Supplementary Information

Versatile roles of elemental doping in the optimization of thermoelectric performance of R-GeTe studied by first principles calculations

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Supplementary Figures

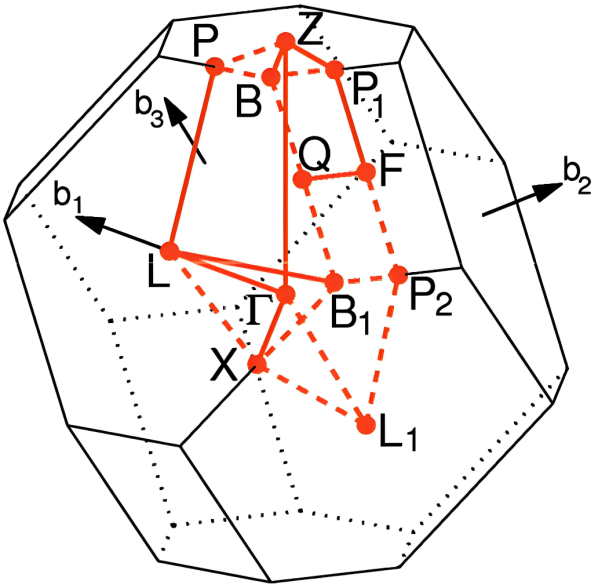

Fig. S1 The Brillouin zone of R-GeTe. K-point Path: Γ–L–B1|B–Z–Γ–X|Q–F–P1–Z|L–P.

