Supporting Information

Novel IV-V-VI Semiconductors with Ultralow Lattice Thermal Conductivity

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Estimation of elastic moduli

According to the Voigt approximation, the bulk modulus (B_{V}) and shear modulus (G_{V}) are defined as[1]

$$B_{\mathrm{V}} = \frac{2\left(c_{11}+c_{12}\right)+c_{33}+4c_{13}}{9}, \qquad (\text{* MERGEFORMAT 1})$$

$$G_{\mathrm{V}} = \frac{c_{11}+c_{12}+2c_{33}+12\left(c_{44}+c_{66}\right)-4c_{13}}{30}, \qquad (\text{* MERGEFORMAT 2})$$

where c_{ij} is the elastic stiffness constant. Within the Reuss model, they can be expressed as[1]

$$B_{\mathrm{R}} = \frac{c_{33}\left(c_{11}+c_{12}\right)-2c_{13}^{2}}{2c_{33}+c_{11}+c_{12}-4c_{13}}, \qquad (\text{* MERGEFORMAT 3})$$

$$G_{\mathrm{R}} = \frac{5\left[c_{33}\left(c_{11}+c_{12}\right)-2c_{13}^{2}\right]\left(c_{44}c_{66}-c_{14}^{2}\right)}{6B_{\mathrm{V}}\left(c_{44}c_{66}-c_{14}^{2}\right)+2\left[c_{33}\left(c_{11}+c_{12}\right)-2c_{13}^{2}\right]\left(c_{44}+c_{66}\right)}. \quad (\text{* MERGEFORMAT 4})$$

The Reuss moduli based on uniform stress indicate the lower limit of actual moduli while Voigt moduli from uniform strain represent the upper limit. Hill proposed a method that is the arithmetic average of Reuss and Voigt values.[2] In this work, the bulk modulus (B_{H}) and shear modulus (G_{H}) are obtained in terms of the Voigt-Reuss-Hill approximation

$$B_{\mathrm{H}} = \frac{B_{\mathrm{V}} + B_{\mathrm{R}}}{2}, \quad (\text{* MERGEFORMAT 5})$$

$$G_{\mathrm{H}} = \frac{G_{\mathrm{V}} + G_{\mathrm{R}}}{2}. \quad (\text{* MERGEFORMAT 6})$$

Young's modulus (E) is determined by

$$E = \frac{9B_{\mathrm{H}}G_{\mathrm{H}}}{3B_{\mathrm{H}} + G_{\mathrm{H}}}. \quad (\text{* MERGEFORMAT 7})$$

Table S1 The used *k*-point meshes for self-consistent field (SCF) as well as 2nd and 3rd order IFC calculations. The size of the supercells employed in the calculations of IFCs is shown in parentheses. We present the specific parameters of q-points and scalebroad (parentheses) for the solution of the BTE as implemented in ShengBTE package.

System	SCF *k*-point mesh	2nd order IFC	3rd order IFC	BTE solution
$A_1B_2C_4$	9×9×3	5×5×3 (2×2×1)	Γ (2×2×1)	17×17×2 (0.5)
$A_1B_4C_7$	9×9×5	5×5×3 (2×2×2)	Γ (2×2×2)	15×15×4 (1.0)
$A_2B_2C_5$	9×9×5	5×5×3 (2×2×2)	Γ (2×2×2)	15×15×5 (1.0)
$A_3B_2C_6$	9×9×3	5×5×3 (2×2×1)	Γ (2×2×1)	15×15×2 (0.2)

Table S2 The complete list of 144 compositions and their competing stable phases as well as the calculated total energy E_{total} (eV/atom) and formation energy. E_{f1} (eV/atom) is the formation energy of a compound with respect to its elements, whereas E_{f2} (meV/atom) corresponds to the formation energy of a compound relative to their competing stable phases.

$A_1B_2C_4$	E_{f1}	Competing Stable Phases			$\lvert E_{total}\rvert$				E_{f2}
SiAsS	-0.244	SiS_2	AsS		4.713	5.336	4.715		267.86
SiAsSe	-0.329	$SiSe_2$	As_2Se_3	As	4.433	4.752	4.346	4.672	117.94
SiAsTe	-0.278	$SiAs_2$	Te		4.18	5.279	3.143		-121.79
SiSbS	-0.350	SiS_2	Sb_2S_3	Sb	4.668	5.336	4.630	4.380	240.67
SiSbSe	-0.444	$SiSe_2$	Sb_2Se_3	Sb	4.396	4.752	4.306	4.380	108.42
SiSbTe	-0.370	Sb_2Te_3	Si	Te	4.12	4.024	5.425	3.143	-22.00
SiBiS	-0.467	SiS_2	Bi_2S_3	Bi	4.715	5.336	4.704	3.833	176.71
SiBiSe	-0.559	$SiSe_2$	Bi_2Se_3	Bi	4.442	4.752	4.398	3.833	53.99
SiBiTe	-0.467	Bi_2Te_3	Si	Te	4.148	4.076	5.425	3.143	-12.93
GeAsS	-0.308	GeS_2	AsS		4.662	4.715	4.715		52.63
GeAsSe	-0.402	$GeSe_2$	As_2Se_3	As	4.391	4.316	4.346	4.672	-27.17
GeAsTe	-0.348	GeTe	As_2Te_3		4.135	4.245	4.100		6.46
GeSbS	-0.441	GeS_2	Sb_2S_3	Sb	4.644	4.715	4.630	4.380	-1.56
GeSbSe	-0.534	GeSe	Sb_2Se_3		4.371	4.508	4.306		-7.16
GeSbTe	-0.451	GeTe	Sb_2Te_3		4.086	4.245	4.024		0.74
GeBiS	-0.569	GeS	Bi_2S_3		4.702	4.819	4.704		34.57
GeBiSe	-0.657	GeSe	Bi_2Se_3		4.425	4.508	4.398		4.34
GeBiTe	-0.554	GeTe	Bi_2Te_3		4.12	4.245	4.076		3.81
SnAsS	-0.354	SnS_2	AsS		4.619	4.650	4.715		67.81

SnAsSe	-0.457	SnSe	As_2Se_3		4.356	4.455	4.346		20.94
SnAsTe	-0.400	SnTe	As_2Te_3		4.097	4.147	4.100		16.49
SnSbS	-0.515	SnS	Sb_2S_3		4.628	4.766	4.630		40.74
SnSbSe	-0.604	SnSe	Sb_2Se_3		4.352	4.455	4.306		-3.13
SnSbTe	-0.510	SnTe	Sb_2Te_3		4.056	4.147	4.024		2.77
SnBiS	-0.654	SnS	Bi_2S_3		4.698	4.766	4.704		23.46
SnBiSe	-0.736	SnSe	Bi_2Se_3		4.414	4.455	4.398		0.37
SnBiTe	-0.618	SnTe	Bi_2Te_3		4.095	4.147	4.076		0.84
PbAsS	-0.377	PbS	As_2S_3		4.602	4.789	4.641		81.29
PbAsSe	-0.488	PbSe	As_2Se_3		4.347	4.514	4.346		46.74
PbAsTe	-0.434	PbTe	As_2Te_3		4.092	4.178	4.100		30.29
PbSbS	-0.560	PbS	Sb_2S_3		4.634	4.789	4.630		41.29
PbSbSe	-0.651	PbSe	Sb_2Se_3		4.359	4.514	4.306		6.67
PbSbTe	-0.551	PbTe	Sb_2Te_3		4.057	4.178	4.024		10.57
PbBiS	-0.711	PbS	Bi_2S_3		4.715	4.789	4.704		13.00
PbBiSe	-0.791	PbSe	Bi_2Se_3		4.429	4.514	4.398		2.17
PbBiTe	-0.664	PbTe	Bi_2Te_3		4.101	4.178	4.076		3.64
$A_1B_4C_7$	E_{f1}	Competing Stable Phases				$\|E_{total}\|$			E_{f2}
SiAsS	-0.253	SiS_2	As_2S_3	AsS	4.671	5.336	4.641	4.715	168.250
SiAsSe	-0.352	$SiSe_2$	As_2Se_3	As	4.396	4.752	4.346	4.672	69.383
SiAsTe	-0.308	$SiAs_2$	As_2Te_3	Te	4.146	5.279	4.100	3.143	-70.292
SiSbS	-0.392	SiS_2	Sb_2S_3	Sb	4.633	5.336	4.630	4.380	159.472
SiSbSe	-0.492	$SiSe_2$	Sb_2Se_3	Sb	4.360	4.752	4.306	4.380	61.869

