

## Supporting Information

### Tailoring high-temperature stability and electrical conductivity of high entropy lanthanum manganite for solid oxide fuel cell cathodes

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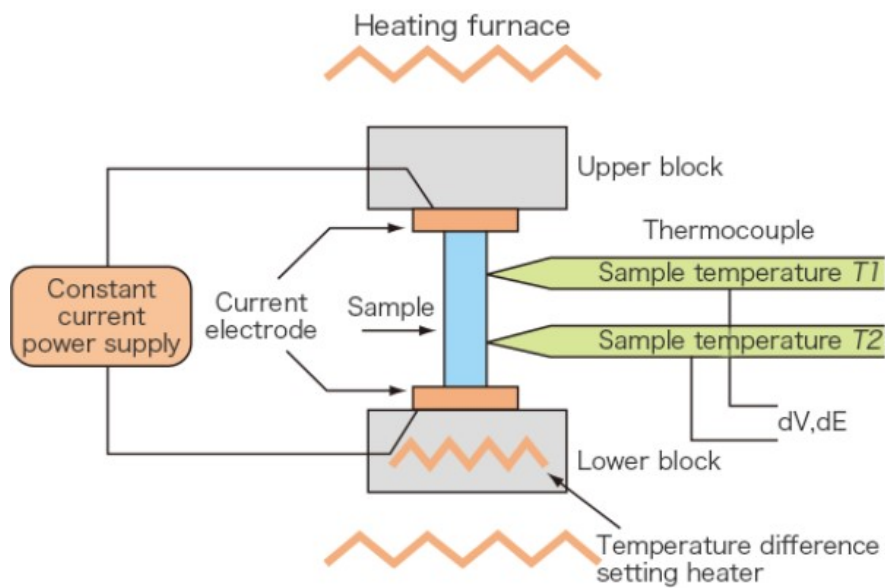
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**Table S1** Average particle/ grain sizes and corresponding calcination/ sintering parameters of single-phase HEALMO and LSM82 powders and pellets. The calcination temperature was chosen as the minimum temperature at which a single-phase structure can be obtained after the precursor was calcinated for 2 h.

Composition	Powder		Pellet	
	Average particle size (nm)	Calcination parameter	Average grain size ( $\mu\text{m}$ )	Sintering parameter
HEALMO-1	520	1200°C for 2 h	3.85	1400°C for 10 h
HEALMO-2	360	1200 C for 2 h	4.28	1400°C for 10 h
HEALMO-3	220	1100 C for 2 h	1.75	1300°C for 10 h
LSM82	660	Unknown	10.74	1400°C for 5 h



**Fig. S1** Schematic diagram of electrical conductivity measurement via Seebeck coefficient/ electrical resistance measuring system, in which the current electrodes and thermocouples are made of platinum-rhodium alloy. The two parallel thermocouples are used to measure the voltage drop, and the corresponding parallel distance is 6 mm.

ADVANCE RIKO, Inc., <https://advance-riko.com/en/products/zem-3/>, (accessed September 2021).

