by a single-band model $n = \frac{1}{R_{\mathrm{H}}e}$, where R_{H} is the hall coefficient.

II. XRD REFINEMENT PATTERNS

Fig. S2 shows the Rietveld refinement XRD patterns of ten samples, the refinement software is FullProf Suite, XRD peak shape is fitting by Pseudo-Voigt function, the refinement results (R_{p}, R_{wp}) have been achieved by least-squares technique and shown in each figure.

Table S1 and Table S2 show the BOSX crystalline information, due to same space group ($I4/mmm$) and similar atomic occupancy as well lattice constants (See table 1 of main text), there is only a slight difference in the angle of the peak position for BOSB and BOSC.

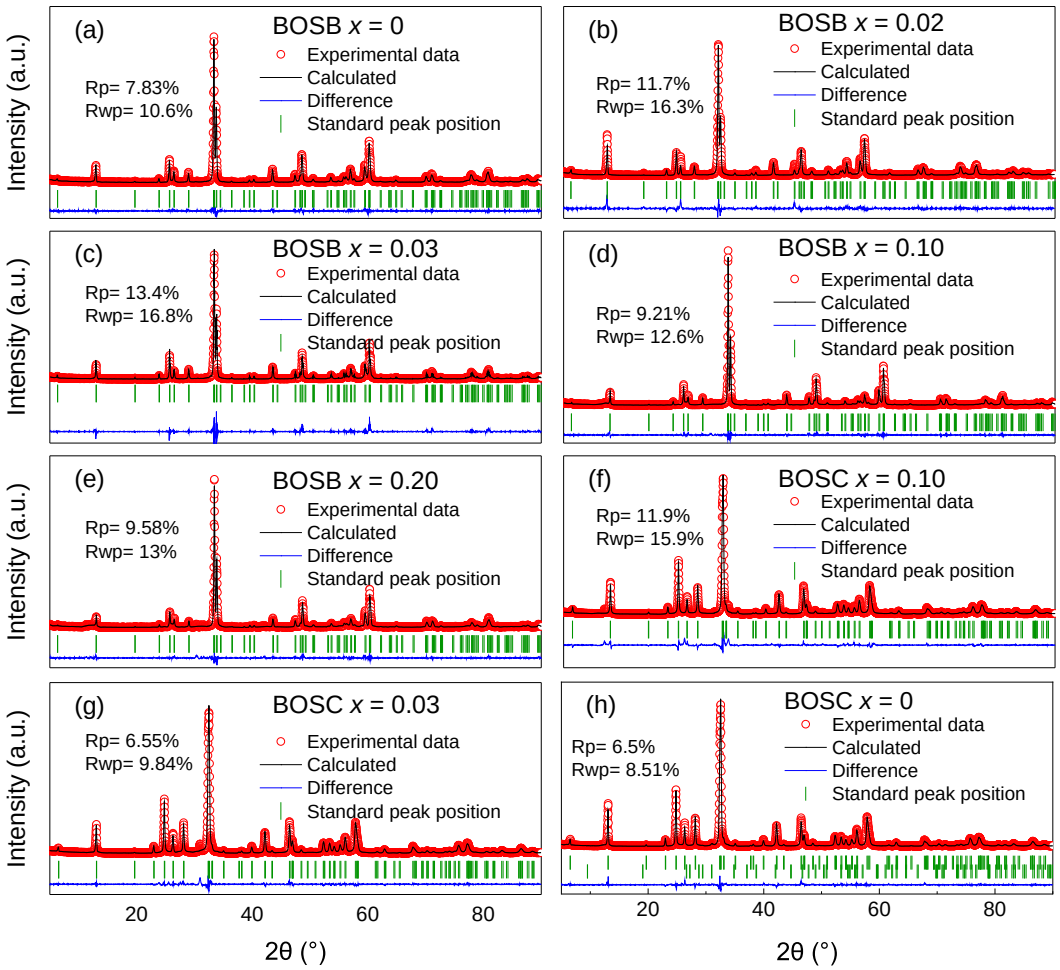

Figure S2. XRD refinement patterns of BOSX (X = Cl, Br; $x = 0, 0.02, 0.03, 0.10, 0.20$).