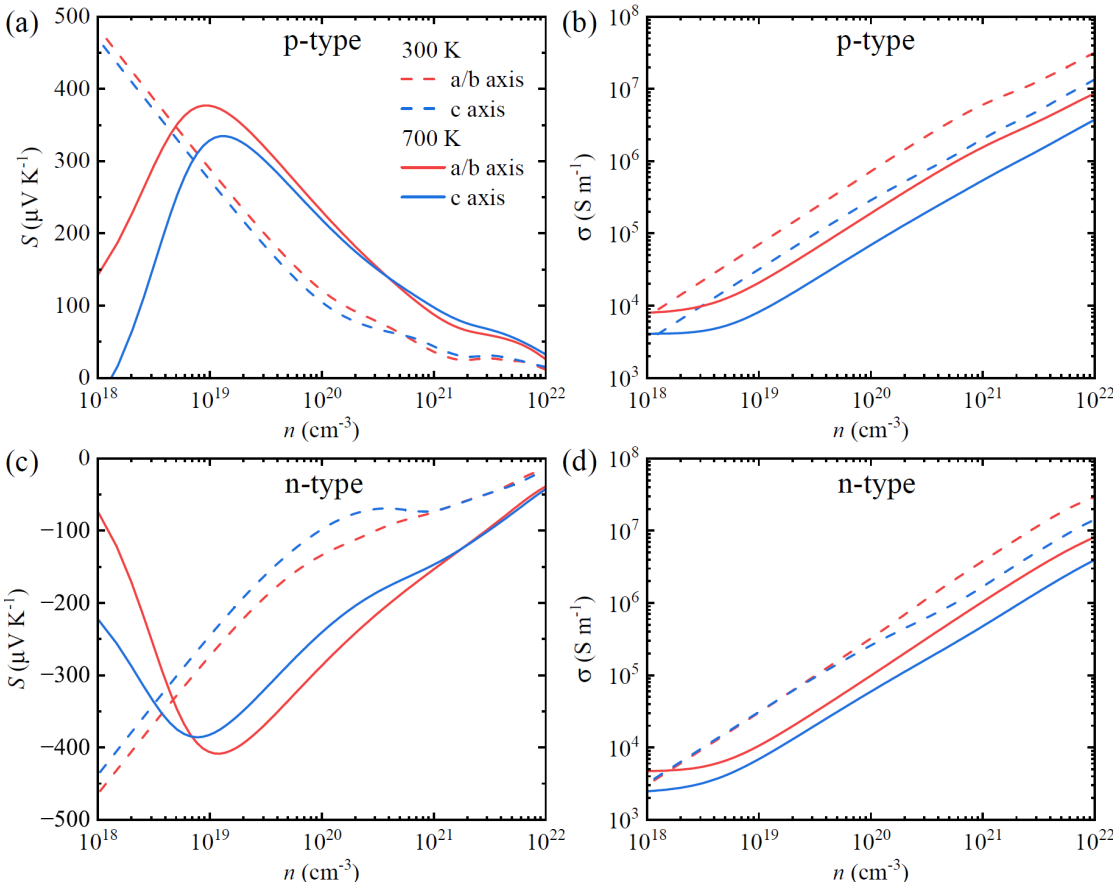

Fig. S2 The calculated (a,c) Seebeck coefficient and (b,d) electrical conductivity as a function of carrier concentration of R-GeTe at 300 K and 700 K.

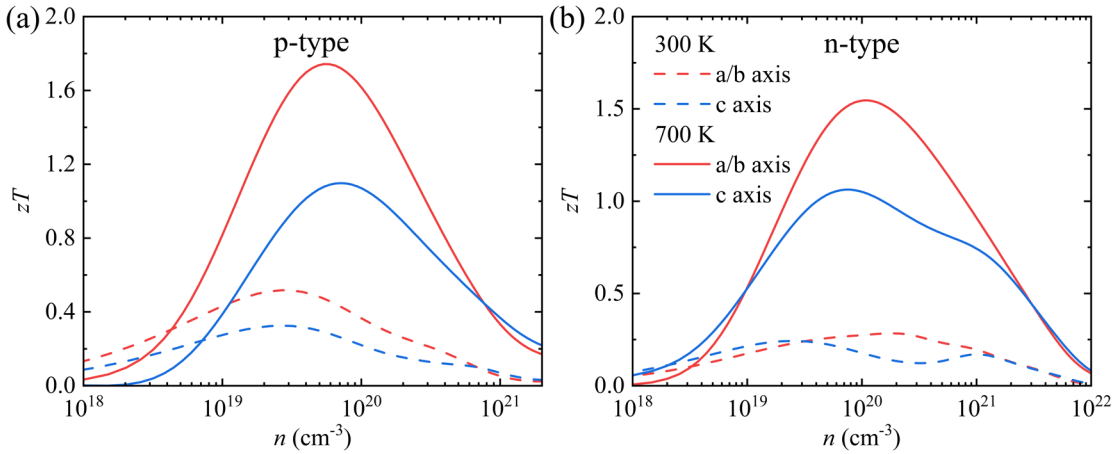

Fig. S3 The *zT* values of R-GeTe at (a) 300 K and (b) 700 K as a function of carrier concentration.

