Supplementary information

Mg₃(Bi,Sb)₂-based thermoelectric modules for efficient and reliable

waste-heat utilization up to 750 K

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This supplement contains Supplementary Figures 1-18 Supplementary Tables 1-3 Supplementary Note Supplementary References



Supplementary Figure 1| Powder X-ray diffraction patterns of $Mg_{3,2}Bi_{1,996-x}Sb_xSe_{0,004}$. All the peaks can be well indexed to Mg_3Bi_2 structure ($P^{3}m1$). No secondary phases are observed within the detection limits of the measurement. With the increase of *x*, the peak position shifts to the large angle because of the smaller lattice size of $Mg_3Sb_2^{-1}$.



Supplementary Figure 2| Microstructure of the polished surface of bulk $Mg_{3.2}Bi_{0.996}SbSe_{0.004}$ and $Mg_{3.2}Bi_{0.496}Sb_{1.5}Se_{0.004}$ samples. a. SEM image, and EDS elemental mapping of b. All elements, c. Mg, d. Bi, e. Sb, and f. Se. The result confirms that Se is homogeneously distributed in the matrix without forming secondary phases, indicating that Se successfully enters the lattice of Mg_3Bi_2 .



Supplementary Figure 3| TE transport properties and cost of n-type Mg_{3.2}Bi_{1.996-x}Sb_xSe_{0.004}. a. Electrical conductivity (σ), b. Seebeck coefficient (α), c. power factor ($\alpha^2 \sigma$), d. total thermal conductivity (κ), and e. lattice and bipolar thermal conductivity ($\kappa_{\text{lat+}}\kappa_{\text{bip}}$), electronic thermal conductivity (κ_e) of Mg_{3.2}Bi_{1.996-x}Sb_xSe_{0.004} samples. f. Summary of zT_{ave} and material cost for Mg₃(Bi,Sb)₂ alloys with different doping elements^{1–16}. The prices are sourced from IYPT 2019¹⁷. Raw materials with the same purity were chosen for calculation.

Mg₃Bi₂ is a semimetal, and Mg₃Sb₂ is a semiconductor¹⁸; and therefore, alloying Mg₃Bi₂ with Mg₃Sb₂ can enhance the bandgap and suppress the bipolar contribution of Bi-rich compositions, pushing the maximum *zT* to higher temperatures¹⁸. The electrical conductivities of Mg_{3.2}Bi_{1.996-x}Sb_xSe_{0.004} samples show decreasing trends with increasing temperature (**Fig. S3a**), implying degenerate semiconductor behavior. There is no thermally activated behavior in the low-temperature electrical conductivity, which is attributed to the large grain size resulting from the optimized sintering process (**Fig. S4**)^{18,19}. The σ values decline with increasing Sb content, showing an opposite trend to that of the Seebeck coefficient (**Fig. S3b**). Room-temperature Hall measurements (**Fig. S5**) indicate that the decrease in σ with increasing Sb content is mainly caused by the decrease in carrier mobility. This is consistent with the general observation that a higher Mg₃Sb₂ content in Mg₃Bi₂-Mg₃Sb₂ alloys results in lower mobility due to the heavier band effective mass of Mg₃Sb₂^{18–20}. In addition, the band gap (*E*_g) of Mg₃Bi₂-Mg₃Sb₂

increases with increasing Mg₃Sb₂ content, from approximately -0.15 eV for pure Mg₃Bi₂ to ~0.5 eV for pure Mg₃Sb₂¹⁹, thereby suppressing thermally excited bipolar conduction. As a result, the peak Seebeck coefficient (α_{max}) and its corresponding temperature (T_{max}) rise with increasing x (Fig. S3b), coinciding with the Goldsmid-Sharp equation²¹, $E_g=2e|\alpha_{max}|T_{max}$ (Fig. S6). Owing to the successful manipulation of the carrier-scattering mechanism and energy band structure, the samples with higher Sb content exhibit lower power factors near room temperature but show significant enhancement at high temperatures (Fig. S3c).