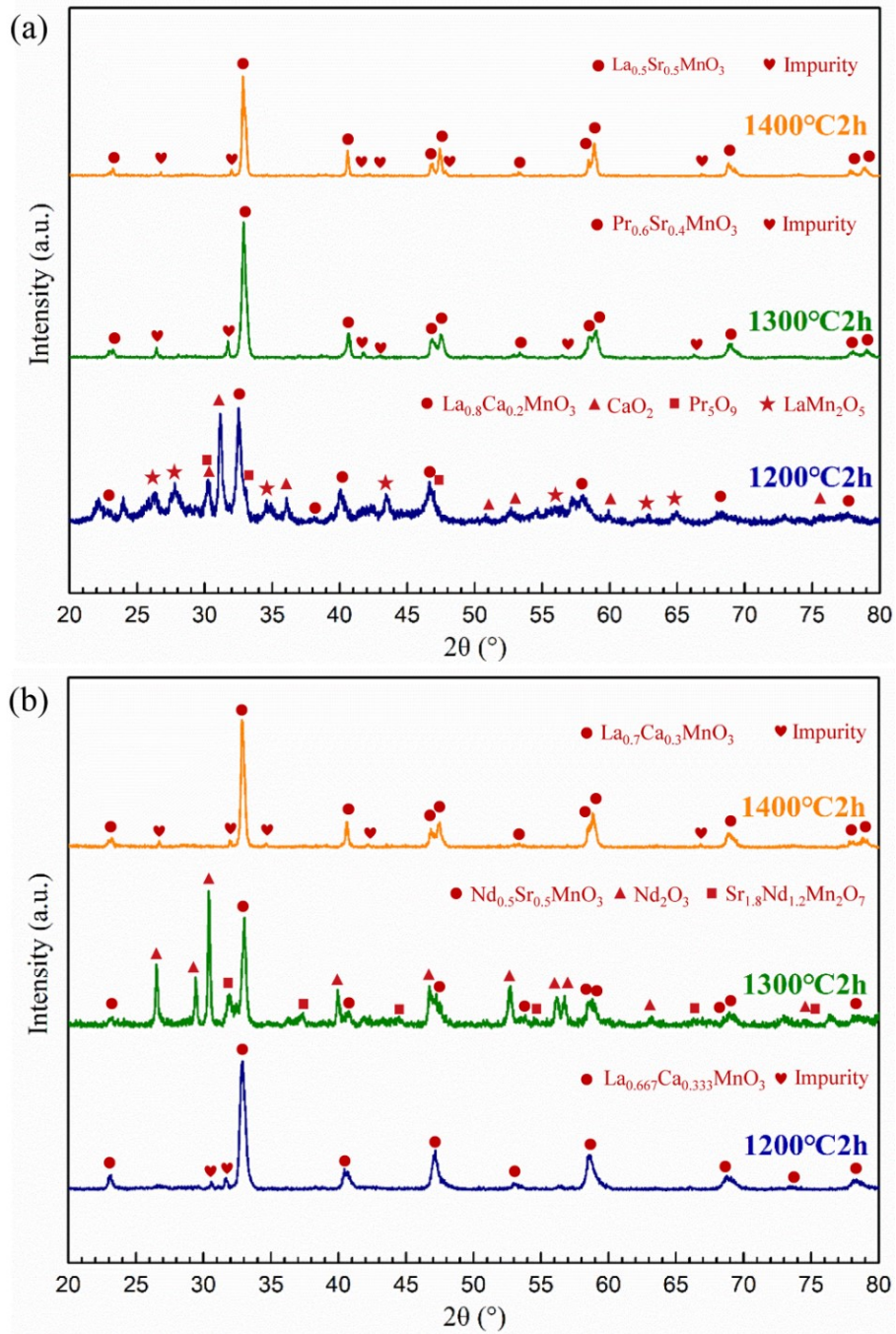
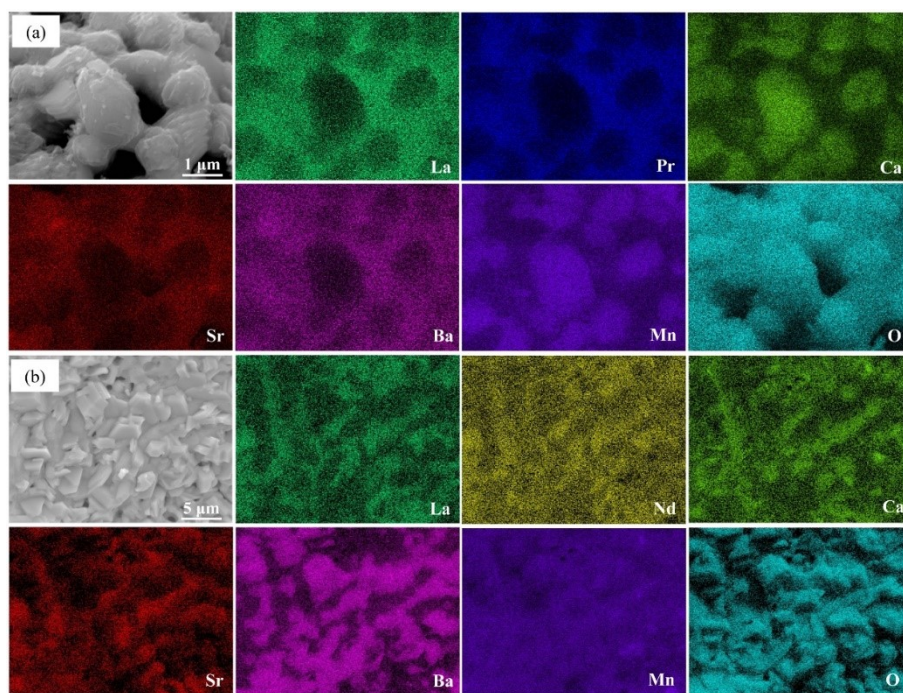