SiSbTe	-0.417	Si	Sb_2Te_3	Te	4.079	5.425	4.024	3.143	-12.000
SiBiS	-0.540	SiS_2	Bi_2S_3	Bi	4.700	5.336	4.704	3.833	113.333
SiBiSe	-0.635	$SiSe_2$	Bi_2Se_3	Bi	4.422	4.752	4.398	3.833	33.161
SiBiTe	-0.535	Si	Bi_2Te_3	Te	4.116	5.425	4.076	3.143	-5.750
GeAsS	-0.291	GeS_2	As_2S_3	AsS	4.641	4.715	4.641	4.715	42.950
GeAsSe	-0.394	$GeSe_2$	As_2Se_3	As	4.371	4.316	4.346	4.672	-14.767
GeAsTe	-0.348	GeTe	As_2Te_3		4.119	4.245	4.100		5.267
GeSbS	-0.446	GeS_2	Sb_2S_3	Sb	4.620	4.715	4.630	4.380	17.172
GeSbSe	-0.546	GeSe	Sb_2Se_3		4.346	4.508	4.306		-6.133
GeSbTe	-0.465	GeTe	Sb_2Te_3		4.060	4.245	4.024		0.433
GeBiS	-0.601	GeS	Bi_2S_3		4.694	4.819	4.704		28.833
GeBiSe	-0.694	GeSe	Bi_2Se_3		4.413	4.508	4.398		3.283
GeBiTe	-0.587	GeTe	Bi_2Te_3		4.101	4.245	4.076		2.683
SnAsS	-0.315	SnS_2	As_2S_3	AsS	4.613	4.650	4.641	4.715	54.725
SnAsSe	-0.423	SnSe	As_2Se_3		4.348	4.455	4.346		15.883
SnAsTe	-0.376	SnTe	As_2Te_3		4.095	4.147	4.100		12.950
SnSbS	-0.489	SnS	Sb_2S_3		4.611	4.766	4.630		41.517
SnSbSe	-0.587	SnSe	Sb_2Se_3		4.335	4.455	4.306		-3.867
SnSbTe	-0.500	SnTe	Sb_2Te_3		4.042	4.147	4.024		2.117
SnBiS	-0.652	SnS	Bi_2S_3		4.693	4.766	4.704		21.017
SnBiSe	-0.740	SnSe	Bi_2Se_3		4.407	4.455	4.398		0.550
SnBiTe	-0.626	SnTe	Bi_2Te_3		4.087	4.147	4.076		0.367
PbAsS	-0.325	PbS	As_2S_3		4.600	4.789	4.641		65.667

PbAsSe	-0.438	PbSe	As_2Se_3		4.340	4.514	4.346		33.683
PbAsTe	-0.395	PbTe	As_2Te_3		4.091	4.178	4.100		22.083
PbSbS	-0.515	PbS	Sb_2S_3		4.613	4.789	4.630		43.333
PbSbSe	-0.613	PbSe	Sb_2Se_3		4.338	4.514	4.306		2.933
PbSbTe	-0.523	PbTe	Sb_2Te_3		4.042	4.178	4.024		7.250
PbBiS	-0.685	PbS	Bi_2S_3		4.702	4.789	4.704		15.833
PbBiSe	-0.772	PbSe	Bi_2Se_3		4.416	4.514	4.398		1.350
PbBiTe	-0.652	PbTe	Bi_2Te_3		4.090	4.178	4.076		2.500
$A_2B_2C_5$	E_{f1}	Competing Stable Phases				$\lvert E_{total}\rvert$			E_{f2}
SiAsS	-0.224	AsS	SiS_2	As	4.762	4.715	5.336	4.672	362.111
SiAsSe	-0.296	As_2Se_3	$SiSe_2$	As	4.479	4.346	4.752	4.672	186.022
SiAsTe	-0.238	Te	SiAs		4.225	3.143	5.396		-80.489
SiSbS	-0.297	Sb_2S_3	SiS_2	Sb	4.717	4.630	5.336	4.380	346.593
SiSbSe	-0.379	Sb_2Se_3	$SiSe_2$	Sb	4.444	4.306	4.752	4.380	170.485
SiSbTe	-0.305	Sb_2Te_3	Si	Te	4.174	4.024	5.425	3.143	-34.667
SiBiS	-0.378	Bi_2S_3	SiS_2	Bi	4.744	4.704	5.336	3.833	252.222
SiBiSe	-0.463	Bi_2Se_3	$SiSe_2$	Bi	4.474	4.398	4.752	3.833	76.430
SiBiTe	-0.378	Bi_2Te_3	Si	Te	4.193	4.076	5.425	3.143	-24.833
GeAsS	-0.329	AsS	GeS_2	As	4.688	4.715	4.715	4.672	21.978
GeAsSe	-0.412	As_2Se_3	$GeSe_2$	As	4.416	4.346	4.316	4.672	-42.044
GeAsTe	-0.349	As_2Te_3	GeTe		4.157	4.100	4.245		7.378
GeSbS	-0.432	Sb_2S_3	GeS_2	Sb	4.674	4.630	4.715	4.380	-24.541
GeSbSe	-0.515	Sb_2Se_3	GeSe		4.401	4.306	4.508		-5.189

GeSbTe	-0.429	Sb_2Te_3	GeTe		4.119	4.024	4.245		2.822
GeBiS	-0.526	Bi_2S_3	GeS		4.714	4.704	4.819		40.889
GeBiSe	-0.608	Bi_2Se_3	GeSe		4.440	4.398	4.508		6.756
GeBiTe	-0.508	Bi_2Te_3	GeTe		4.144	4.076	4.245		6.656
SnAsS	-0.409	AsS	SnS_2	SnS	4.629	4.715	4.650	4.766	75.433
SnAsSe	-0.502	As_2Se_3	SnSe		4.367	4.346	4.455		27.356
SnAsTe	-0.432	As_2Te_3	SnTe		4.101	4.100	4.147		19.867
SnSbS	-0.546	Sb_2S_3	SnS		4.648	4.630	4.766		42.378
SnSbSe	-0.625	Sb_2Se_3	SnSe		4.372	4.306	4.455		0.522
SnSbTe	-0.523	Sb_2Te_3	SnTe		4.074	4.024	4.147		4.311
SnBiS	-0.655	Bi_2S_3	SnS		4.703	4.704	4.766		28.378
SnBiSe	-0.729	Bi_2Se_3	SnSe		4.422	4.398	4.455		1.467
SnBiTe	-0.609	Bi_2Te_3	SnTe		4.106	4.076	4.147		1.144
PbAsS	-0.457	As_2S_3	PbS		4.615	4.641	4.789		91.778
PbAsSe	-0.560	As_2Se_3	PbSe		4.363	4.346	4.514		57.489
PbAsTe	-0.490	As_2Te_3	PbTe		4.097	4.100	4.178		37.556
PbSbS	-0.622	Sb_2S_3	PbS		4.662	4.630	4.789		38.556
PbSbSe	-0.703	Sb_2Se_3	PbSe		4.388	4.306	4.514		10.656
PbSbTe	-0.590	Sb_2Te_3	PbTe		4.079	4.024	4.178		13.000
PbBiS	-0.744	Bi_2S_3	PbS		4.730	4.704	4.789		11.556
PbBiSe	-0.815	Bi_2Se_3	PbSe		4.446	4.398	4.514		3.600
PbBiTe	-0.681	Bi_2Te_3	PbTe		4.116	4.076	4.178		4.833
$A_3B_2C_6$	E_{f1}	Competing Stable Phases				$\lvert E_{total}\rvert$			E_{f2}

