Supporting Information

Designing Rare Earth Free High Entropy Oxide with Tungsten Bronze Structure for Thermoelectric Application

*Subhra Sourav Jana and Tanmoy Maiti**

Plasmonics and Perovskites Laboratory, Department of Materials Science and Engineering,

IIT Kanpur, U.P. 208016, India.

Experimental methods:

$(SrBaLiKNa)_{0.2}Nb_2O_6$ has been synthesized through solid state processing technique using stoichiometric ratio of $SrCO_3$ (Sigma-Aldrich), $BaCO_3$ (Sigma-Aldrich), Li_2CO_3 (Sigma-Aldrich), Na_2CO_3 (Sigma-Aldrich), K_2CO_3 (Sigma-Aldrich) and Nb_2O_5 (Sigma-Aldrich). All the precursor raw materials have been mixed properly in alcohol medium using ZrO_2 balls as grinding media. The powder mixture is calcined at $1423K$ for 8 hours in reducing atmosphere. The calcined powder is vigorously ground and the final powder is pressed into $15mm$ diameter pellets under application of 8 tons of load. The green pellets are finally sintered in $1473K$ for 10 hours in reducing atmosphere.

* Corresponding author Telephone: +91-512-259-6599; Email address: tmaiti@iitk.ac.in

Crystal structure of the sintered pellet has been determined using Pan analytical XRD with Cu Kα radiation. Microstructure of the fractured sample has been examined using Nova NanoSEM 450 (FESEM) at IIT Kanpur. Further, nanoscale structure has been observed under FEI-Titan G2 60-300 KV TEM (HRTEM, IIT Kanpur). Oxidation states of elements have been identified by X-ray Photoelectron Spectroscopy (PHI 5000 Versa Probe II, FEI Inc., IIT Kanpur). The pellet is machined in the dimension of $3mm \times 3mm \times 12mm$ for the thermoelectric measurement. Electrical conductivity and Seebeck coefficient have been measured in ZEM-3M10R, ULVAC-RICO Inc. apparatus, IIT Kanpur. Thermal diffusivity and specific heat capacity have been estimated using TC-1200RH and ADVANCE RIKO and HDSC PT 1600 (LINSEIS), respectively.

Thermodynamic Calculation:

The coefficient required for calculation of enthalpy and entropy change have been estimated by fitting Cp with the equation (4) in manuscript. The fitted curve for HETB is shown in **fig.S1**.

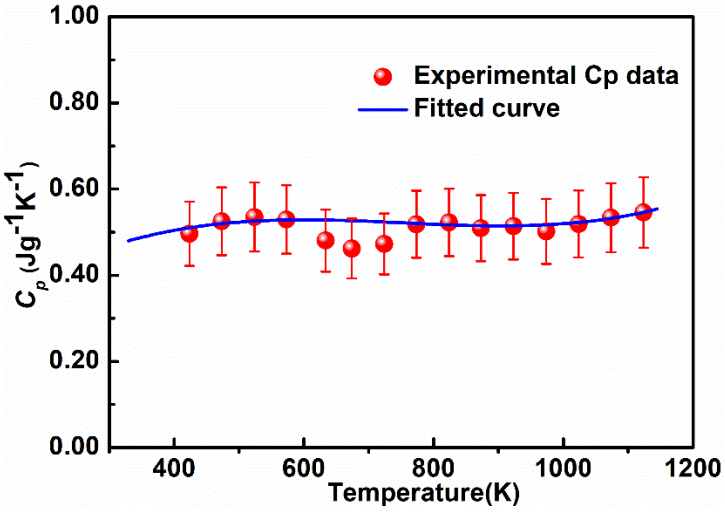

Fig.S1: Fitting curve of specific heat (Cp) for *HETB*.

Table S1: A, B, C, D, E, F, G and H_f of all the precursor oxides including *HETB*.