Fig. S2 XRD patterns of non-single-phase HEALMOs:

(a) HEALMO-4 and (b) HEALMO-5.



**Fig. S3** Elemental distribution in non-single-phase HEALMOs:

(a) HEALMO-4 and (b) HEALMO-5.

**Table S2** Average relative acidity of A site oxides in HEALMOs, and relative acidity of oxides related to HEALMOs.

Composition	Relative acidity	Composition	Relative acidity
HEALMO-1	1.252	Sm <sub>2</sub> O <sub>3</sub>	1.274
HEALMO-2	0.995	Nd <sub>2</sub> O <sub>3</sub>	1.139
HEALMO-3	1.069	CaO	1.099
HEALMO-4	0.987	Pr <sub>2</sub> O <sub>3</sub>	1.064
HEALMO-5	1.002	SrO	0.978
Y <sub>2</sub> O <sub>3</sub>	1.591	BaO	0.938
Gd <sub>2</sub> O <sub>3</sub>	1.402	La <sub>2</sub> O <sub>3</sub>	0.855

**Table S3** Oxidation state, coordination number, ionic radii of A site cations, and prototype structure of the corresponding manganite associated with HEALMO-4 and HEALMO-5.

A site cation	Coordination number <sup>1,2</sup>	Ionic radii ( $\text{\AA}$ ) <sup>1,2</sup>
La <sup>3+</sup>	XII	1.36
Pr <sup>3+</sup>	XII	1.32
Nd <sup>3+</sup>	XII	1.27
Ca <sup>2+</sup>	XII	1.34
Sr <sup>2+</sup>	XII	1.44
Ba <sup>2+</sup>	XII	1.61

**Table S4** Crystal structure, space group, Goldschmidt's tolerance factor and cation size difference of conventional and high entropy perovskite oxides. To facilitate the comparison, Goldschmidt's tolerance factor ( $t$ ) and cation size difference ( $\delta$ ) of reported materials from the literature were re-calculated according to Equation (3) and (4) in the manuscript using the ion radius values in Table S5.