SiAsS	-0.210	SiS_2	As		4.792	5.336	4.672		423.273
SiAsSe	-0.274	$SiSe_2$	As		4.507	4.752	4.672		230.618
SiAsTe	-0.212	Si	SiAs	Te	4.252	5.425	5.396	3.143	-82.127
SiSbS	-0.265	SiS_2	Sb		4.751	5.336	4.380		411.182
SiSbSe	-0.339	$SiSe_2$	Sb		4.476	4.752	4.380		208.527
SiSbTe	-0.264	Sb_2Te_3	Si	Te	4.208	4.024	5.425	3.143	-42.364
SiBiS	-0.325	SiS_2	Bi		4.767	5.336	3.833		295.727
SiBiSe	-0.405	$SiSe_2$	Bi		4.497	4.752	3.833		88.073
SiBiTe	-0.323	Si	Bi_2Te_3	Te	4.223	5.425	4.076	3.143	-33.773
GeAsS	-0.341	GeS_2	As		4.704	4.715	4.672		3.018
GeAsSe	-0.420	$GeSe_2$	As		4.433	4.316	4.672		-52.600
GeAsTe	-0.350	GeTe	As_2Te_3		4.171	4.245	4.100		7.964
GeSbS	-0.427	GeS_2	Sb		4.693	4.715	4.380		-39.073
GeSbSe	-0.503	GeSe	Sb_2Se_3		4.420	4.508	4.306		-3.845
GeSbTe	-0.415	GeTe	Sb_2Te_3		4.140	4.245	4.024		4.145
GeBiS	-0.501	GeS	Bi_2S_3		4.723	4.819	4.704		43.545
GeBiSe	-0.578	GeSe	Bi_2Se_3		4.451	4.508	4.398		6.836
GeBiTe	-0.480	GeTe	Bi_2Te_3		4.160	4.245	4.076		7.736
SnAsS	-0.447	SnS_2	AsS	SnS	4.639	4.650	4.715	4.766	76.645
SnAsSe	-0.534	SnSe	As_2Se_3		4.377	4.455	4.346		28.436
SnAsTe	-0.454	SnTe	As_2Te_3		4.104	4.147	4.100		21.564
SnSbS	-0.566	SnS	Sb_2S_3		4.661	4.766	4.630		43.145
SnSbSe	-0.640	SnSe	Sb_2Se_3		4.386	4.455	4.306		1.573

SnSbTe	-0.532	SnTe	Sb_2Te_3	4.086	4.147	4.024	4.745
SnBiS	-0.656	SnS	Bi_2S_3	4.707	4.766	4.704	30.691
SnBiSe	-0.725	SnSe	Bi_2Se_3	4.427	4.455	4.398	2.255
SnBiTe	-0.603	SnTe	Bi_2Te_3	4.113	4.147	4.076	1.336
PbAsS	-0.515	PbS	As_2S_3	4.631	4.789	4.641	90.727
PbAsSe	-0.613	PbSe	As_2Se_3	4.380	4.514	4.346	57.509
PbAsTe	-0.529	PbTe	As_2Te_3	4.103	4.178	4.100	39.364
PbSbS	-0.663	PbS	Sb_2S_3	4.682	4.789	4.630	34.636
PbSbSe	-0.737	PbSe	Sb_2Se_3	4.407	4.514	4.306	12.645
PbSbTe	-0.616	PbTe	Sb_2Te_3	4.094	4.178	4.024	13.545
PbBiS	-0.764	PbS	Bi_2S_3	4.739	4.789	4.704	11.182
PbBiSe	-0.831	PbSe	Bi_2Se_3	4.457	4.514	4.398	4.327
PbBiTe	-0.692	PbTe	Bi_2Te_3	4.126	4.178	4.076	5.136

Table S3 Calculated lattice parameters of the 14 documented compounds. The available experimental data are listed in parentheses for comparison.[3-8]

Compound	*a* (Å)	*c* (Å)
$Ge_1Sb_2Te_4$	4.22 (4.25)	41.25 (41.00)
$Ge_1Bi_2Te_4$	4.28 (4.32)	41.83 (41.38)
$Sn_1Bi_2Te_4$	4.36 (4.41)	42.32 (41.51)
$Pb_1Bi_2Te_4$	4.38 (4.44)	42.67 (41.68)
$Ge_1Sb_4Te_7$	4.23 (4.21)	24.06 (23.65)
$Ge_1Bi_4Te_7$	4.30 (4.35)	24.41 (23.93)
$Sn_1Bi_4Te_7$	4.35 (4.39)	24.58 (23.98)
$Pb_1Bi_4Te_7$	4.36 (4.42)	24.70 (24.04)
$Pb_2Bi_2Se_5$	4.20 (4.22)	16.68 (16.42)
$Ge_2Sb_2Te_5$	4.21 (4.25)	17.16 (17.27)
$Pb_2Sb_2Te_5$	4.36 (4.40)	17.79 (17.50)
$Pb_2Bi_2Te_5$	4.42 (4.46)	17.91 (17.52)
$Ge_3Sb_2Te_6$	4.21 (4.25)	61.83 (62.60)
$Ge_3Bi_2Te_6$	4.24 (4.28)	62.48 (62.57)

Table S4 Electronic band gap E_g (eV) using HSE06 functional, mechanical properties including bulk modulus B_H (GPa), shear modulus G_H (GPa) and Young's modulus E (GPa), longitudinal group velocity v_L (ms^{-1}), transverse group velocity v_T (ms^{-1}) and mean group velocity v_m (ms^{-1}) as well as the room-temperature total mode Grüneisen parameter γ and lattice thermal conductivity κ_l ($Wm^{-1}K^{-1}$) for 70 stable compounds. The calculated bulk modulus and band gap of $Ge_2Sb_2Te_5$ agree well with experiments (parentheses).[9,10]