A significant decrease in the κ of Mg_{3.2}Bi_{1.996-x}Sb_xSe_{0.004} with increasing Sb content can be observed (**Fig. S3d**), which is attributed to the substantial reduction in κ_{lat} and κ_{bip} (**Fig. S3e**). κ_{bip} appears in the samples with x=0.3 and 0.5 (**Fig. S3e**), but is significantly reduced when $x\geq 1$ due to the increase in the bandgap (**Fig. S6**). Meanwhile, the strong phonon scattering due to the mass and strain fluctuations caused by Bi/Sb substitution has a beneficial effect on reducing $\kappa_{\text{lat}}^{18,21}$. As a result, a low $\kappa_{\text{lat}}+\kappa_{\text{bip}}$ of 0.54 Wm⁻¹K⁻¹ is obtained at 700 K, approaching the minimum lattice thermal conductivity calculated from Cahill's formula².

In addition to TE properties, material cost is another essential metric for assessing the commercial feasibility of TE materials^{1,22}. We compared the zT_{ave} values and material costs of Mg₃Bi₂-Mg₃Sb₂ alloys with different doping elements^{1–16} (**Fig. S3f**). Some material systems have achieved high zT_{ave} values of over 1.0 but at the same time have high costs, *e.g.*, Sc-doped and Te&Hf dual-doped samples. Apparently, the materials located in the upper left region of **Fig. S3f** are ideal for assembling devices and practical applications. In previous reports, this could only be achieved by doping with Te. However, in the present work, we achieved a comparable performance by using Se doping. The reduced cost of Se seems negligible when comparing to only 0.5% Te doping. However, the advantage in cost will become more apparent when kilogram-scale raw materials are required for subsequent batch preparation to meet industrial applications. Therefore, Se is considered a better choice for long-term development given the price fluctuations caused by the low crustal abundance of Te^{23,24}. Moreover,

higher zT_{ave} can also be achieved by further doping (such as Mn, Cu, or Fe) at the cation site of Se-doped Mg₃(Bi,Sb)₂, leading to better performance, low cost and non-toxicity. Therefore, we developed TE power generation modules for mid-temperature applications using Mg_{3.2}Bi_{0.996}SbSe_{0.004} in this work. Once the path from highperformance Mg₃(Bi,Sb)₂-based materials to high-performance Mg₃(Bi,Sb)₂-based modules is opened up, reliable modules with higher efficiency can be achieved immediately whenever the materials with higher zT_{ave} are available.



Supplementary Figure 4| Scanning electron microscopy images of the polished surfaces after etching. a. $Mg_{3.2}Bi_{0.996}SbSe_{0.004}$. b. $Mg_{3.2}Bi_{0.496}Sb_{1.5}Se_{0.004}$. An average grain size of ~10 μ m is achieved for our samples.



Supplementary Figure 5| Room temperature carrier concentration $(n_{\rm H})$ and mobility $(\mu_{\rm H})$ of bulk Mg_{3.2}Bi_{1.996-x}Sb_xSe_{0.004} samples. As x increases, the carrier concentration is nearly unchanged while carrier mobility decreases because of the band effective mass of individual bands $m_{\rm b}^*$ increases with Mg₃Sb₂ alloying¹⁸.



Supplementary Figure 6| Calculated bandgap (*E*_g) of Mg_{3.2}Bi_{1.996-x}Sb_xSe_{0.004} samples.



Supplementary Figure 7| Temperature dependent carrier concentration and carrier mobility of our $Mg_{3.2}Bi_{0.496}Sb_{1.5}Se_{0.004}$ sample in comparison with the literature results^{25,26}.