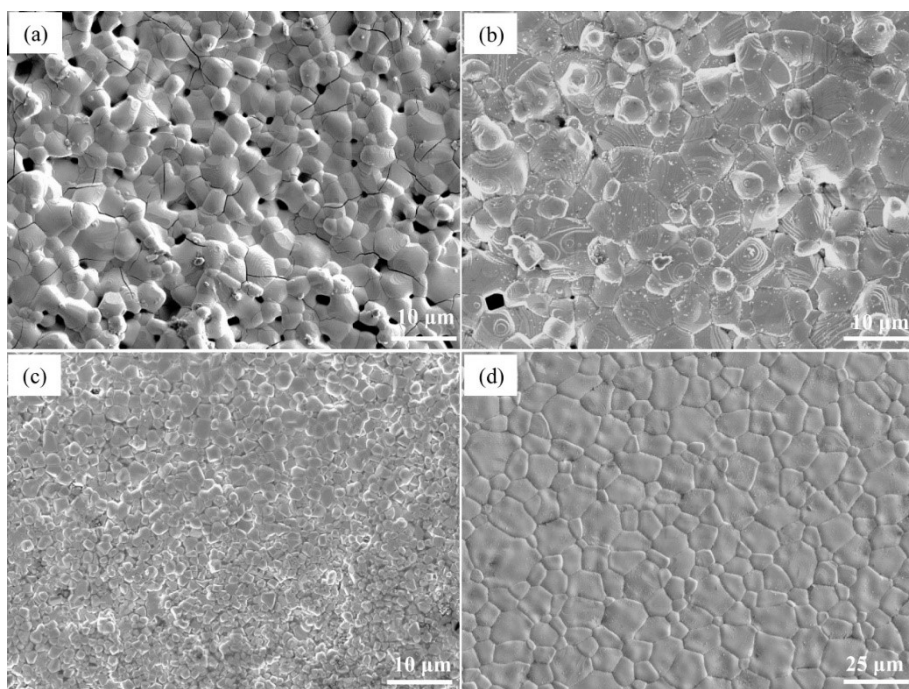
Composition	Crystal structure	SG	Goldschmidt's tolerance factor ( $t$ )	Cation size difference ( $\delta$ )	Reference
(La <sub>0.9</sub> Ca <sub>0.1</sub> )MnO <sub>3</sub>	Orthorhombic	-	0.969	0.44%	3
(La <sub>0.6</sub> Ca <sub>0.4</sub> )MnO <sub>3</sub>	Orthorhombic	<i>Pbnm</i>	0.967	0.72%	4
(La <sub>0.9</sub> Sr <sub>0.1</sub> )MnO <sub>3</sub>	Orthorhombic	<i>Pbnm</i>	0.972	1.75%	5
(La <sub>0.9</sub> Ba <sub>0.1</sub> )MnO <sub>3</sub>	Orthorhombic	<i>Pnma</i>	0.978	5.42%	6
(La <sub>0.8</sub> Ca <sub>0.2</sub> )MnO <sub>3</sub>	Orthorhombic	<i>Pnma</i>	0.968	0.59%	7
(La <sub>0.7</sub> Ca <sub>0.3</sub> )MnO <sub>3</sub>	Orthorhombic	<i>Pnma</i>	0.967	0.68%	
(La <sub>0.6</sub> Sr <sub>0.4</sub> )MnO <sub>3</sub>	Orthorhombic	-	0.981	2.82%	8
(La <sub>0.5</sub> Sr <sub>0.5</sub> )MnO <sub>3</sub>	Orthorhombic	-	0.984	2.86%	
(Pr <sub>0.9</sub> Sr <sub>0.1</sub> )MnO <sub>3</sub>	Orthorhombic	-	0.960	2.70%	
(Pr <sub>0.8</sub> Sr <sub>0.2</sub> )MnO <sub>3</sub>	Orthorhombic	-	0.964	3.57%	
(Pr <sub>0.7</sub> Sr <sub>0.3</sub> )MnO <sub>3</sub>	Orthorhombic	-	0.968	4.06%	
(Pr <sub>0.6</sub> Sr <sub>0.4</sub> )MnO <sub>3</sub>	Orthorhombic	-	0.973	4.30%	
(Pr <sub>0.5</sub> Sr <sub>0.5</sub> )MnO <sub>3</sub>	Orthorhombic	-	0.977	4.35%	
(Nd <sub>0.9</sub> Sr <sub>0.1</sub> )MnO <sub>3</sub>	Orthorhombic	-	0.944	3.96%	
(Nd <sub>0.8</sub> Sr <sub>0.2</sub> )MnO <sub>3</sub>	Orthorhombic	-	0.950	5.21%	
(Nd <sub>0.7</sub> Sr <sub>0.3</sub> )MnO <sub>3</sub>	Orthorhombic	-	0.956	5.90%	
(Nd <sub>0.6</sub> Sr <sub>0.4</sub> )MnO <sub>3</sub>	Orthorhombic	-	0.962	6.22%	
(Nd <sub>0.5</sub> Sr <sub>0.5</sub> )MnO <sub>3</sub>	Orthorhombic	-	0.968	6.27%	
(Sm <sub>0.9</sub> Sr <sub>0.1</sub> )MnO <sub>3</sub>	Orthorhombic	-	0.935	4.76%	
(Sm <sub>0.8</sub> Sr <sub>0.2</sub> )MnO <sub>3</sub>	Orthorhombic	-	0.942	6.25%	
(Sm <sub>0.7</sub> Sr <sub>0.3</sub> )MnO <sub>3</sub>	Orthorhombic	-	0.948	7.05%	
(Sm <sub>0.6</sub> Sr <sub>0.4</sub> )MnO <sub>3</sub>	Orthorhombic	-	0.955	7.42%	
(Sm <sub>0.5</sub> Sr <sub>0.5</sub> )MnO <sub>3</sub>	Orthorhombic	-	0.963	7.46%	
(Gd <sub>0.9</sub> Sr <sub>0.1</sub> )MnO <sub>3</sub>	Orthorhombic	-	0.944	3.96%	
(Gd <sub>0.8</sub> Sr <sub>0.2</sub> )MnO <sub>3</sub>	Orthorhombic	-	0.950	5.21%	
(Gd <sub>0.7</sub> Sr <sub>0.3</sub> )MnO <sub>3</sub>	Orthorhombic	-	0.956	5.90%	
(Gd <sub>0.6</sub> Sr <sub>0.4</sub> )MnO <sub>3</sub>	Orthorhombic	-	0.962	6.22%	
(Gd <sub>0.5</sub> Sr <sub>0.5</sub> )MnO <sub>3</sub>	Orthorhombic	-	0.968	6.27%	
(Gd <sub>0.5</sub> Sr <sub>0.5</sub> )CoO <sub>3</sub>	Orthorhombic	<i>Pnma</i>	0.985	6.27%	9
(Nd <sub>0.5</sub> Ba <sub>0.5</sub> )CoO <sub>3</sub>	Orthorhombic	<i>Pmmm</i>	1.016	11.81%	
(Gd <sub>0.5</sub> Ba <sub>0.5</sub> )CoO <sub>3</sub>	Orthorhombic	<i>Pmmm</i>	1.016	11.81%	
(La <sub>0.5</sub> Sr <sub>0.5</sub> )CoO <sub>3</sub>	Rhombohedral	$R\bar{3}c$	1.001	2.86%	
(Pr <sub>0.5</sub> Sr <sub>0.5</sub> )CoO <sub>3</sub>	Rhombohedral	$R\bar{3}c$	0.994	4.35%	
(Nd <sub>0.5</sub> Sr <sub>0.5</sub> )CoO <sub>3</sub>	Rhombohedral	$R\bar{3}c$	0.985	6.27%	
(La <sub>0.5</sub> Ba <sub>0.5</sub> )CoO <sub>3</sub>	Rhombohedral	$R\bar{3}c$	1.032	8.42%	
(La <sub>0.8</sub> Ba <sub>0.2</sub> )MnO <sub>3</sub>	Rhombohedral	$R\bar{3}c$	0.987	7.09%	



