Supporting Information

Thermoelectric behavior of $(Ba_{0.2}Sr_{0.2}Ca_{0.2}La_{0.2}Na_{0.2})CoO_3$ high entropy cobaltate-based perovskite

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S1. Calculation of thermal enthalpy and thermal entropy:

(i) $SrCO_3$:

Change in enthalpy (ΔH) and entropy (ΔS) of $SrCO_3$ follows the following equations:

$$\Delta H_{SrCO3} = 21.42T + 4.28 \times 10^{-3}T^2 + 3.396 \times 10^{5}T^{-1} - 7905 \ldots (S1)$$

$$\Delta S_{SrCO3} = 21.42lnT + 8.56 \times 10^{-3}T + 1.698 \times 10^{5}T^{-2} \ldots (S2)$$

The change in enthalpy for $SrCO_3$ cannot be obtained simply by extrapolating S1 up to 1323K, because of a phase transition of $SrCO_3$ at 1197 K. Orthorhombic $SrCO_3$ transitions to Hexagonal crystal structure at 1197 K. That's why ΔH_{SrCO3} has been calculated as-

$$\Delta H_{SrCO3,1323} = \Delta H_{298K \rightarrow 1323K} + \Delta H_{orthorhombic \rightarrow hexagonal,at1197K}.$$

$$= 139 \text{ KJ/mol} \ldots (S3)$$

Similarly, ΔS_{SrCO3} has been calculated as-

$$\Delta S_{SrCO3,1323} = \Delta S_{298K \rightarrow 1323K} + \Delta S_{orthorhombic \rightarrow hexagonal,at1197K}.$$

$$= 128.77 \text{ J/mol-K} \ldots (S4)$$

(ii) $BaCO_3$:

$$\Delta H_{BaCO3} = 20.77T + 5.85 \times 10^{-3}T^2 + 2.86 \times 10^{5}T^{-1} - 7670 \ldots (S5)$$

$$\Delta S_{BaCO3} = 20.77lnT + 11.7 \times 10^{-3}T + 1.43 \times 10^{5}T^{-2} \ldots (S6)$$

The phase transitions occur at 1079 K and 1241 K for $BaCO_3$. As a result of that ΔH_{BaCO3} and ΔS_{BaCO3} can be written as a similar fashion to that of equation S3 and S4.

$$\Delta H_{BaCO3,1323} = \Delta H_{298K \rightarrow 1323K} + \Delta H_{orthorhombic \rightarrow hexagonal,at1079K} + \Delta H_{hexagonal \rightarrow cubic,at1241K}$$

$$= 152.57 \text{ KJ/mol} \ldots (S7)$$

$$\Delta S_{BaCO3,1323} = \Delta S_{298K \rightarrow 1323K} + \Delta S_{orthorhombic \rightarrow hexagonal,at1079K} + \Delta S_{hexagonal \rightarrow cubic,at1241K}$$

$$= 129.08 \text{ J/mol-K} \ldots (S8)$$

(iii) La_2O_3:

$\Delta H_{La_2O_3,1323} = [28.86T + 0.0015T^2 + 3.275 \times 10^5 T^{-1} - 9971]_{T=1323K}$=131.67 KJ/mol …(S9)

$\Delta S_{La_2O_3,1323} = [28.86lnT + 0.003076T + 1.63 \times 10^5 T^{-2}]_{T=1323K}$= 192.45 J/mol-K …(S10)

(iv) $CaCO_3$:

$\Delta H_{CaCO_3,1323}$=$\left[-184.79T + 0.162T^2 + 3.688 \times 10^6 T^{-1} - (4.3 \times 10^{-5})T^3 + 7767T^{\frac{1}{2}} - 104608\right]_{T=1323K} = 120.19\ KJ/mol$ …(S11)

$\Delta S_{CaCO_3,1323} = \left[-184.79lnT + 0.323T + 1.844 \times 10^6 T^{-2} - (0.6485 \times 10^{-4})T^2 - 7767T^{-\frac{1}{2}} + 1478\right]_{T=1323K}$=164.13 J/mol-K …(S12)

(v) Na_2CO_3 and Co_3O_4:

The fitting parameters for the calculation of ΔH and ΔS for Na_2CO_3 and Co_3O_4 in the temperature range 298 K to 1323 Khas been tabulated in table S1, which follows equation 2 and 3 of the main manuscript.

Table S1. The values of A, B, C, D, E, F, G and H_f of Na_2CO_3 and Co_3O_4.