Supplementary Figure 8| Thermoelectric properties of $Mg_{3.2}Bi_{1-p}SbSe_p$. Temperature dependence of **a**. Electrical conductivity (σ), **b**. Seebeck coefficient (α), **c**. power factor ($\alpha^2 \sigma$), **d**. total thermal conductivity (κ), **e**. lattice and bipolar thermal conductivity ($\kappa_{lat}+\kappa_{bip}$), and **f**. zT and zT_{ave} (the inset). We did not further decrease Se concentration because we found that the zT_{ave} of $Mg_{3.2}Bi_{1-y}SbSe_y$ samples did not change much when the Se concentration varied between 0.004 and 0.012. Therefore, from the perspective of controlled and reproducible preparation, we balanced the difficulty of material synthesis with the thermoelectric properties and ended up using $Mg_{3.2}Bi_{0.996}SbSe_{0.004}$ for module fabrication.



Supplementary Figure 9| Thermoelectric properties of Mg_{3,2}Bi_{0,996}SbSe_{0,004} with different sizes and measured along different directions. Temperature dependence of a. Electrical conductivity (σ), b. Seebeck coefficient (α), c. power factor ($\alpha^2 \sigma$), d. total thermal conductivity (κ), and e. zT_{ave} and compared with literature results^{25–27}. Small samples are in a typical dimension – a disk with a diameter of 10 mm and a thickness of 2 mm, while large samples have the thickness of 12 mm and diameter of 10 mm.

Note that the small-sized sample and the large-sized sample are prepared separately. We used the same sintering temperature and pressure to prepare them, but we increased the holding time to 6 min when preparing the large-sized sample. This ensures that the large-sized sample has the comparable density with the small-sized sample. However, the extended holding time led to more loss of Mg, resulting in a lower carrier concentration for the large-sized samples. As a result, the large-sized sample shows a lower electrical conductivity and a higher Seebeck coefficient. But the zT_{ave} value of the large-sized sample ($zT_{ave}=1.0$) and the small-sized sample ($zT_{ave}=1.03$) is comparable (Fig. S9e). Therefore, instead of further optimizing the Mg content, we are working on the module research with the aim of transforming the high-performance materials into high-efficiency modules.



Supplementary Figure 10| Detailed microstructure and element distribution of 8 kinds of diffusion barrier materials. a. W, b. Nb, c. Ni, d. Mo, e. Fe, f. Ti, g. Cu, h. Cr.



Supplementary Figure 11| More element distribution results of 4 kinds of diffusion barrier materials classified into the third category. a. Fe, b. Mo, c. Cr, d. Nb.



Supplementary Figure 12 | Microstructure of the $Mg_{3,2}Bi_{0,996}SbSe_{0.004}/Nb$ interface. SEM image, and EDS elemental mapping of **a**. as-sintered sample, and **b**. the sample after thermal aging at 773 K for 360 h. The result confirms that Nb is almost chemical inert to $Mg_3(Bi,Sb)_2$, showing no obvious interdiffusion at high temperature. Besides, no obvious cracks were found near the interface.



Supplementary Figure 13 Pictures of a 2-pairs thermoelectric module. a. Before, and b. after filling the glass fiber.



Supplementary Figure 14| Pictures of a commercial measurement system developed by Shanghai Fuyue Vacuum Technology Ltd. This measurement system was calibrated by comparing it with a commercial Mini-PEM apparatus (Ulvac-Riko, Japan) before being put into use. The results obtained from two instruments are shown in Fig. S18 below.



Supplementary Figure 15| Summary of the operating temperature of existing Mg₃(Bi,Sb)₂-based TE modules for power generation^{24,28,29}.



Supplementary Figure 16 Evolution of conversion efficiency of existing thermoelectric modules for mid-temperature power generation over time.



Supplementary Figure 17 Thermoelectric properties of p-type $Ce_{0.9}Fe_3CoSb_{12}$, which are measured along pressing direction. Temperature dependence of a. electrical conductivity (σ), b. Seebeck coefficient (α), c. total thermal conductivity (κ), d. zT.