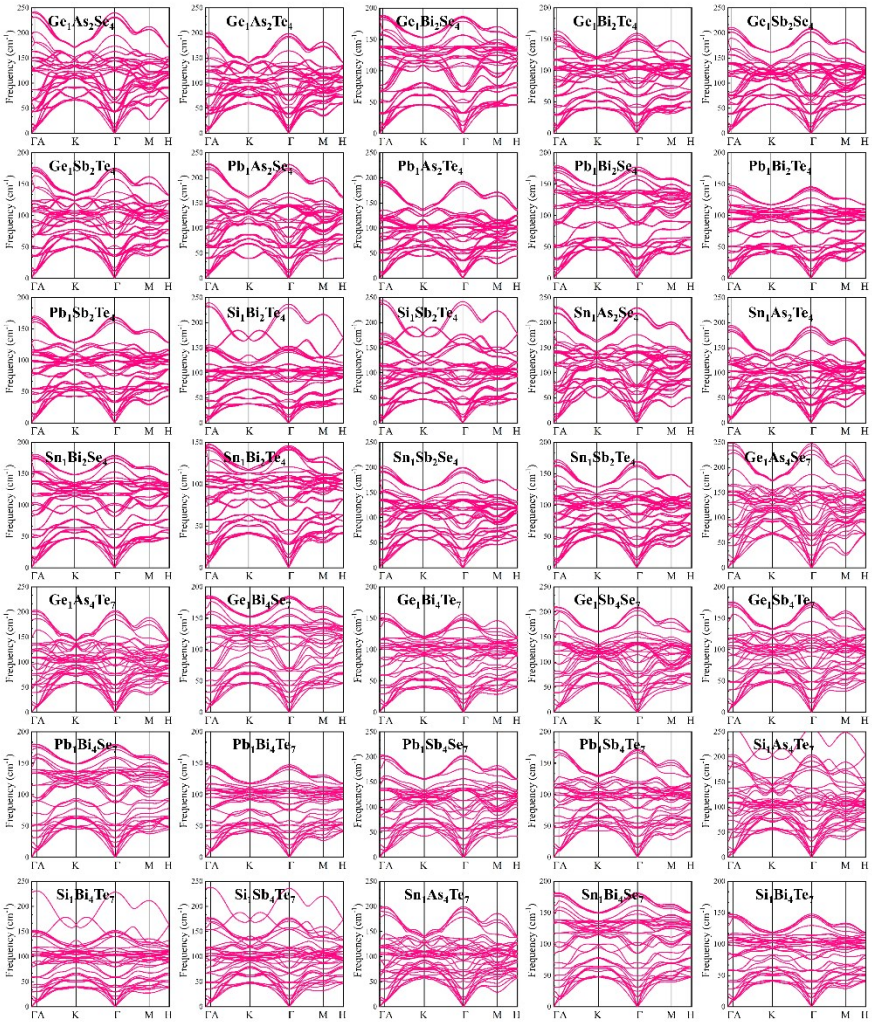
$A_1B_2C_4$	E_g	B_H	G_H	E	v_L	v_T	v_m	γ	κ_l
GeAsSe	0.89	51	39	93	4075	2635	2891	1.79	0.82
GeAsTe	0.75	49	30	75	3448	2188	2407	1.59	1.15
GeBiSe	0.87	36	26	63	2960	1906	2093	1.42	0.92
GeBiTe	1.03	37	24	59	2813	1793	1971	1.33	0.95
GeSbSe	0.55	47	28	69	3429	2164	2382	1.54	1.00
GeSbTe	0.61	44	30	72	3347	2140	2351	1.39	1.16
SiBiTe	0.95	41	28	68	3035	1940	2131	1.41	0.75
SiSbTe	0.45	43	33	78	3529	2281	2503	1.44	0.89
SnAsSe	0.69	48	30	75	3581	2272	2499	1.83	0.63
SnAsTe	0.68	34	29	68	3244	2124	2327	1.62	0.95
SnBiSe	0.76	32	20	49	2602	1652	1817	1.25	1.16
SnBiTe	0.89	37	22	55	2719	1719	1891	1.29	0.88
SnSbSe	0.48	40	23	59	3126	1973	2171	1.45	0.96
SnSbTe	0.57	33	21	52	2821	1791	1970	1.37	0.97
PbAsSe	0.90	51	31	78	3453	2185	2404	1.76	0.66
PbAsTe	0.95	43	23	58	2888	1809	1993	1.55	0.90
PbBiSe	0.90	44	27	67	2914	1847	2032	1.19	1.28
PbBiTe	1.03	38	18	46	2405	1491	1644	1.25	0.91
PbSbTe	0.70	37	22	55	2794	1766	1943	1.36	0.85
$A_1B_4C_7$	E_g	B_H	G_H	E	v_L	v_T	v_m	γ	κ_l
GeAsSe	0.72	46	34	81	3813	2455	2696	1.78	0.83
GeAsTe	0.76	49	31	77	3476	2209	2429	1.52	1.09
GeBiSe	0.75	31	23	55	2729	1758	1930	1.26	1.02
GeBiTe	0.89	33	13	35	2133	1311	1447	1.23	0.85
GeSbSe	0.29	37	27	65	3306	2128	2337	1.43	0.95
GeSbTe	0.46	37	24	59	3028	1926	2117	1.31	0.98
SiAsTe	0.50	43	29	71	3382	2159	2372	1.55	0.97
SiBiTe	0.86	39	23	58	2777	1755	1931	1.29	0.71
SiSbTe	0.37	42	28	69	3305	2109	2318	1.35	0.86
SnAsTe	0.65	40	21	53	2875	1796	1979	1.55	0.87

SnBiSe	0.63	39	24	60	2842	1803	1983	1.13	1.23
SnBiTe	0.76	39	21	54	2671	1678	1848	1.19	0.83
SnSbSe	0.20	44	26	66	3307	2091	2300	1.38	0.91
SnSbTe	0.33	40	10	28	2064	1241	1372	1.29	0.87
PbBiSe	0.72	36	22	55	2653	1682	1849	1.10	1.30
PbBiTe	0.85	32	19	47	2430	1531	1685	1.17	0.83
PbSbSe	0.29	33	23	55	2946	1886	2072	1.37	0.91
PbSbTe	0.42	33	15	39	2400	1486	1639	1.29	0.83
$A_2B_2C_5$	E_g	B_H	G_H	E	v_L	v_T	v_m	γ	κ_l
GeAsSe	0.73	52	36	88	3928	2513	2761	1.93	0.75
GeBiSe	0.69	46	34	82	3445	2222	2439	1.87	0.62
GeBiTe	0.92	43	28	69	3075	1957	2152	1.62	0.99
GeSbSe	0.34	50	33	81	3702	2358	2592	1.85	0.89
GeSbTe	0.46(0.50[9])	39(44[10])	29	70	3284	2114	2321	1.64	1.20
SiBiTe	0.65	45	31	75	3278	2096	2303	1.69	0.66
SiSbTe	0.17	43	28	70	3374	2152	2365	1.73	0.75
SnAsSe	0.58	43	25	63	3257	2056	2263	2.15	0.37
SnAsTe	0.54	42	25	62	3093	1954	2150	1.80	0.71
SnBiSe	0.46	47	27	68	3104	1956	2153	1.49	1.11
SnBiTe	0.60	36	8	22	1744	1043	1154	1.52	0.92
SnSbSe	0.20	50	28	71	3409	2146	2362	1.66	1.00
SnSbTe	0.36	40	23	59	3009	1898	2089	1.57	0.90
PbAsSe	0.69	38	28	67	3098	1997	2192	2.35	0.28
PbAsTe	0.76	36	26	64	2941	1893	2078	1.55	1.65
PbBiSe	0.80	49	25	65	2848	1780	1961	1.49	1.68
PbBiTe	0.94	37	20	51	2510	1574	1734	1.71	1.00
PbSbS	0.91	44	29	71	3417	2175	2392	2.11	0.60
PbSbSe	0.47	51	28	71	3175	1994	2195	1.43	2.02
PbSbTe	0.60	39	22	56	2765	1743	1919	1.50	1.00
$A_3B_2C_6$	E_g	B_H	G_H	E	v_L	v_T	v_m	γ	κ_l
GeAsSe	0.68	22	27	58	3181	2174	2368	1.97	0.78
GeBiTe	0.86	42	32	76	3255	2101	2306	1.77	0.93
GeSbTe	0.50	46	34	81	3539	2279	2503	1.76	1.09
SnAsSe	0.61	44	30	73	3475	2220	2439	2.32	0.29
SnAsTe	0.51	45	27	68	3222	2040	2244	1.78	0.75
SnBiSe	0.42	47	27	67	3114	1962	2159	1.55	1.23
SnBiTe	0.55	22	22	50	2639	1765	1929	1.56	1.08
SnSbSe	0.32	48	10	27	2100	1253	1387	1.68	1.08

SnSbTe	0.42	40	25	63	3100	1970	2166	1.61	1.04
PbAsTe	0.70	47	27	68	3002	1895	2085	1.78	0.67
PbBiSe	0.83	47	29	72	2981	1887	2076	1.43	1.25
PbSbSe	0.58	51	30	75	3206	2024	2227	1.63	0.83
PbSbTe	0.70	40	24	60	2826	1789	1968	1.59	0.81

Table S5 The calculated average –IpCOHP (eV) and bond length (Å) of different atomic interactions for four GST compounds.

