Supporting Information

Graphene-Assisted Synergistic Electronic DOS Modulation and Phonon Scattering to Improve the Thermoelectric Performance of Mg_3Sb_2-Based Materials

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1 Experimental section and theoretical calculation

First-principles calculations

Some basic information regarding the first-principles calculations is given below: **Tabs.1-4** and **Figs. 1-4.**

Tabs. 1 Parameters of Mg_3Sb_2 and graphene crystal structure

Items	Structure parameter
Mg_3Sb_2	Space group P-3m1 (No. 164)
	Lattice constant (Å) a=b=4.55 c=7.24
	α=β=90.000°, γ=120.000°
Mg (I)	(0, 0, 0)
Mg (II)	(0.3333, 0.6667, 0.3669)
Sb	(0.3333, 0.6667, 0.7738)
Graphene	Space group P6mm
	Lattice constant (Å) a=b=7.38
	γ=120.000°
C (I)	(0.3333, 0.6667,0)
C (II)	(0.6667, 0.3333, 0)

Tabs. 2 Parameters of geometrical optimization

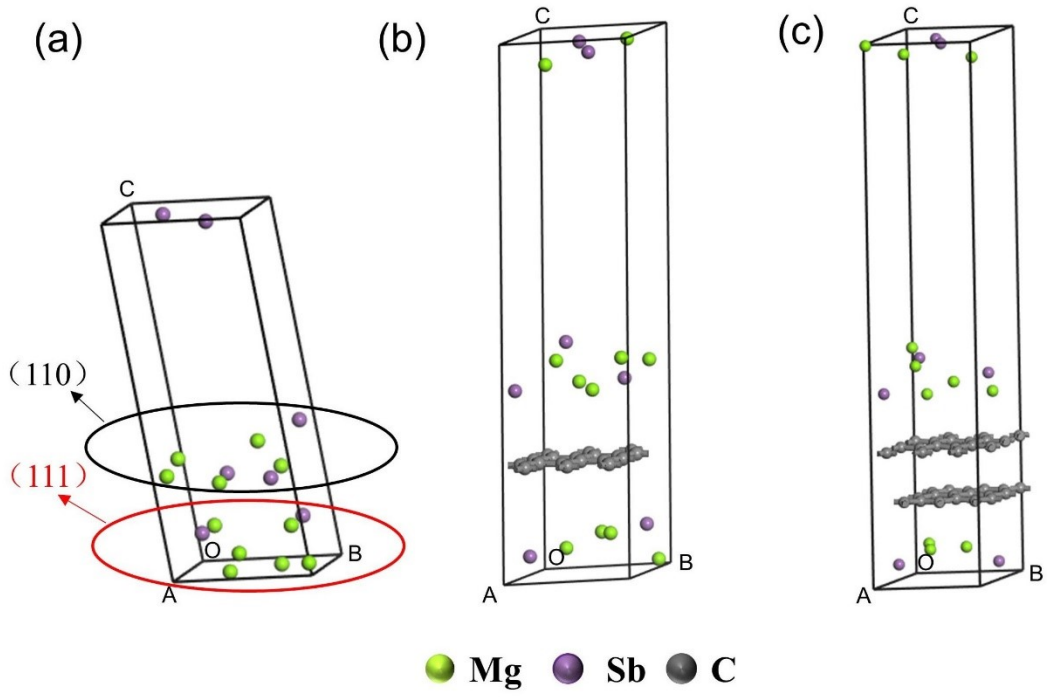
Items	Parameters
Functional	GGA-PBE
Plane-wave cutoff energy	400 eV
Self-consistent field	Fine
	1×10^{-5} eV/atom
Monkhorst-Pack *k*-point mesh	1×1×1
Pseudopotential	norm-conserving

Tabs. 3 Parameters of calculation for energy band structure

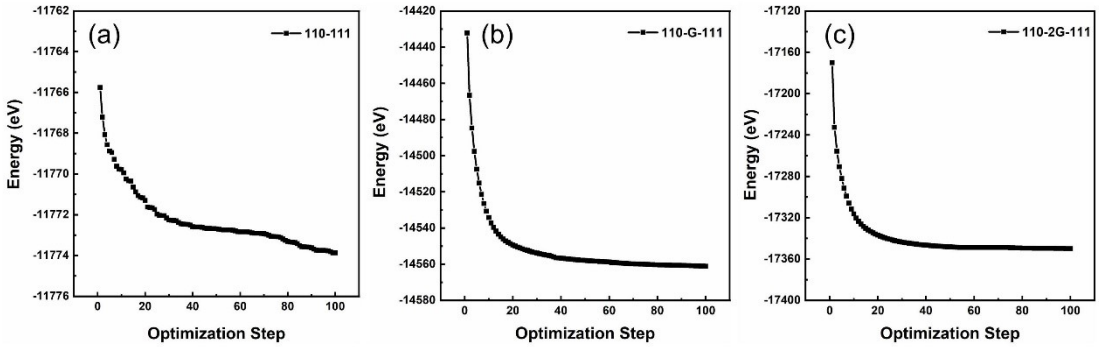
Items	Parameters
Functional	GGA-PBE
Interval	0.015/Å
High symmetry points	Γ, K, H, A
Path	Γ-K-H-A-Γ