Supplementary Figure 18 Comparison of the power-generating performance of a TE module measured from our equipment and the Mini-PEM (Advance Riko, Japan). Temperature gradient dependent **a.** open-circuit voltage V_{oc} , **b**. device resistance R_{in} , **c**. maximum power output P_{max} , **d**. cold-side heat flow Q_c , **e**. hot-side heat flow Q_h , and **f**. maximum efficiency η_{max} .

 $\label{eq:supplementary} \begin{array}{l} \textbf{Supplementary Table 1} \mid A \mbox{ short summary of nominal compositions and preparation} \\ methods used \mbox{ when synthesizing n-type polycrystalline $Mg_3(Bi,Sb)_2$-based alloys in some} \end{array}$

literature.							
Nominal composition	Author (et al.)	Preparation method	Reference				
$Mg_{3.2}Sb_{1.5}Bi_{0.49}Te_{0.01}$	H. Tamaki	BM+HP	Adv. Mater., 2016, 28, 10182				
$Mg_{3.2}Sb_{1.5}Bi_{0.49}Te_{0.01}$	J. Mao	BM+HP	PNAS, 2017, 114, 10548				
$Mg_{3.2}Sb_{1.5}Bi_{0.49}Te_{0.01}$	J. Mao	BM+HP	ACS Energy Lett. 2017, 2, 2245				
$Mg_{3.2}Sb_{1.5}Bi_{0.49}Te_{0.01}$	J. Shuai	BM+HP	Energy Environ. Sci., 2017, 10, 799				
$Mg_{3.01}Sb_{1.5}Bi_{0.49}Te_{0.01}$	K. Imasato	BM+HP	APL Materials, 2018, 6, 016106				
$Mg_{3.2}Bi_{1.498}Sb_{0.5}Te_{0.002}$	J. Mao	BM+HP	Science, 2019, 365, 495				
$Mg_{3.2}Sb_{1.5}Bi_{0.49}Se_{0.01}$	F. Zhang	BM+HP	Adv. Funct. Mater., 2020, 30, 1906143				
$Mg_{3.175}Mn_{0.025}Sb_{1.5}Bi_{0.49}Te_{0.01}$	X. Chen	BM+SPS	Nano energy, 2018, 52, 246				
$Mg_{3.02}Sb_{1.5}Bi_{0.49}Te_{0.01}$: $Mn_{0.01}$	R. Shu	BM+SPS	Adv. Funct. Mater., 2019, 29, 1807235				
$Mg_{3.2}Sb_{1.5}Bi_{0.49}Te_{0.01}Cu_{0.01}$	Z. Liu	BM+SPS	Joule 2021, 5, 1196				
$Mg_{3,2}Bi_{1,5}Sb_{0,498}Te_{0,002}Cu_{0,01}$	Z. Liu	BM+SPS	Nat Commun 2022, 13, 1120				
$Mg_{3.07}Sb_{1.48}Bi_{0.48}Se_{0.04}$	J. Zhang	AM+BM+SPS	Chem. Mater., 2017, 29, 5371				
$Mg_{3.032}Y_{0.018}SbBi$	X. Shi	Melting+HP	Adv. Mater., 2019, 31, 1903387				
$Mg_{3.5}Sc_{0.04}Sb_{1.97}Te_{0.03}$	J. Zhang	SPS	Angew. Chem. Int. Ed., 2020, 59, 4278				

BM: ball milling, HP: hot press, AM: arc-melting, SPS: spark plasma sintering.

x in Mg _{3.2} Bi _{1.996-x} Sb _x Se _{0.004}	Sintering temperature		
0.3	973 K		
0.5	973 K		
1	1023 K		
1.5	1073 K		
1.7	1073 K		

Supplementary Table 2| Sintering temperature of our Mg_{3.2}Bi_{1.996-x}Sb_xSe_{0.004} samples.