$(\text{La}_{0.7}\text{Ba}_{0.3})\text{MnO}_3$	Rhombohedral	$R\bar{3}C$	0.996	7.98%	
$(\text{La}_{0.7}\text{Sr}_{0.3})\text{MnO}_3$	Rhombohedral	$R\bar{3}C$	0.978	2.65%	7
$(\text{Sr}_{0.9}\text{Ho}_{0.1})\text{CoO}_3$	Cubic	$Pm\bar{3}m$	1.008	4.44%	10
$(\text{Sm}_{0.4}\text{Sr}_{0.6})\text{CoO}_3$	Cubic	-	0.987	7.20%	
$(\text{Sm}_{0.3}\text{Sr}_{0.7})\text{CoO}_3$	Cubic	-	0.994	6.64%	
$(\text{Sm}_{0.2}\text{Sr}_{0.8})\text{CoO}_3$	Cubic	-	1.001	5.71%	
$(\text{Sm}_{0.1}\text{Sr}_{0.9})\text{CoO}_3$	Cubic	-	1.008	4.23%	11
$(\text{Dy}_{0.3}\text{Sr}_{0.7})\text{CoO}_3$	Cubic	-	0.994	6.64%	
$(\text{Dy}_{0.2}\text{Sr}_{0.8})\text{CoO}_3$	Cubic	-	1.001	5.71%	
$(\text{Dy}_{0.1}\text{Sr}_{0.9})\text{CoO}_3$	Cubic	-	1.008	4.23%	
$(\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2}\text{Gd}_{0.2})\text{CoO}_3$	Orthorhombic	$Pbnm$	0.945	7.49%	
$(\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2}\text{Gd}_{0.2})\text{CrO}_3$	Orthorhombic	$Pbnm$	0.927	7.49%	
$(\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2}\text{Gd}_{0.2})\text{FeO}_3$	Orthorhombic	$Pbnm$	0.936	7.49%	
$\text{La}(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})\text{O}_3$	Orthorhombic	$Pbnm$	0.978	2.63%	12
$\text{Gd}(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})\text{O}_3$	Orthorhombic	$Pbnm$	0.946	2.63%	
$\text{Sm}(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})\text{O}_3$	Orthorhombic	$Pbnm$	0.935	2.63%	
$\text{Nd}(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})\text{O}_3$	Orthorhombic	$Pbnm$	0.946	2.63%	
$\text{Y}(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2})\text{O}_3$	Orthorhombic	$Pbnm$	0.880	2.63%	
$(\text{La}_{0.2}\text{Pr}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Sr}_{0.2})\text{MnO}_{3-\delta}$	Orthorhombic	$Pnma$	0.958	5.30%	13
$\text{La}(\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2})\text{O}_{3-\delta}$	Hexagonal	$R\bar{3}cH$	0.966	9.15%	14
$\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.2}\text{Sn}_{0.2}\text{Hf}_{0.2}\text{Y}_{0.2})\text{O}_3$	Cubic	$Pm\bar{3}m$	1.001	13.30%	
$\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.2}\text{Sn}_{0.2}\text{Hf}_{0.2}\text{Nb}_{0.2})\text{O}_3$	Cubic	$Pm\bar{3}m$	1.026	6.50%	15
$\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.2}\text{Sn}_{0.2}\text{Hf}_{0.2}\text{Ta}_{0.2})\text{O}_3$	Cubic	$Pm\bar{3}m$	1.026	6.50%	
$\text{Sr}(\text{Zr}_{0.2}\text{Sn}_{0.2}\text{Ti}_{0.2}\text{Hf}_{0.2}\text{Mn}_{0.2})\text{O}_3$	Cubic	$Pm\bar{3}m$	0.972	7.34%	
$\text{Sr}(\text{Zr}_{0.2}\text{Sn}_{0.2}\text{Ti}_{0.2}\text{Hf}_{0.2}\text{Nb}_{0.2})\text{O}_3$	Cubic	$Pm\bar{3}m$	0.968	6.50%	
$\text{Ba}(\text{Zr}_{0.2}\text{Sn}_{0.2}\text{Ti}_{0.2}\text{Hf}_{0.2}\text{Ce}_{0.2})\text{O}_3$	Cubic	$Pm\bar{3}m$	1.004	11.92%	16
$\text{Ba}(\text{Zr}_{0.2}\text{Sn}_{0.2}\text{Ti}_{0.2}\text{Hf}_{0.2}\text{Y}_{0.2})\text{O}_{3-x}$	Cubic	$Pm\bar{3}m$	1.001	13.30%	
$\text{Ba}(\text{Zr}_{0.2}\text{Sn}_{0.2}\text{Ti}_{0.2}\text{Hf}_{0.2}\text{Nb}_{0.2})\text{O}_3$	Cubic	$Pm\bar{3}m$	1.026	6.50%	