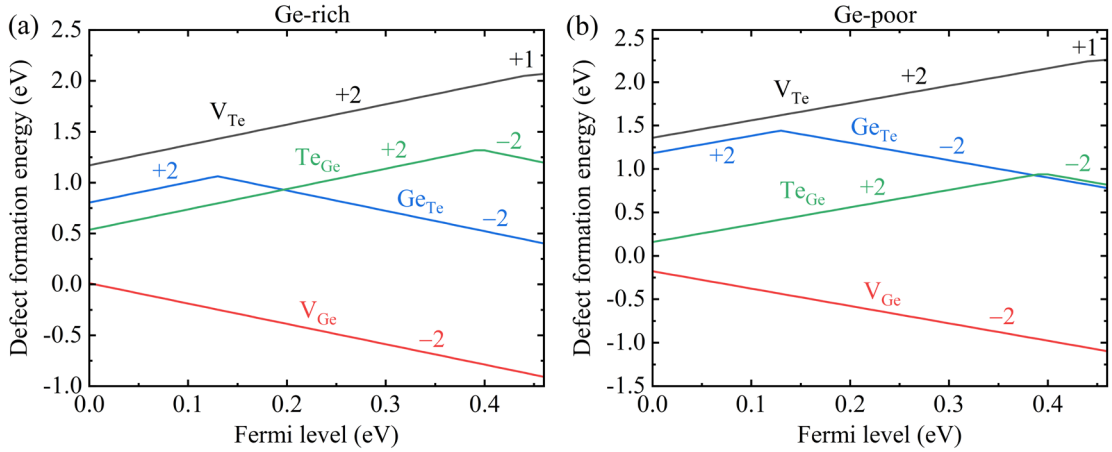

Fig. S4 The calculated defect formation energy as a function of the Fermi level under Ge-rich and Ge-poor conditions for R-GeTe.

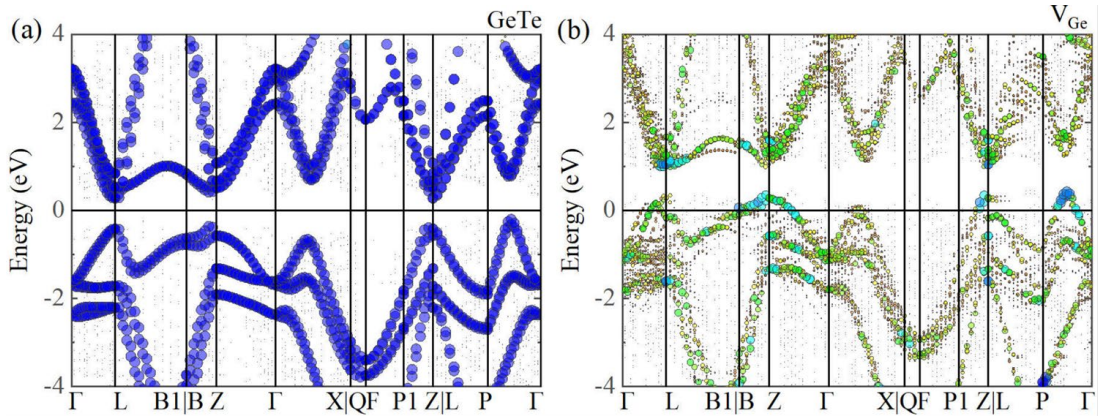

Fig. S5 (a) The intrinsic band structure and (b) the band structure containing a Ge vacancy V_{Ge} in R-GeTe (The calculated supercell band is unfolded to the first Brillouin zone).

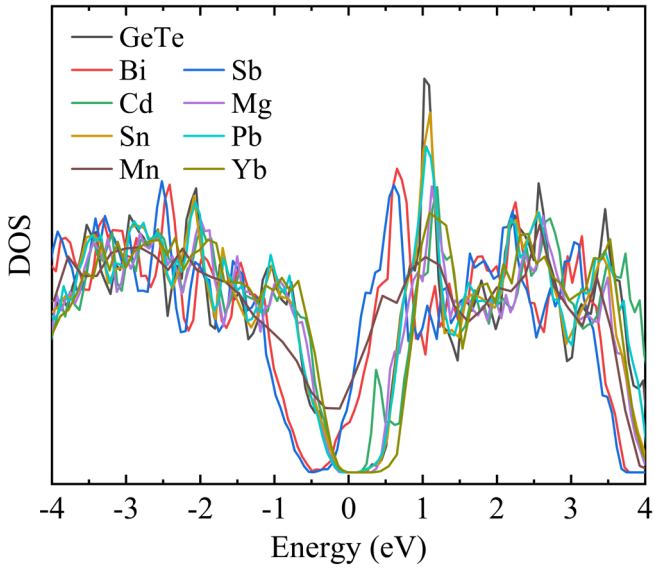

Fig. S6 The density of states (DOS) of doped R-GeTe.