Supplementary Note

The power-cost ratio of different TE modules plotted in Fig. 1 is calculated by:

$$Power - Cost \ ratio = \frac{P_{max}}{Price_p + Price_n}$$
$$Price_{p(n)} = \frac{\sum n_i M_i P_i}{\sum n_i M_i} V \rho N$$

Where n_i , M_i , P_i are the stoichiometric ratio, molar mass (g/mol), and price (\$/kg) of each element in TE materials, respectively. V and ρ is volume and density of single TE leg. N is the number of TE pairs in the module. Detailed information of different modules is shown in Supplementary Table 3 below.

Module		Volume	Density (g cm ⁻³)		Ref.
	Material	(mm ³)		Pairs	
РЬТе	n-type PbTe doped with 0.2% PbI ₂	8.8	8.08		30
	p-type PbTe–2% MgTe doped with 4% Na	8.8	8.08	8	
PbTe	n-type Pb _{0.93} Sb _{0.05} S _{0.5} Se _{0.5}	180.5	7.74	r	22
	p-type Na-doped PbTe	180.5	8.08	2	
РЬТе	n-type PbTe _{0.9964} I _{0.0036}	12.8	8.06	0	31
	p-type Pb _{0.953} Na _{0.040} Ge _{0.007} Te	12.8	8.06	8	
CoSb ₃	n-type Yb _{0.3} Co ₄ Sb ₁₂	120	7.6	8	32
	p-type Ce _{0.85} Fe ₃ CoSb ₁₂	200	7.6		
CoSb ₃	n-type Yb _{0.3} Co ₄ Sb ₁₂ /0.5%MWCNTs	192	7.46	8	33
	p-type Ce _{0.9} Fe ₃ CoSb ₁₂	192	7.6		
CoSb ₃	$\begin{array}{c} n\text{-type} \\ Yb_{0.2}Ca_{0.1}Al_{0.1}Ga_{0.1}In_{0.1}Fe_{0.25}Co_{3.75}Sb_{12} \end{array}$	175	7.6	32	34
	p-type Pr _{0.8} Ti _{0.1} Ga _{0.1} Ba _{0.1} Fe ₃ CoSb ₁₂	175	7.6		
GeTe	n-type Yb _{0.3} Co ₄ Sb ₁₂	64	7.6	Q	35
	p-type Ge _{0.92} Sb _{0.04} Bi _{0.04} Te _{0.95} Se _{0.05}	128	5.91	0	
half-Heusler	n-type Hf _{0.5} Zr _{0.5} NiSn _{0.98} Sb _{0.02}	188.8	8.9	0	36
	p-type (Nb _{0.8} Ta _{0.2}) _{0.8} Ti _{0.2} FeSb	188.8	8.4	8	
half-Heusler	n-type Hf _{0.6} Zr _{0.4} NiSn _{0.98} Sb _{0.02}	128	9.1		37
	p-type FeNb _{0.88} Hf _{0.12} Sb	128	8.5	8	
Cu ₂ Se	n-type Yb _{0.3} Co ₄ Sb ₁₂	40	7.6		38
	p-type Cu ₂ Se	160	6.6	8	
Mg ₃ (Bi,Sb) ₂	n-type Mg _{3.2} SbBi _{0.996} Se _{0.004}	54	4.9	2	This
	p-type Ce _{0.9} Fe ₃ CoSb ₁₂	17.34	7.6	2	work

Supplementary Table 3| Detailed parameters of different modules used for the

calculation in Fig. 1b.