Compound	-IpCOHP (eV)			Bond length (Å)		
	Ge-Te	Sb-Te	Te-Te	Ge-Te	Sb-Te	Te-Te
$Ge_1Sb_2Te_4$	1.774	1.658	0.146	2.958	3.071	3.830
$Ge_1Sb_4Te_7$	1.772	1.660	0.154	2.958	3.070	3.820
$Ge_2Sb_2Te_5$	1.780	1.659	0.148	2.957	3.071	3.830
$Ge_3Sb_2Te_6$	1.780	1.670	0.140	2.957	3.071	3.830


Ge1As2Se4
Ge1As2Te4
Ge1Bi2Se4
Ge1Bi2Te4
Ge1Sb2Se4
Ge1Sb2Te4
Pb1As2Se4
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Pb1Bi2Se4
Pb1Bi2Te4
Pb1Sb2Te4
Si1Bi2Te4
Si1Sb2Te4
Sn1As2Se4
Sn1As2Te4
Sn1Bi2Se4
Sn1Bi2Te4
Sn1Sb2Se4
Sn1Sb2Te4
Ge1As4Se7
Ge1As4Te7
Ge1Bi4Se7
Ge1Bi4Te7
Ge1Sb4Se7
Ge1Sb4Te7
Pb1Bi4Se7
Pb1Bi4Te7
Pb1Sb4Se7
Pb1Sb4Te7
Si1As4Te7
Si1Bi4Te7
Si1Sb4Te7
Sn1As4Te7
Sn1Bi4Se7
Si1Bi4Te7
Frequency (cm-1)
ΓA K Γ M H

Fig. S1 Phonon dispersions of all 70 stable compounds.

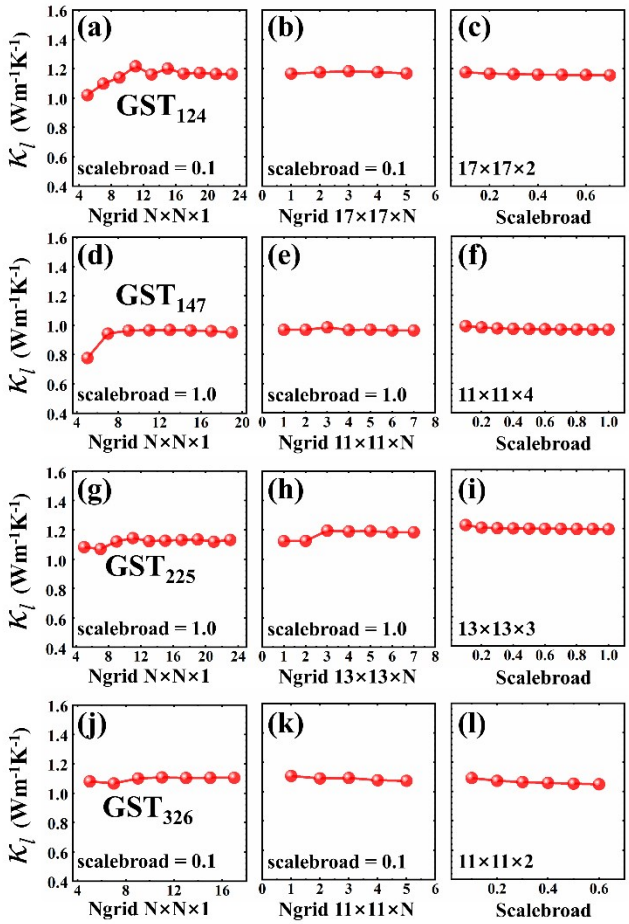

Fig. S2 The convergence tests of κ_l with respect to the q-point grid and scalebroad for (a-c) $Ge_1Sb_2Te_4$, (d-f) $Ge_1Sb_4Te_7$, (g-i) $Ge_2Sb_2Te_5$ and (j-l) $Ge_3Sb_2Te_6$, respectively.

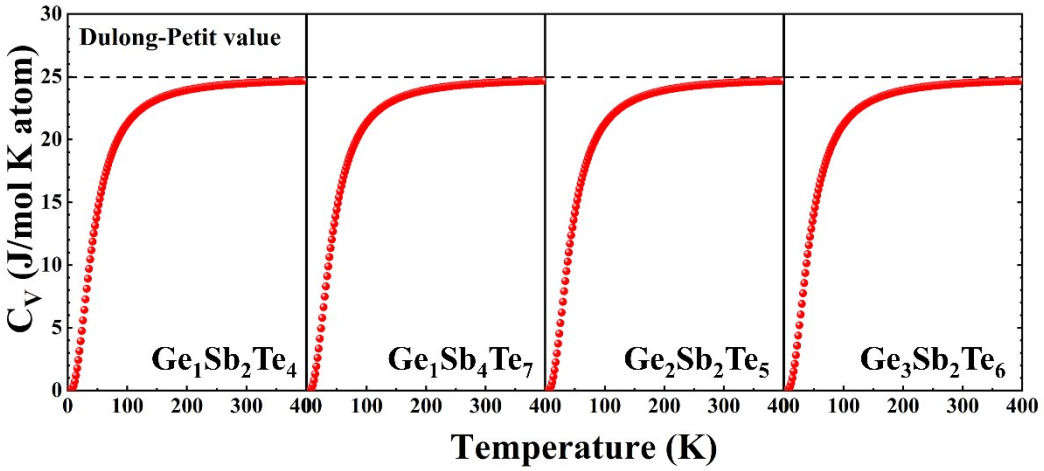

Fig. S3 Calculated heat capacity at constant volume of four GST compounds as a function of temperature.

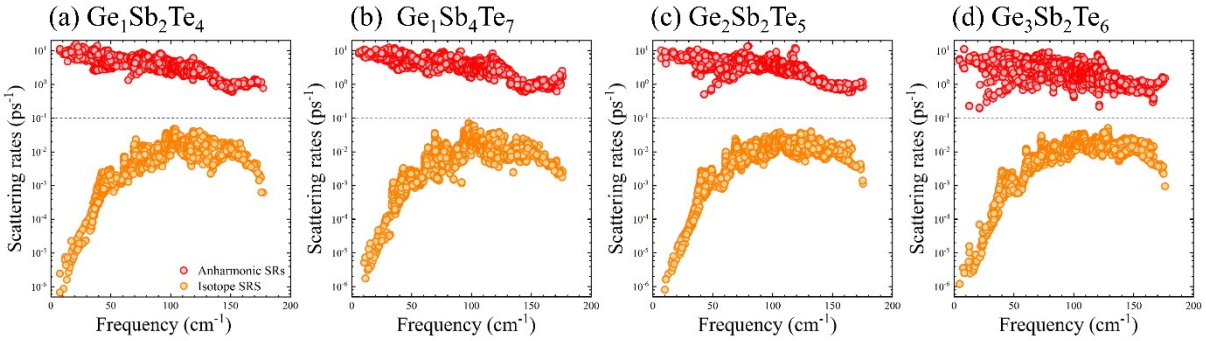

Fig. S4 Anharmonic scattering rates (SRs) and isotope SRs of four GST compounds as a function of phonon frequency.