Tabs. 4 Parameters of calculation for density of states

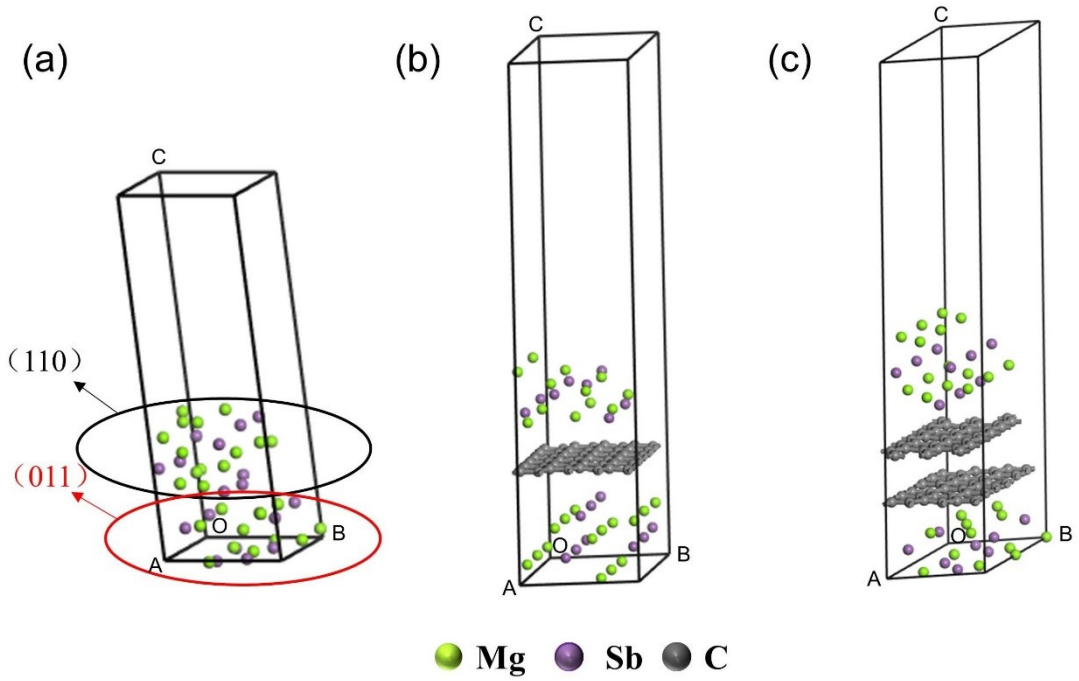
Item	Parameters
Functional	GGA-PBE
k-point mesh	8x8x8



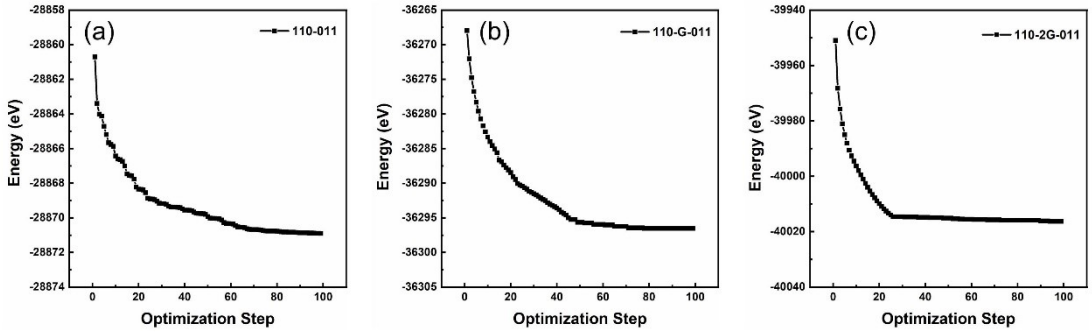
Figs. 1 Unit cell of three interface structures: (a) Mg_3Sb_2(110)|Mg_3Sb_2(111), (b) Mg_3Sb_2(110)|G(1layer)|Mg_3Sb_2(111), (c) Mg_3Sb_2(110)|G(2layers)|Mg_3Sb_2(111).



Figs. 2 Geometry optimization processes for the three interface structures: (a) $Mg_3Sb_2(110)|Mg_3Sb_2(111)$, (b) $Mg_3Sb_2(110)|G(1layer)|Mg_3Sb_2(111)$, (c) $Mg_3Sb_2(110)|G(2layers)|Mg_3Sb_2(111)$.