Supplementary References

- J. Zhang, L. Song, S. H. Pedersen, H. Yin, L. T. Hung and B. B. Iversen, *Nat. Commun.*, 2017, 8, 13901.
- 2 H. Tamaki, H. K. Sato and T. Kanno, Adv. Mater., 2016, 28, 10182-10187.
- 3 J. Mao, Y. Wu, S. Song, Q. Zhu, J. Shuai, Z. Liu, Y. Pei and Z. Ren, *ACS Energy Lett.*, 2017, **2**, 2245–2250.
- 4 X. Shi, C. Sun, X. Zhang, Z. Chen, S. Lin, W. Li and Y. Pei, *Chem. Mater.*, 2019, **31**, 8987– 8994.
- 5 F. Zhang, C. Chen, S. Li, L. Yin, B. Yu, J. Sui, F. Cao, X. Liu, Z. Ren and Q. Zhang, *Adv. Electron. Mater.*, 2020, **6**, 1901391.
- 6 T. Kanno, H. Tamaki, H. K. Sato, S. D. Kang, S. Ohno, K. Imasato, J. J. Kuo, G. J. Snyder and Y. Miyazaki, *Appl. Phys. Lett.*, 2018, **112**, 033903.
- 7 X. Shi, T. Zhao, X. Zhang, C. Sun, Z. Chen, S. Lin, W. Li, H. Gu and Y. Pei, *Adv. Mater.*, 2019, 31, 1903387.
- 8 X. Chen, H. Wu, J. Cui, Y. Xiao, Y. Zhang, J. He, Y. Chen, J. Cao, W. Cai, S. J. Pennycook, Z. Liu, L.-D. Zhao and J. Sui, *Nano Energy*, 2018, **52**, 246–255.
- 9 K. Imasato, M. Wood, J. J. Kuo and G. J. Snyder, J. Mater. Chem. A, 2018, 6, 19941-19946.
- 10 K. Imasato, S. Ohno, S. D. Kang and G. J. Snyder, APL Mater., 2018, 6, 016106.
- 11 J. Mao, J. Shuai, S. Song, Y. Wu, R. Dally, J. Zhou, Z. Liu, J. Sun, Q. Zhang, C. dela Cruz, S. Wilson, Y. Pei, D. J. Singh, G. Chen, C.-W. Chu and Z. Ren, *Proc. Natl. Acad. Sci.*, 2017, **114**, 10548–10553.
- 12 R. Shu, Y. Zhou, Q. Wang, Z. Han, Y. Zhu, Y. Liu, Y. Chen, M. Gu, W. Xu, Y. Wang, W. Zhang, L. Huang and W. Liu, *Adv. Funct. Mater.*, 2019, **29**, 1807235.
- 13 J. Zhang, L. Song, K. A. Borup, M. R. V. Jørgensen and B. B. Iversen, *Adv. Energy Mater.*, 2018, 8, 1702776.
- 14 X. Shi, C. Sun, Z. Bu, X. Zhang, Y. Wu, S. Lin, W. Li, A. Faghaninia, A. Jain and Y. Pei, *Adv. Sci.*, 2019, **6**, 1802286.
- 15 J. Li, F. Jia, S. Zhang, S. Zheng, B. Wang, L. Chen, G. Lu and L. Wu, J. Mater. Chem. A, 2019, 7, 19316–19323.
- 16 J. Shuai, J. Mao, S. Song, Q. Zhu, J. Sun, Y. Wang, R. He, J. Zhou, G. Chen, D. J. Singh and Z. Ren, *Energy Environ. Sci.*, 2017, **10**, 799–807.
- 17 #ChemistryAdvent #IYPT2019 Day 23, https://www.compoundchem.com/2019advent/day23/, (accessed January 6, 2022).
- 18 K. Imasato, S. D. Kang and G. J. Snyder, Energy Environ. Sci., 2019, 12, 965–971.
- 19 A. Li, C. Fu, X. Zhao and T. Zhu, Research, 2020, 2020, 1–22.
- 20 Y. Pan, M. Yao, X. Hong, Y. Zhu, F. Fan, K. Imasato, Y. He, C. Hess, J. Fink, J. Yang, B. Büchner, C. Fu, G. J. Snyder and C. Felser, *Energy Environ. Sci.*, 2020, **13**, 1717–1724.
- 21 K. Imasato, S. D. Kang, S. Ohno and G. J. Snyder, Mater. Horiz., 2018, 5, 59-64.
- 22 B. Jiang, X. Liu, Q. Wang, J. Cui, B. Jia, Y. Zhu, J. Feng, Y. Qiu, M. Gu, Z. Ge and J. He, *Energy Environ. Sci.*, 2020, **13**, 579–591.
- 23 Q. Yan and M. G. Kanatzidis, Nat. Mater., , DOI:10.1038/s41563-021-01109-w.
- 24 P. Ying, R. He, J. Mao, Q. Zhang, H. Reith, J. Sui, Z. Ren, K. Nielsch and G. Schierning, *Nat. Commun.*, 2021, **12**, 1121.