Oxides	A	B	C	D	E	F	G	H_f
Li_2O	68.69	5.46	23.18	9.49	-1.60	-625.03	109.39	598.73
Na_2O	2240.95	-3209.97	1803.69	-359.07	-386.24	-1877.63	2421.66	-417.98
K_2O	72.55	41.39	0.72	0.21	0.06	-386.16	170.56	363.17
BaO	47.42	13.13	3.79	0.72	-0.33	-563.93	123.79	-548.10
SrO	48.55	8.74	0.89	0.11	-0.50	-608.63	108.74	-592.03
Nb_2O_5	116	117.18	-71.76	15.30	-1.16	-1942.64	239.33	-1899.54
HETB	30	325	-446	196	0.01	1463.44	220	-1443.65

Table S2: Mixing enthalpy of binary alloys

Binary alloys	ΔH_{AB}^{mix}
Na-Li	3.43
Na-K	1.515
Na-Sr	-1.756
Na-Ba	-2.595
Li-K	10.892
Li-Sr	-0.277
Li-Ba	-0.143
K-Sr	7.248
K-Ba	5.93
Sr-Ba	0.042

Crystal structure analysis:

Table S3: Refined parameters of *HETB*

Elements	**x(±0.0001)**	**y(±0.0001)**	**z(±0.0001)**
Sr/Ba/Na/K/Li	0	0	0
Sr/Ba/Na/K/Li	0.17282	0.67282	0.0031
Sr/Ba/Na/K/Li	0.3152	0.1558	0.9997
Nb1	0.0746	0.2114	0.4994
Nb2	0.5	0	0.502
O1	0.3438	0.0055	0.4456
O2	0.139	0.0682	0.4626
O3	0.7195	0.2195	0.4766
O4	0.0165	0.5165	0.9857
O5	0.0988	0.1928	0.0028
O6	0.0542	0.217	0.0211
Space group		P4bm	
Crystal structure		Tetragonal	
Lattice parameter		a=b=12.4756Å(±0.0002), c=3.9568Å (±0.0002)	
Reliability parameters		R_{exp}=4.6, R_p=4.3, R_{wp}= 5.6, $\chi = 1.46$	

XPS analysis:

Table S4: Oxidation states and binding energies of Nb and O, as estimated from the XPS analysis.

Element	**Bond**	**Binding Energy (eV) (± 0.5)**	**% Area (± 2)**
Nb	$Nb^{+4}3d_{5/2}$	206.26	23
	$Nb^{+5}3d_{5/2}$	207.22	42
	$Nb^{+4}3d_{3/2}$	209.15	12
	$Nb^{+5}3d_{3/2}$	209.9	23
O	O1s	529.3	77
	Oxygen vacancy	531.27	12
	Adsorped O	532.07	11

Thermal transport:

Thermal conductivity is computed using the equation S(2)

$$\text{Thermal conductivity, } \kappa = D\rho C_p \ldots\ldots\ldots (S1)$$

Specific heat (C_p) and thermal diffusivity (D) of *HETB* are measured, as shown in fig.S2(a&b). Lorenz number (fig.S2(c)) has been calculated from Seebeck coefficient to estimate the κ_e. κ_e with temperature of HETB has been presented in fig.S2(d).