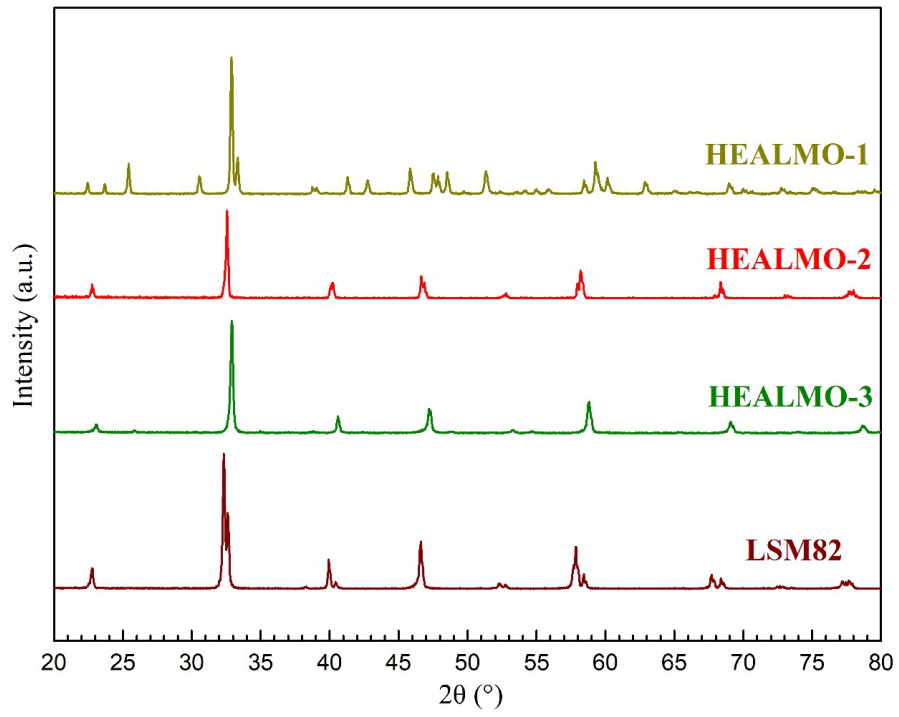
**Table S5** Ion radius values used to re-calculate Goldschmidt's tolerance factor ( $t$ ) and cation size difference ( $\delta$ ) of reported materials are listed in Table S2. The "LS" in Table means "low spin", and "HS" means "high spin".

