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Supplementary Information

Plastically $Mg_3(Sb,Bi)_2$-based thermoelectric compounds with enhanced texture via cold-deformation

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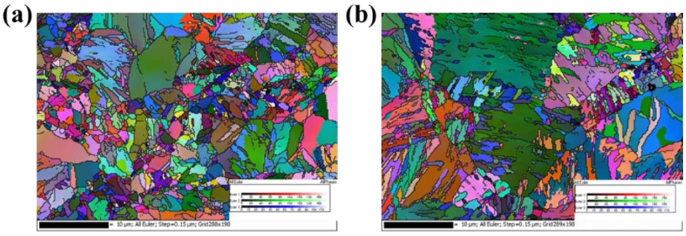

Fig. S1 EBSD images of $Mg_{3.1}Bi_{1.5}Sb_{0.49}Te_{0.01}$ (a) +600 mn sample and (b) +20 mn sample.

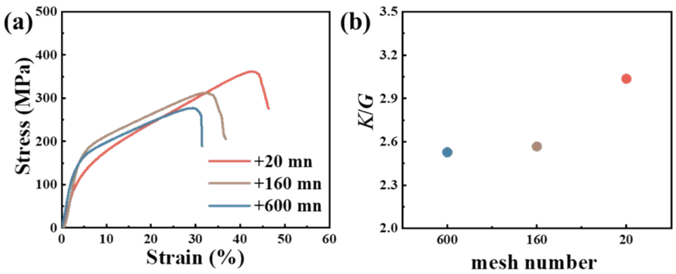

Fig. S2 (a) Stress-strain curves and (b) calculated *K*/*G* of $Mg_{3.1}Bi_{1.5}Sb_{0.49}Te_{0.01}$ samples with different particle size.

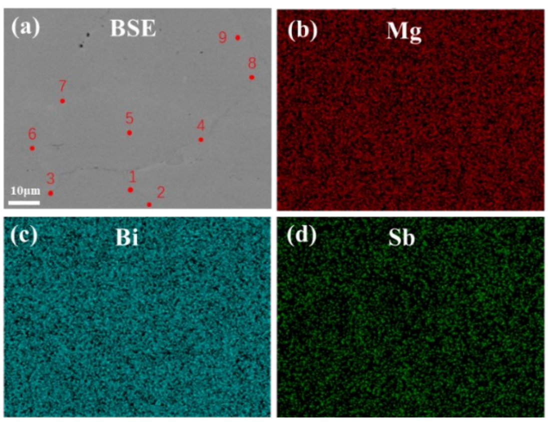

Fig. S3 (a) SEM image and corresponding EDS composition mapping of (b) Mg, (c) Bi, (d) Sb elements of $Mg_{3.1}Bi_{1.5}Sb_{0.49}Te_{0.01}$.

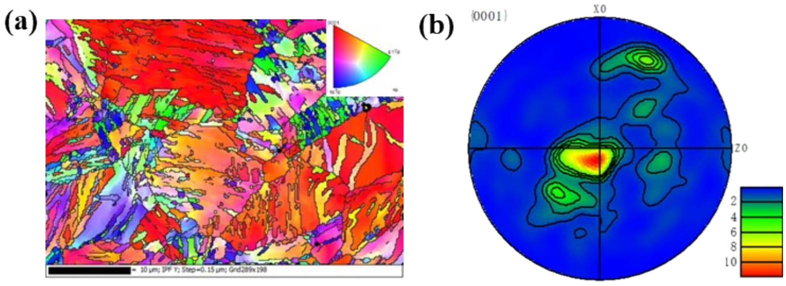

Fig. S4 (a) Orientation imaging microscopy map and (b) pole figure of (000l) plane obtained from EBSD analysis of +20 mn sample.

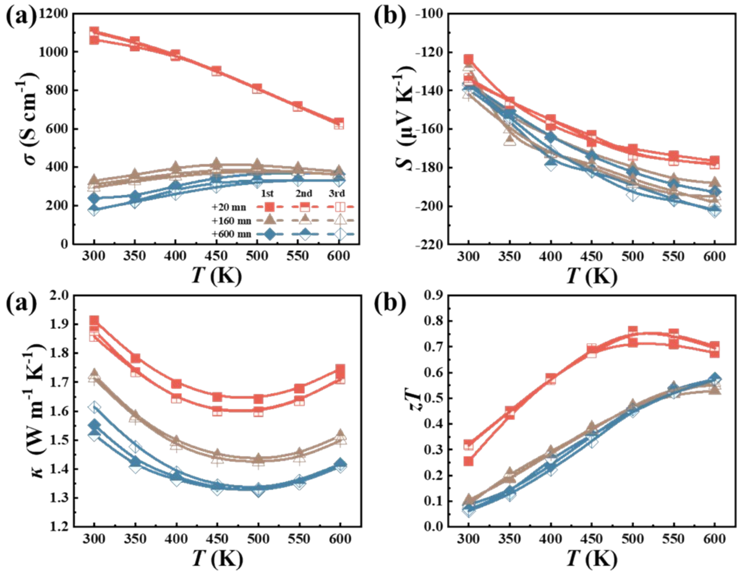

Fig. S5 Repeated tests of (a) electrical conductivity (b) Seebeck coefficient (c) thermal conductivity and (d) calculated zT of $Mg_{3.1}Bi_{1.5}Sb_{0.49}Te_{0.01}$ samples in ⊥F.