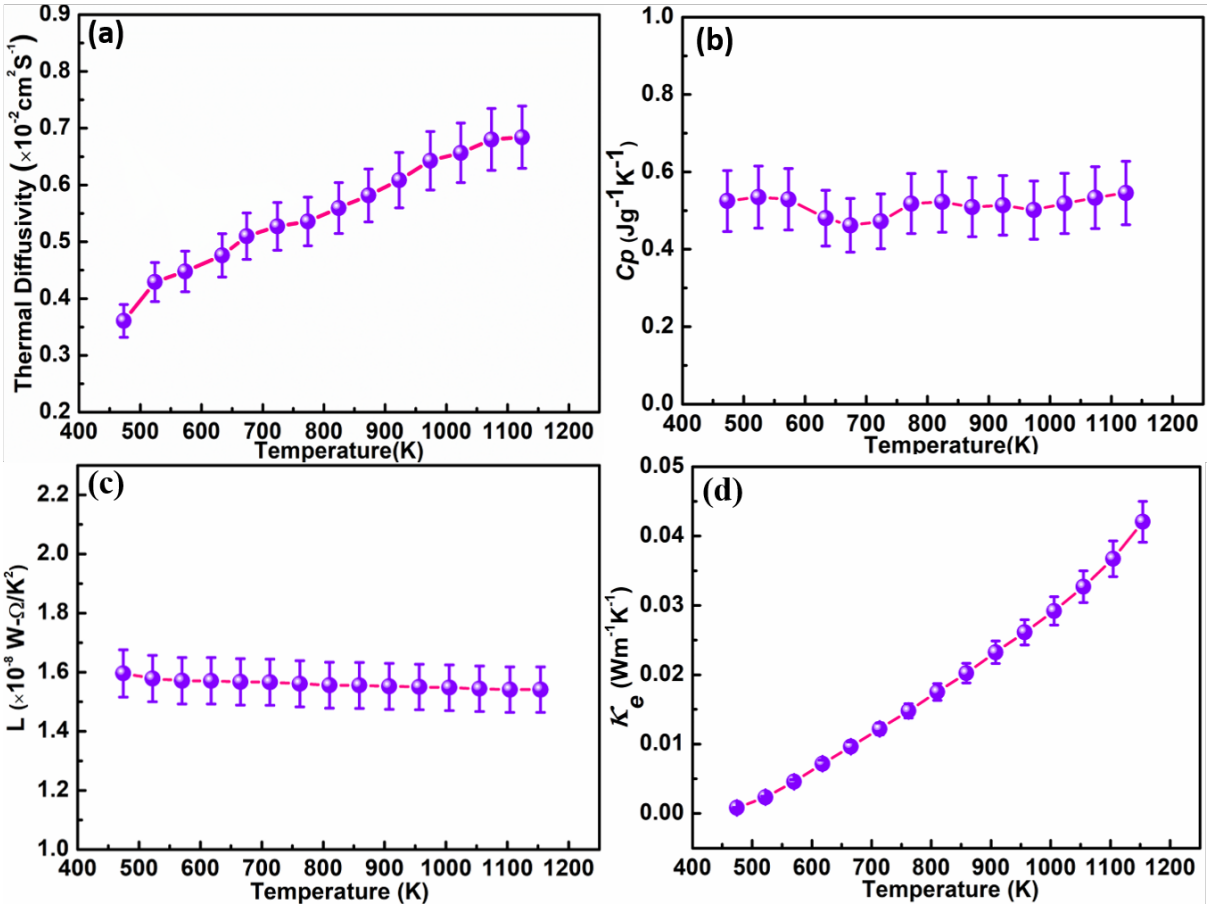

Fig.S2: (a) Thermal diffusivity (b) specific heat (c) Lorenz number and (d) κ_e of *HETB* with temperature

Determination of mean velocity (υ_m)

Mean velocity (υ_m) of sound within the material has been estimated using nano hardness measurement (applying a load of 1 mN using a Nano-Indentor). The following four equations are used to compute υ_m.[1]

$$\text{Poisson}'\text{sratio}, \nu = \frac{(3B - 2G)}{(6B + 2G)} \ldots\ldots\ldots\ldots\ldots (S2)$$

B and G are Bulk modulus Shear modulus, respectively.

$$\upsilon_m = \left[\frac{1}{3}\left(\frac{2}{\upsilon_t^3} + \frac{1}{\upsilon_l^3}\right)\right]^{-\frac{1}{3}} \ldots\ldots\ldots\ldots\ldots (S3)$$

Where, υ_l & υ_t are longitudinal and transverse velocity, respectively.

$$\upsilon_l = \left(\frac{B + \frac{4}{3}G}{\rho}\right)^{1/2} \ldots\ldots\ldots\ldots\ldots (S4)$$

$$\upsilon_t = \left(\frac{G}{\rho}\right)^{1/2} \ldots\ldots\ldots\ldots\ldots (S5)$$

Where, ***h***= Planck's constant, ***ρ*** = density

Table S5*:* The values of Bulk modulus *(B),* Shear modulus *(G),* longitudinal *(v_l),* transverse (v_t)**,** mean velocity(v_m), as calculated for *HETB* system.

B (Gpa)	G (GPa)	Density (Kg/m^3)	v_l (m/s)	v_t (m/s)	v_m (m/s)
34 ± 3	22 ± 2	4700±50	3675 ±180	2171 ± 100	2405 ± 120

Reference:

1. Anderson, O.; Schreiber, E.; Soga, N., Elastic Constants and Their Measurements. McGraw-Hill, New York: 1973.