Oxides	Temp, Range	A	B	C	D	E	F	G	H_f
Na_2CO_3	298-723	175.2	-348.1	743.1	-305.6	-1.63	-1179	415.06	-1130.7
	723-1123	-1067	2469.3	-1829.1	505.7	100.2	-607.1	-1356.4	
	1123-1323	189.5	-7×10^{-6}	2×10^{-6}	-5.2×10^{-9}	3×10^{-6}	-1183.1	343	
Co_3O_4	298-1323	177.095	-100.43	185.78	-49.05	-3.48	-971.54	331.28	-910

By putting the fitting parameter values from the table, change of enthalpy for Na_2CO_3 ($\Delta H_{Na_2CO_3,1323}$) and Co_3O_4 ($\Delta H_{Co_3O_4,1323}$) has been calculated in equation S13 and S14.

$\Delta H_{Na_2CO_3,1323} = 176.4\ KJ/mol$ … $(S13)$

$\Delta H_{Co_3O_4,1323} = 194.2\ KJ/mol$ … $(S14)$

Similarly, entropy change for the above-mentioned oxides has been written in equation S15 and S16.

$\Delta S_{Na_2CO_3,1323} = 256.2\ J/mol\ K$ ... $(S15)$

$\Delta S_{Co_3O_4,1323} = 251\ J/mol\ K$ ... $(S16)$

(vi) HEP:

Table S2: Variation of specific heat with temperature.

Temperature (t=T/1000) (K)	**Specific heat (J/mol K)**
0.37341	152.58626
0.42324	141.75865
0.47328	135.30894
0.52331	125.85744
0.57319	122.80999
0.62318	120.30945
0.67306	115.57576
0.72325	109.89884
0.77301	114.46133
0.82323	117.8193
0.87323	123.07239
0.92331	123.20704
0.97311	126.40214
1.023	126.40214

S2. Thermal conductivity:

To evaluate the thermal conductivity of the BSCLN sample thermal diffusivity (D), specific heat (C_p) and density (ρ) are measured in the temperature range of 323 K to 1023 K. Thermal conductivity is calculated by using the following equation (S17):

$$K = \rho C p D \ldots (S17)$$

Wiedemann Franz law (ke = LσT) has been used to calculate the electronic thermal conductivity of the BSCLN sample where the temperature dependent Lorentz number has been calculated using the equation (S18):

$$L = 1.5 + exp\left[-\frac{|S|}{116}\right] \ldots (S18)$$

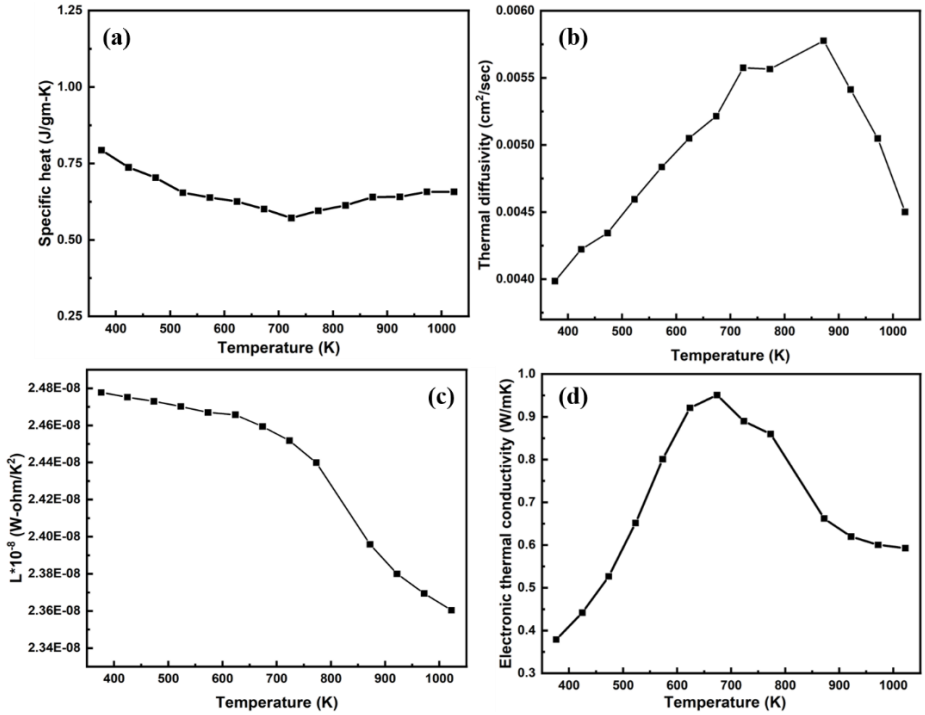

Fig. S1: (a) Specific heat (C_p), (b) thermal diffusivity (D), (c) Lorentz's number and (d) electronic thermal conductivity of BSCLN ceramics.