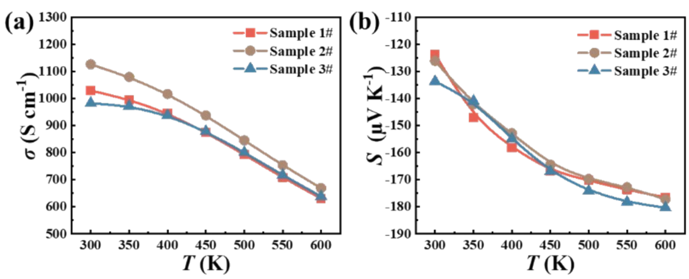

Fig. S6 Measurement results of (a) electrical conductivity, (b) Seebeck coefficient of the reproduced +20 mn samples.

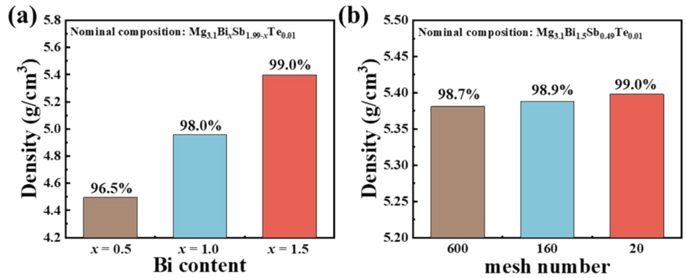

Fig. S7 Measured densities of the samples of (a) $Mg_{3.1}Bi_xSb_{1.99\text{-}x}Te_{0.01}$ (x = 0.5, 1.0, 1.5) and (b) $Mg_{3.1}Bi_{1.5}Sb_{0.49}Te_{0.01}$ with different particle size. The relative densities of all the samples are marked above the columns.

Table. S1 Corresponding chemical compositions of the marked points in Fig. S3(a).

Position	1	2	3	4	5	6	7	8	9	Average	theoretical
Mg (at%)	62.9	63.8	63.6	62.7	62.7	62.3	62.6	63.4	63.8	63.1	60.8
Bi (at%)	26.4	27.6	25.8	29.0	28.6	29.8	27.7	27.4	25.5	27.5	29.4
Sb (at%)	10.7	8.5	10.6	8.2	8.7	7.9	9.7	9.2	10.7	9.4	9.8
O (at%)	0	0.1	0	0	0	0	0	0	0	0	0

Table. S2 Grain boundary content (t_{GB}) and potential barrier height (E_{bh}) in ⊥F and ∥F of $Mg_{3.1}Bi_{1.5}Sb_{0.49}Te_{0.01}$ samples with different particle size.

	Grain boundary content (t_{GB})		Potential barrier height (E_{bh})	
	⊥F	∥F	⊥F	∥F
+20 mn	0.00008	0.0003	3.0 meV	17.4 meV
+160 mn	0.00085	0.0017	34.6 meV	44.3 meV
+600 mn	0.0013	0.0035	62.1 meV	79.0 meV

Notes

According to typical band transport equations,[1] the electrical conductivity of each phase can be expressed as:

$$\sigma_i = \sigma_{E_0}(T) s F_{s-1}(\eta_i) \quad \text{(S1)}$$

And the Seebeck coefficient can be expressed as:

$$S_i = \frac{k_B}{e}\left[\frac{(s+1)F_s(\eta_i)}{sF_{s-1}(\eta_i)} - \eta_i\right] \quad \text{(S2)}$$

where the subscript i denotes the phase (bulk phase and GB phase), σ_{E0} is a transport coefficient that determines the magnitude of conductivity, η is the reduced Fermi-level, F_j is the Fermi-Dirac integral, s is a parameter for the conduction mechanism and k_B is the Boltzmann constant.

Treating the two phases as the series circuit configuration, the total electrical conductivity σ can be calculated by:

$$\sigma^{-1} = (1 - t_{GB})\sigma_G^{-1} + t_{GB}\sigma_{GB}^{-1} \quad \text{(S3)}$$

where the subscripts G and GB refer to the bulk phase and grain boundary phase, respectively. t_{GB} is the size fraction of the GB phase.

The potential barrier height, which is used to describe the intensity of GBS, was calculated with the following equation:[2]

$$E_{bh} = \begin{cases} \dfrac{e^2 d^2 N}{8\varepsilon} & dN < Q_t \\ \dfrac{e^2 Q_t^2}{8N\varepsilon} & dN > Q_t \end{cases} \quad \text{(S4)}$$

where E_{bh} is the potential barrier height, e is the elementary charge, d is the grain size, ε is the static dielectric constant, Q_t is the density of trapping states at the grain boundaries and N is the concentration of ionized impurity atoms.

The total thermal conductivity κ and Seebeck coefficient S can be further expressed as:

$$\kappa^{-1} = (1 - t_{GB})\kappa_G^{-1} + t_{GB}\kappa_{GB}^{-1} \quad \text{(S5)}$$

$$S = \frac{S_G \dfrac{1 - t_{GB}}{\kappa_G} + S_{GB}\dfrac{t_{GB}}{\kappa_{GB}}}{\dfrac{1 - t_{GB}}{\kappa_G} + \dfrac{t_{GB}}{\kappa_{GB}}} \quad \text{(S6)}$$

Since t_{GB} is very small and S_i and κ_i are similar in orders of magnitude between the bulk phase and the GB phase, eqn (S6) can be reduced to:[3]

$$S \approx S_G \quad \text{(S7)}$$

Reference

1. S. D. Kang and G. J. Snyder, *Nat. Mater.*, 2016, **16**, 252-257.
2. C. L. Hu, K. Y. Xia, C. G. Fu, X. B. Zhao and T. J. Zhu, *Energy Environ. Sci.*, 2022, **15**, 1406-1422.
3. J. J. Kuo, S. D. Kang, K. Imasato, H. Tamaki, S. Ohno, T. Kanno and G. J. Snyder, *Energy Environ. Sci.*, 2018, **11**, 429-434.