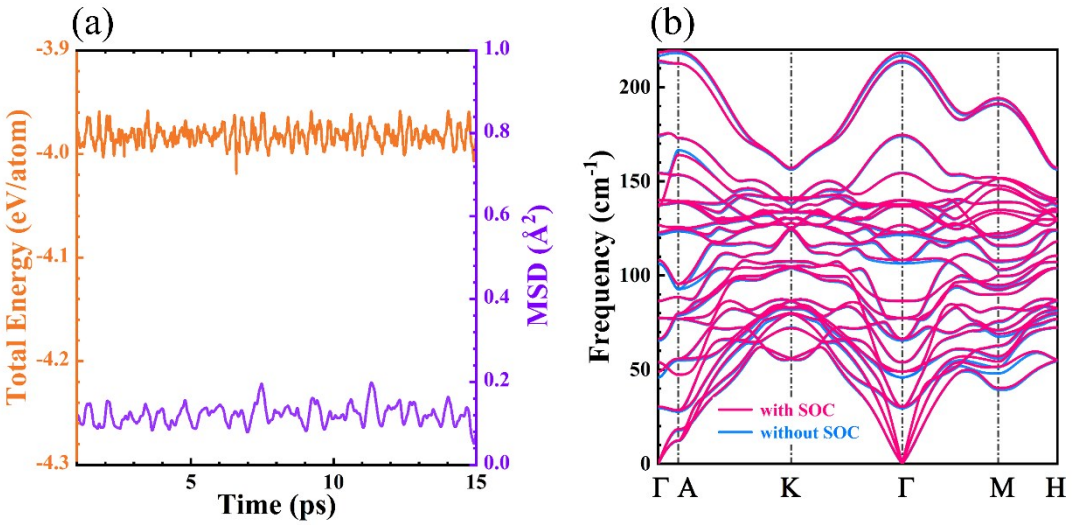

Fig. S5 (a) Evolution of total energy and average atomic mean-square displacement of $Sn_2As_2Se_5$ as a function of time in AIMD simulation. (b) Phonon dispersion curves of $Sn_2As_2Se_5$ with SOC and without SOC.

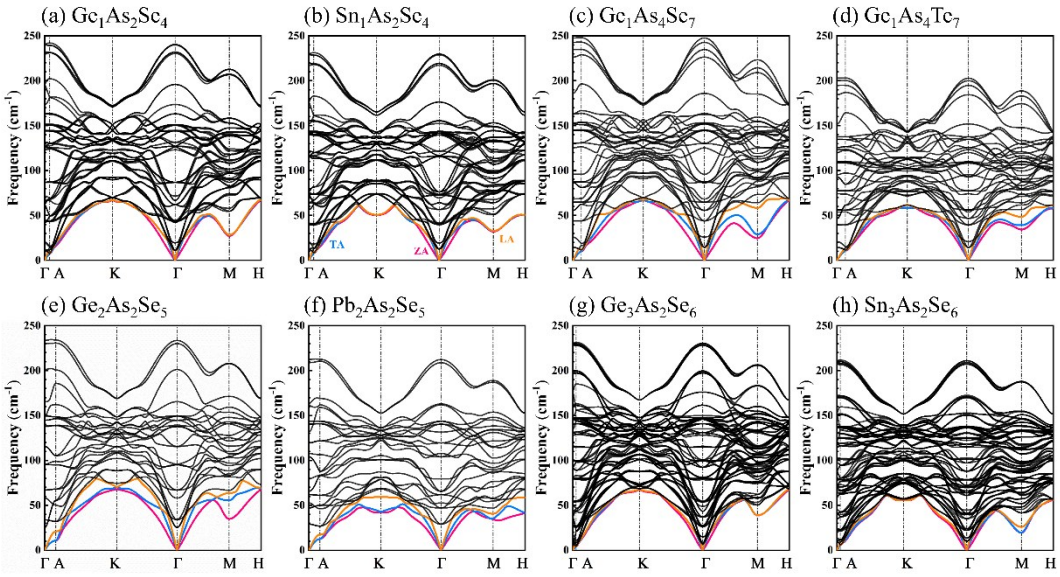

Fig. S6 Phonon dispersion curves of some low-κ_l compounds. The red, green and orange colors denote the acoustic branches of ZA, TA and LA, respectively.

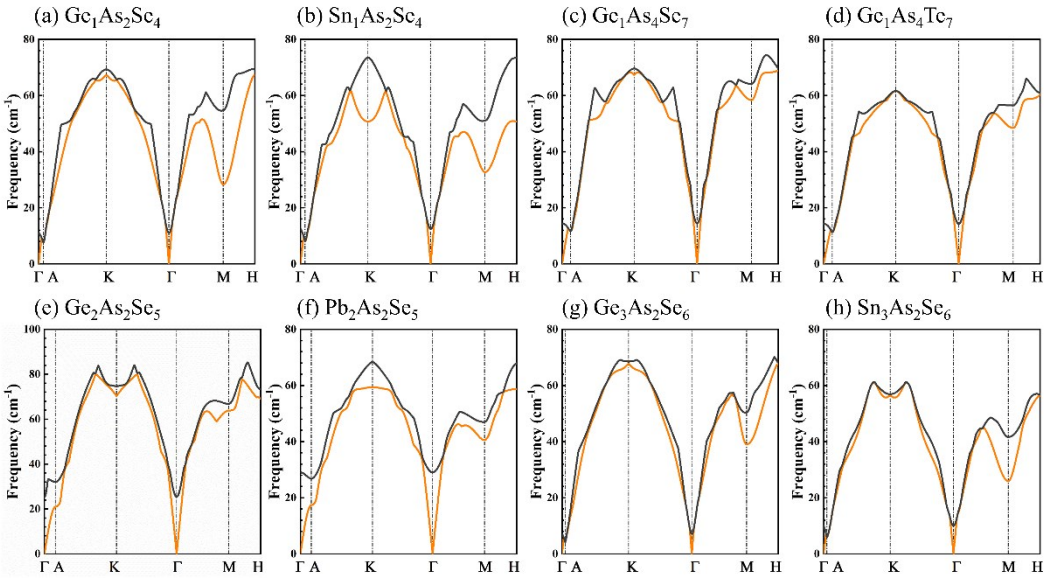

Fig. S7 Illustration of avoided-crossing between low-lying optic phonons and acoustic modes.

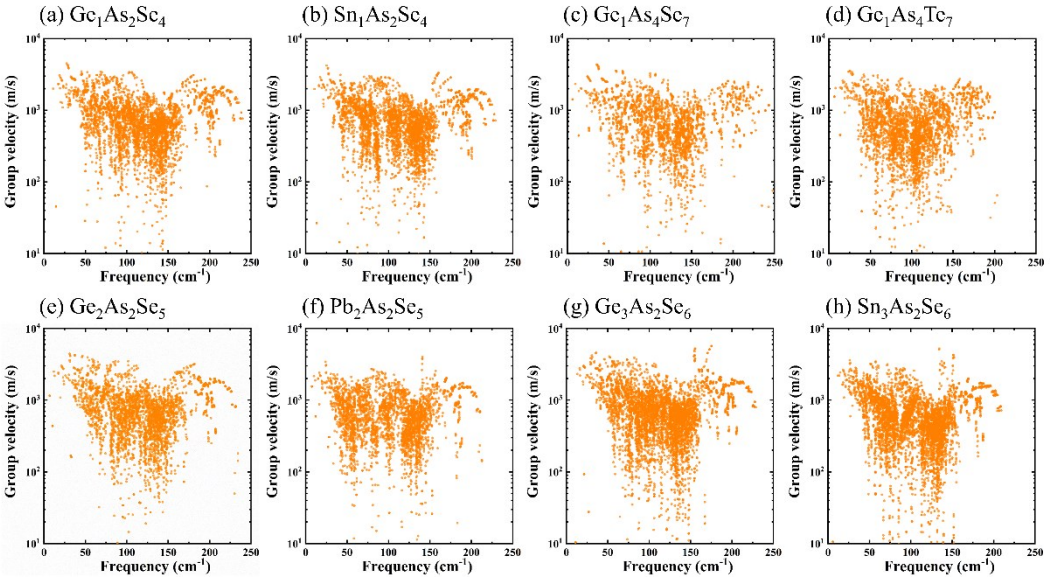

Fig. S8 Phonon group velocity as a function of phonon frequency at 300 K.