Cation	Coordination number <sup>1,2</sup>	Ionic radii ( $\text{Å}$ ) <sup>1,2</sup>
La <sup>3+</sup>	XII	1.36
Nd <sup>3+</sup>	XII	1.27
Sm <sup>3+</sup>	XII	1.24
Gd <sup>3+</sup>	XII	1.27
Pr <sup>3+</sup>	XII	1.32
Ca <sup>2+</sup>	XII	1.34
Sr <sup>2+</sup>	XII	1.44
Ba <sup>2+</sup>	XII	1.61
Ho <sup>3+</sup>	XII	1.23
Dy <sup>3+</sup>	XII	1.24
Y <sup>3+</sup>	IX	1.075
Y <sup>3+</sup>	VI	0.90
Ti <sup>4+</sup>	VI	0.605
Zr <sup>4+</sup>	VI	0.72
Sn <sup>4+</sup>	VI	0.69
Hf <sup>4+</sup>	VI	0.71
Nb <sup>5+</sup>	VI	0.64
Ta <sup>5+</sup>	VI	0.64
Ce <sup>4+</sup>	VI	0.87
Cr <sup>3+</sup>	VI	0.615
Fe <sup>3+</sup>	VI	0.55 <sup>LS</sup> , 0.645 <sup>HS</sup>
Co <sup>3+</sup>	VI	0.545 <sup>LS</sup> , 0.61 <sup>HS</sup>
Ni <sup>3+</sup>	VI	0.56 <sup>LS</sup> , 0.60 <sup>HS</sup>
Mn <sup>3+</sup>	VI	0.58 <sup>LS</sup> , 0.645 <sup>HS</sup>
O <sup>2-</sup>	VI	1.40



**Fig. S4** Morphology of sintered pellets of HEALMOs and LSM82:

(a) HEALMO-1, (b) HEALMO-2, (c) HEALMO-3 and (d) LSM82.



**Fig. S5** XRD patterns of HEALMOs and LSM82 rectangle bars after electrical conductivity and Seebeck coefficient measurement.

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