Table S1. BOSB crystalline information

Number	Element	Label	x	y	z	Occ.	U	Site	Sym
1	Bi	Bi1	1.00000	1.00000	0.56827	1.00000	0.00700	4e	4mm
2	Bi	Bi2	0.50000	0.50000	0.66148	1.00000	0.01300	4e	4mm
3	Se	Se1	0.50000	0.50000	0.50000	0.52000	0.00800	2a	4/mmm
4	Se	Se2	1.00000	1.00000	0.70961	0.24200	0.00900	4e	4mm
5	O	O1	0.50000	1.00000	0.61190	1.00000	0.00800	8g	2mm
6	Br	Br1	0.50000	0.50000	0.50000	0.48000	0.00800	2a	4/mmm
7	Br	Br2	1.00000	1.00000	0.70961	0.75800	0.00900	4e	4mm

Space group $I4/mmm$, BOSB lattice constants $a = b = 3.93007$ Å

$c = 28.1763$ Å, $V = 435.196$ Å^3, $\rho_{density} = 8.6899$ g/cm^3

Table S2. BOSC crystalline information

Number	Element	Label	x	y	z	Occ.	U	Site	Sym
1	Bi	Bi1	1.00000	1.00000	0.56819	1.00000	0.007	4e	4mm
2	Bi	Bi2	0.50000	0.50000	0.65656	1.00000	0.01300	4e	4mm
3	Se	Se1	0.50000	0.50000	0.50000	0.59000	0.00800	2a	4/mmm
4	Se	Se2	1.00000	1.00000	0.70662	0.21000	0.00900	4e	4mm
5	O	O1	0.50000	1.00000	0.60895	1.00000	0.00800	8g	2mm
6	Cl	Cl1	0.50000	0.50000	0.50000	0.41000	0.00800	2a	4/mmm
7	Cl	Cl2	1.00000	1.00000	0.70662	0.79000	0.00900	4e	4mm

Space group $I4/mmm$, BOSC lattice constants $a = b = 3.89373$ Å

$c = 27.02904$ Å, $V = 410.84$ Å^3, $\rho_{density} = 8.4862$ g/cm^3

III. CALCULATION OF EFFECTIVE MASS AND LORENZ NUMBER

In the context of the single parabolic band assumption, the effective mass (m^*) and Lorenz number (L) can be determined by the following expressions:

$$m^* = \frac{h^2}{2k_{\mathrm{B}}T}\left[\frac{n}{4\pi F_{1/2}(\eta)}\right]^{2/3} \tag{1}$$

$$S = \pm\frac{k_{\mathrm{B}}}{e}\left[\frac{(r+5/2)\,F_{r+3/2}(\eta)}{(r+3/2)\,F_{r+1/2}(\eta)} - \eta\right] \tag{2}$$

$$F_n(\eta) = \int_0^\infty \frac{\chi^n}{1+\exp(\chi-\eta)}\mathrm{d}\chi \tag{3}$$

$$L = \left(\frac{k_{\mathrm{B}}}{e}\right)^2\left\{\frac{(r+7/2)F_{5/2+r}(\eta)}{(r+3/2)F_{1/2+r}(\eta)} - \left[\frac{(r+5/2)F_{3/2+r}(\eta)}{(r+3/2)F_{1/2+r}(\eta)}\right]^2\right\} \tag{4}$$

where η denotes the reduced Fermi level, which is calculated as the ratio of Fermi energy E_{F} to $k_{\mathrm{B}}T$ (the Boltzmann constant multiplied by the temperature in Kelvin). The remaining physical parameters used in the equations include h (the Planck constant), F_n (the nth order Fermi integral), χ (reduced energy, defined as $\chi = E/k_{\mathrm{B}}T$) and e (the elementary charge). Additionally, the scattering exponent $r = -1/2$, where Acoustic Phonon Scattering (APS) is the dominant carrier scattering mechanisms in the samples.