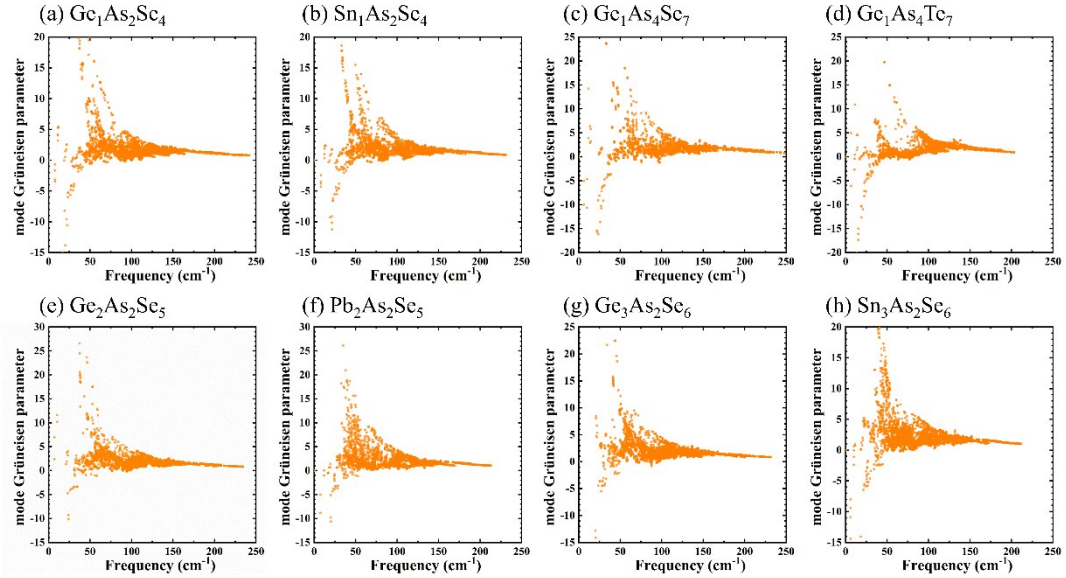

Fig. S9 Room-temperature mode Grüneisen parameter versus phonon frequency.

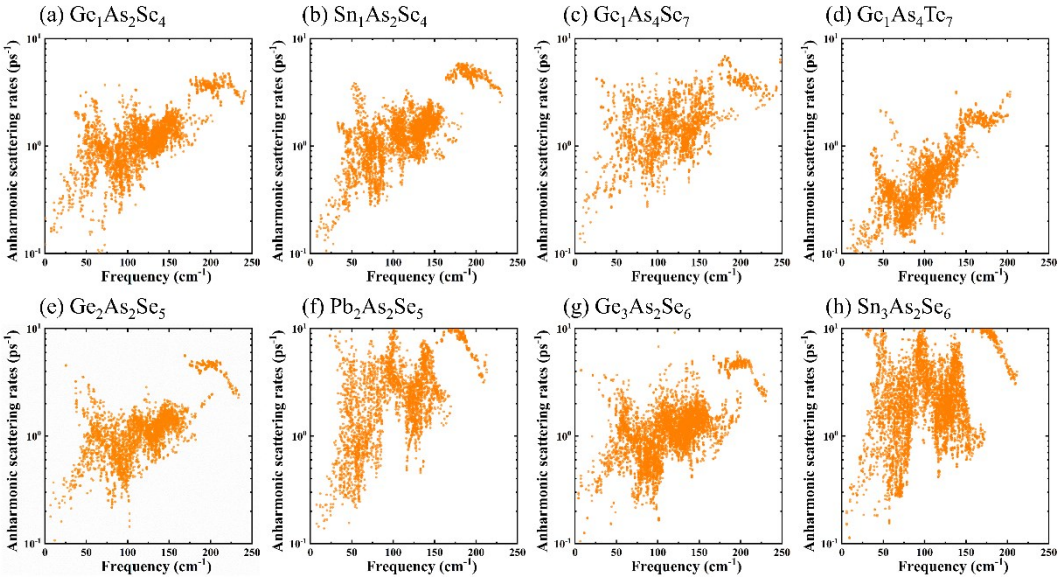

Fig. S10 Anharmonic phonon scattering rates at 300 K *vs* phonon frequency.

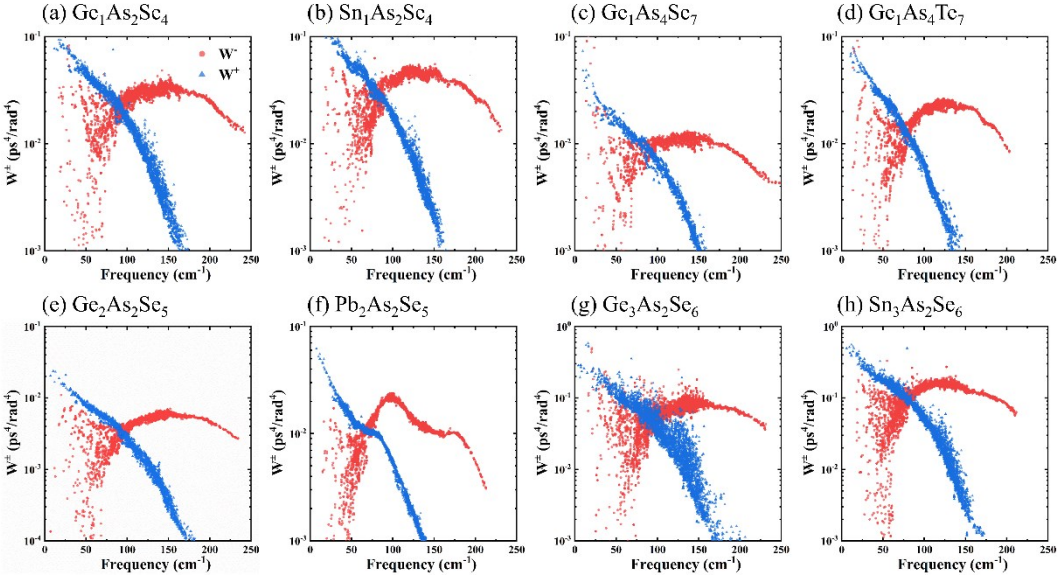

Fig. S11 Weighted phase space at 300K *vs* phonon frequency.

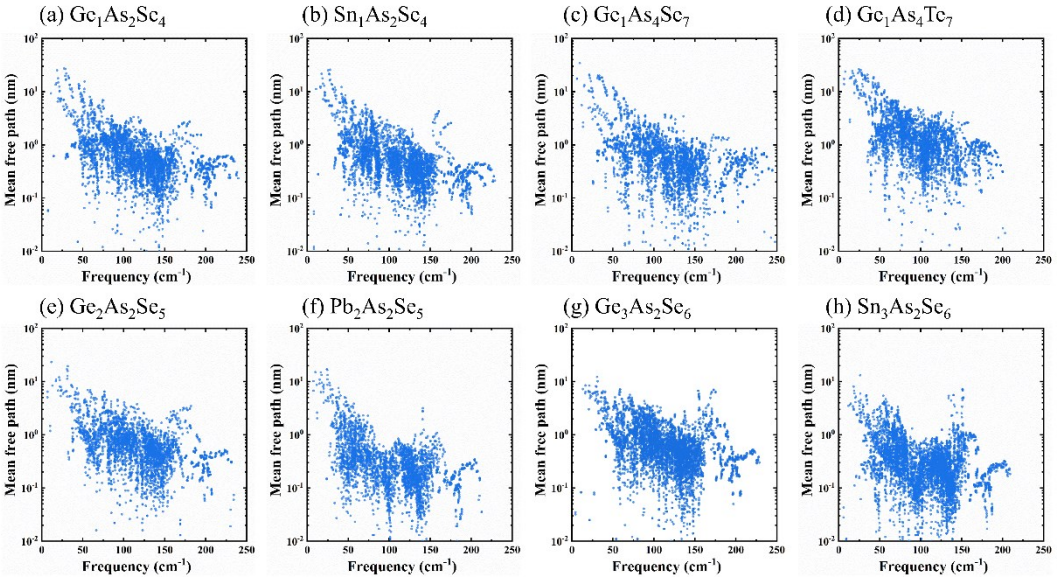

Fig. S12 Phonon mean free path at 300K *vs* phonon frequency.