Supplementary Tables

Table S1 The high symmetry K point of R-GeTe. (Where, $\eta = 0.703,\ \nu = 0.398$)

K point	$\times \mathbf{b_1}$	$\times \mathbf{b_2}$	$\times \mathbf{b_3}$	K point	$\times \mathbf{b_1}$	$\times \mathbf{b_2}$	$\times \mathbf{b_3}$
Γ	0	0	0	**L**	0.5	0	0
B_1	0.5	1−η	η−1	**B**	η	0.5	1−η
Z	0.5	0.5	0.5	**X**	ν	0	−ν
Q	1−ν	ν	0	**F**	0.5	0.5	0
P	η	ν	ν	**P_1**	1−ν	1−ν	1−η
P_2	ν	ν	η−1	**L_1**	0	0	-0.5

Table S2 The calculated elastic constant C_β (eV Å^{-3}), the DP constant E_β (eV), the carrier effective mass m* (m_e) and the relaxation time τ (fs) of R-GeTe.

Type	Axis	m*	C_β	E_β	τ (300 K)	τ (700 K)
p-type	a/b	0.71	0.55	10.05	50.12	14.06
	c	0.71	0.24	8.49	30.19	8.47
n-type	a/b	0.96	0.55	10.67	28.46	7.98
	c	0.96	0.24	9.64	15.00	4.21

Table S3 The p-type optimum *zT*, corresponding carrier concentration and thermoelectric transport coefficients at 300 K and 700 K of R-GeTe (where, n is the carrier concentration (10^{19} cm^{-3}), $\boldsymbol{S}$ is the Seebeck coefficient (μV K^{-1}), $\boldsymbol{\sigma}$ is the electrical conductivity (10^4 S m^{-1}), $\boldsymbol{PF}$ is the power factor (mW m^{-1} K^{-2}), and $\boldsymbol{\kappa}$ is the thermal conductivity (W m^{-1} K^{-1})).

T	Axis	n	$\boldsymbol{S}$	$\boldsymbol{\sigma}$	$\boldsymbol{PF}$	$\boldsymbol{\kappa}$	$(\boldsymbol{zT})_{max}$
300	a/b	2.66	211	18.81	8.37	4.85	0.5
	c	2.66	195	8.29	3.14	2.89	0.3
700	a/b	5.93	270	11.32	8.07	3.33	1.7
	c	7.14	243	5.02	2.96	1.88	1.1

Table S3 The calculated elastic constants C_{ij} (GPa) of GeTe-based materials.

Dopants	C_{11}	C_{12}	C_{13}	C_{14}	C_{44}	C_{66}
Bulk	89.71	18.49	19.37	-15.93	25.84	35.48
Bi	59.85	19.90	22.13	-13.17	19.85	19.75
Sb	58.72	21.18	23.26	-11.35	18.90	18.61
Cd	75.11	23.39	18.62	-5.06	13.12	25.96
Mg	81.79	19.77	19.70	-10.64	21.79	31.19
Sn	83.47	17.54	19.24	-15.08	24.83	32.99
Pb	80.11	17.40	19.06	-14.10	23.68	31.29
Mn	89.17	19.74	25.42	-13.47	17.46	34.56
Yb	76.03	17.42	22.30	-14.64	27.74	29.26

Table S4 The calculated structure parameters and bond length between doping atom and Te atom (d_{X-Te1} and d_{X-Te2}) of GeTe-based materials.

Dopants	a	γ	γ_1	γ_2	d_{X-Te1}	d_{X-Te2}
Bulk	8.750	57.77	57.77	57.77	2.854	3.254
Bi	8.879	57.23	55.70	58.07	3.101	3.241
Sb	8.786	57.76	56.79	58.20	3.045	3.195
Cd	8.751	57.98	56.32	57.16	2.938	3.239
Mg	8.671	58.48	57.90	57.83	2.943	3.094
Sn	8.823	57.81	57.04	58.92	3.025	3.262
Pb	8.877	57.67	56.35	59.36	3.098	3.289
Mn	8.540	58.05	59.56	53.83	2.608	2.839
Yb	8.804	58.02	57.77	59.72	3.144	3.113