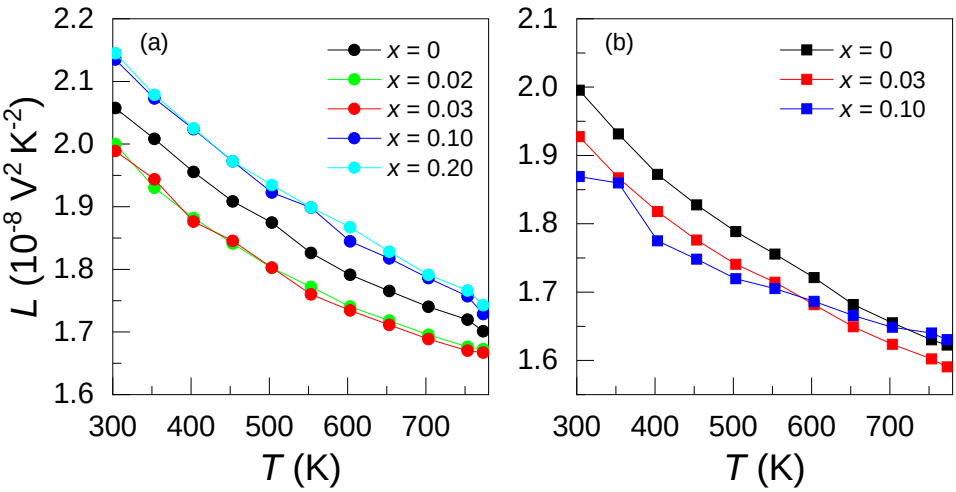

Figure S3. The temperature-dependent the Lorentz number for BOSC and BOSB ($x = 0$, 0.02, 0.03, 0.10, 0.20).

IV. ELASTIC CONSTANTS

For BOSC with $I4/mmm$ space group, there are six independent elastic constants C_{11}, C_{12}, C_{13}, C_{33}, C_{44} and C_{66} corresponding to 144.83, 71.69, 39.83, 63.72, 21.16 and 58.89 GPa. The elastic stability criteria for tetragonal crystal system are shown as follows[1]:

$$C_{11} > |C_{12}| \tag{5}$$

$$2 * C_{13}^2 < C_{33} * (C_{11} + C_{12}) \tag{6}$$

$$C_{44} > 0 \tag{7}$$

$$C_{66} > 0 \tag{8}$$

Average mechanical properties[2] of bulk BOSC polycrystal include bulk modulus (B) 57.54 GPa, shear modulus (G) 27.77 GPa, longitudinal velocity (v_l), transverse sound velocity (v_t) and average sound velocity (v_a) [3], which can be calculated by formula (9)-(13).

$$B = (2C_{11} + C_{33} + 2C_{12} + 4C_{13})/9 \tag{9}$$

$$G = (2C_{11} + C_{33} - C_{12} - 2C_{13} + 6C_{44} + 3C_{66})/15 \tag{10}$$

$$v_\mathrm{l} = \sqrt{\frac{(B + (4/3)G)}{\rho_\mathrm{density}}} \tag{11}$$

$$v_\mathrm{t} = \sqrt{\frac{G}{\rho_\mathrm{density}}} \tag{12}$$

$$v_{\mathrm{a}} = \left[\frac{1}{3}\left(\frac{1}{v_{\mathrm{l}}^3} + \frac{2}{v_{\mathrm{t}}^3}\right)\right]^{-\frac{1}{3}} \tag{13}$$

References

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[3] Y. Duan, Y. Sun, M. Peng, and S. Zhou, J. Alloys Compd. **595**, 14 (2014).