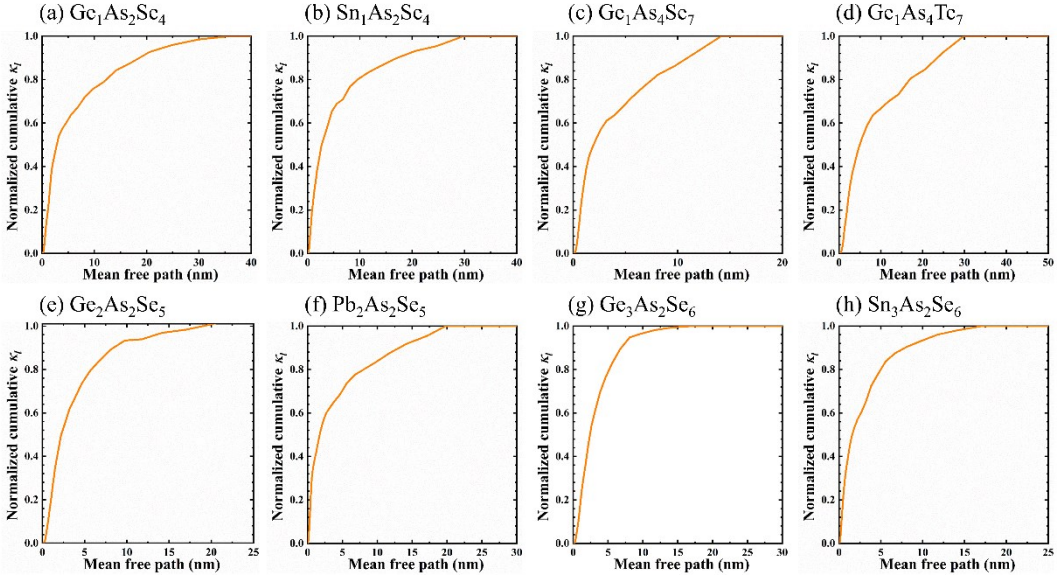

Fig. S13 Normalized cumulative room-temperature thermal conductivity with respect to phonon MFP.

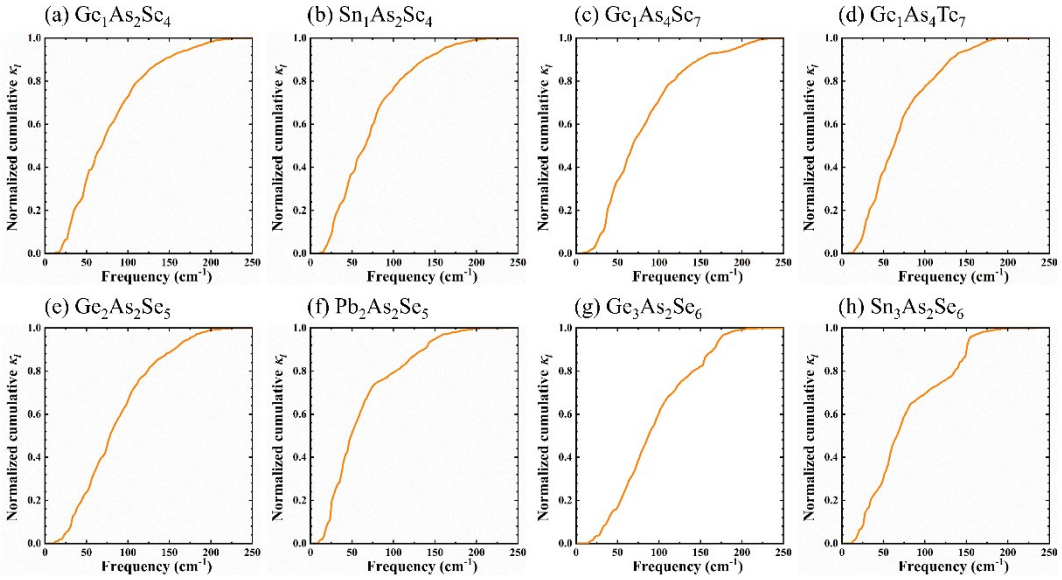

Fig. S14 Normalized cumulative room-temperature thermal conductivity with respect to phonon frequency.

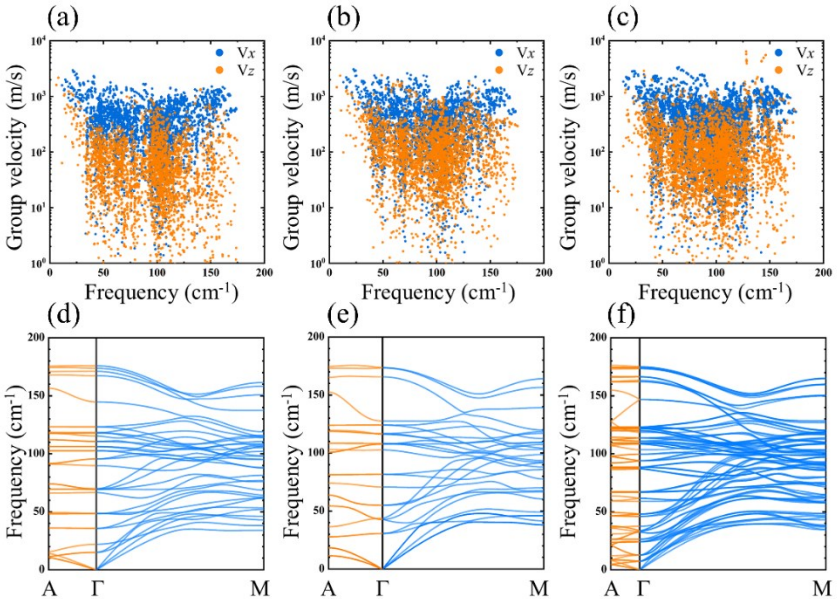

Fig. S15 Room-temperature phonon group velocities along the *a*-axis (v_x) and the *c*-axis (v_z) as well as phonon dispersion curves of (a, d) $Ge_1Sb_4Te_7$, (b, e) $Ge_2Sb_2Te_5$ and (c, f) $Ge_3Sb_2Te_6$.

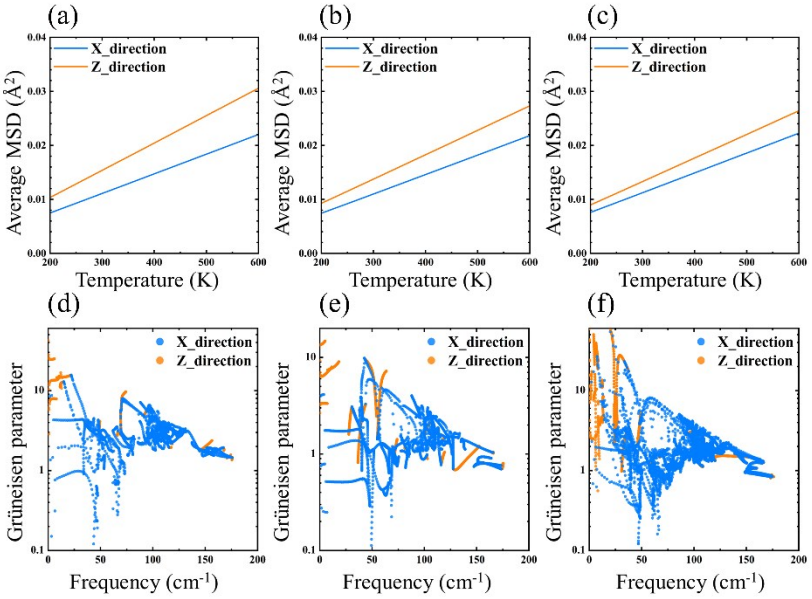

Fig. S16 Temperature-dependent averaged atomic mean-square displacements and phonon Grüneisen parameters of (a, d) $Ge_1Sb_4Te_7$, (b, e) $Ge_2Sb_2Te_5$ and (c, f) $Ge_3Sb_2Te_6$.

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