- 25 J. Zhang, L. Song, A. Mamakhel, M. R. V. Jørgensen and B. B. Iversen, *Chem. Mater.*, 2017, 29, 5371–5383.
- 26 F. Zhang, C. Chen, H. Yao, F. Bai, L. Yin, X. Li, S. Li, W. Xue, Y. Wang, F. Cao, X. Liu, J. Sui and Q. Zhang, *Adv. Funct. Mater.*, 2020, **30**, 1906143.
- 27 J. Liang, H. Yang, C. Liu, L. Miao, J. Chen, S. Zhu, Z. Xie, W. Xu, X. Wang, J. Wang, B. Peng and K. Koumoto, ACS Appl. Mater. Interfaces, 2020, 12, 21799–21807.
- 28 Z. Liu, N. Sato, W. Gao, K. Yubuta, N. Kawamoto, M. Mitome, K. Kurashima, Y. Owada, K. Nagase, C.-H. Lee, J. Yi, K. Tsuchiya and T. Mori, *Joule*, 2021, 5, 1196–1208.
- 29 Z. Bu, X. Zhang, Y. Hu, Z. Chen, S. Lin, W. Li and Y. Pei, *Energy Environ. Sci.*, 2021, 14, 6506–6513.
- 30 X. Hu, P. Jood, M. Ohta, M. Kunii, K. Nagase, H. Nishiate, M. G. Kanatzidis and A. Yamamoto, *Energy Environ. Sci.*, 2016, 9, 517–529.
- 31 P. Jood, M. Ohta, A. Yamamoto and M. G. Kanatzidis, Joule, 2018, 2, 1339–1355.
- 32 J. Chu, J. Huang, R. Liu, J. Liao, X. Xia, Q. Zhang, C. Wang, M. Gu, S. Bai, X. Shi and L. Chen, *Nat. Commun.*, 2020, **11**, 2723.
- 33 Q. Zhang, Z. Zhou, M. Dylla, M. T. Agne, Y. Pei, L. Wang, Y. Tang, J. Liao, J. Li, S. Bai, W. Jiang, L. Chen and G. Jeffrey Snyder, *Nano Energy*, 2017, 41, 501–510.
- 34 G. Nie, W. Li, J. Guo, A. Yamamoto, K. Kimura, X. Zhang, E. B. Isaacs, V. Dravid, C. Wolverton, M. G. Kanatzidis and S. Priya, *Nano Energy*, 2019, 66, 104193.
- 35 T. Xing, Q. Song, P. Qiu, Q. Zhang, M. Gu, X. Xia, J. Liao, X. Shi and L. Chen, *Energy Environ. Sci.*, 2021, 14, 995–1003.
- 36 J. Yu, Y. Xing, C. Hu, Z. Huang, Q. Qiu, C. Wang, K. Xia, Z. Wang, S. Bai, X. Zhao, L. Chen and T. Zhu, *Adv. Energy Mater.*, 2020, 10, 2000888.
- 37 C. Fu, S. Bai, Y. Liu, Y. Tang, L. Chen, X. Zhao and T. Zhu, Nat. Commun., 2015, 6, 8144.
- 38 P. Qiu, T. Mao, Z. Huang, X. Xia, J. Liao, M. T. Agne, M. Gu, Q. Zhang, D. Ren, S. Bai, X. Shi, G. J. Snyder and L. Chen, *Joule*, 2019, 3, 1538–1548.