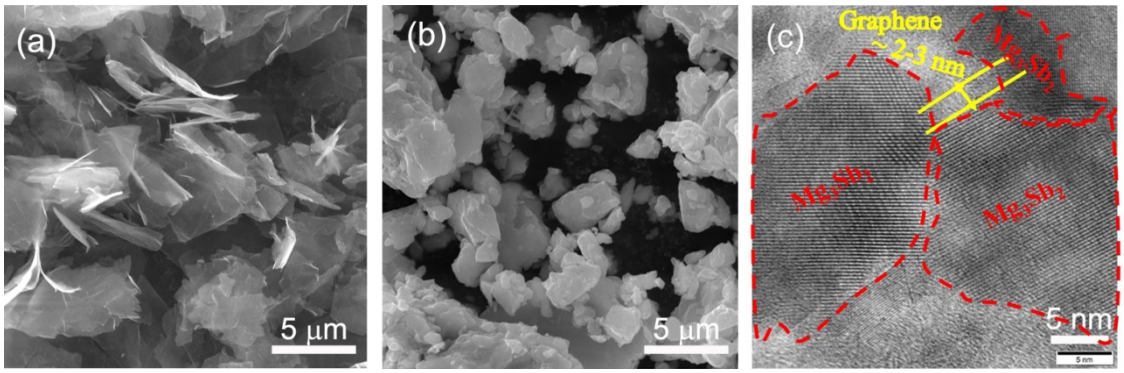
Figs. 3 Unit cell of three interface structures: (a) $Mg_3Sb_2(110)|Mg_3Sb_2(011)$, (b) $Mg_3Sb_2(110)|G(1layer)|Mg_3Sb_2(011)$, (c) $Mg_3Sb_2(110)|G(2layers)|Mg_3Sb_2(011)$.



Figs. 4 Geometry optimization processes for the three interface structures: (a) $Mg_3Sb_2(110)|Mg_3Sb_2(011)$, (b) $Mg_3Sb_2(110)|G(1layer)|Mg_3Sb_2(011)$, (c) $Mg_3Sb_2(110)|G(2layers)|Mg_3Sb_2(011)$.

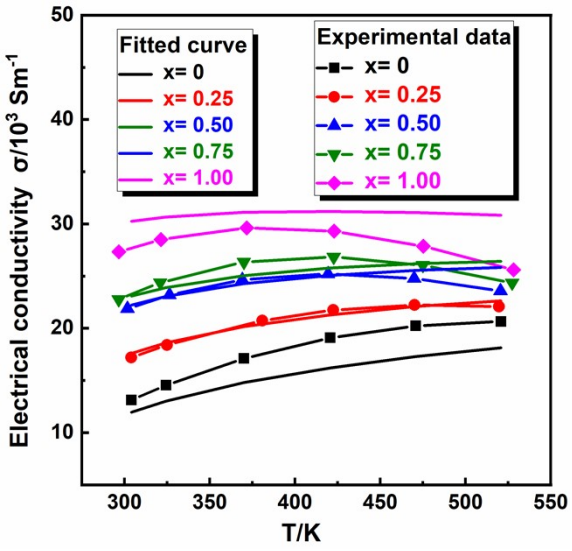
2 Results and Discussion

2.1 Phase composition and microstructure characterization



Figs. 5 (a) 2-dimenstional graphene raw materials; (b) morphology of BM-ed powders of $Mg_{3.24}Sb_{1.5}Bi_{0.49}Te_{0.01}$/1.0 vol% G; (c) TEM photos of grain boundary graphene for the $Mg_{3.24}Sb_{1.5}Bi_{0.49}Te_{0.01}$/1.0 vol% G sample.

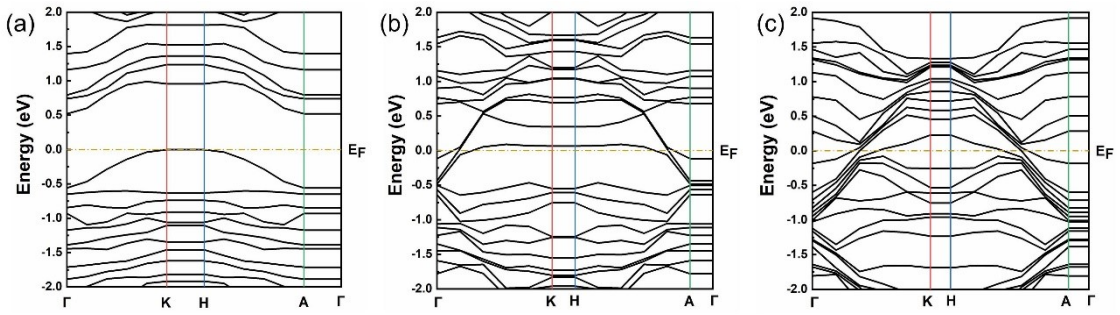
2.2 Electrical transport properties of $Mg_{3.24}Sb_{1.5}Bi_{0.49}Te_{0.01}$/x vol% G (x=0-1.25) samples



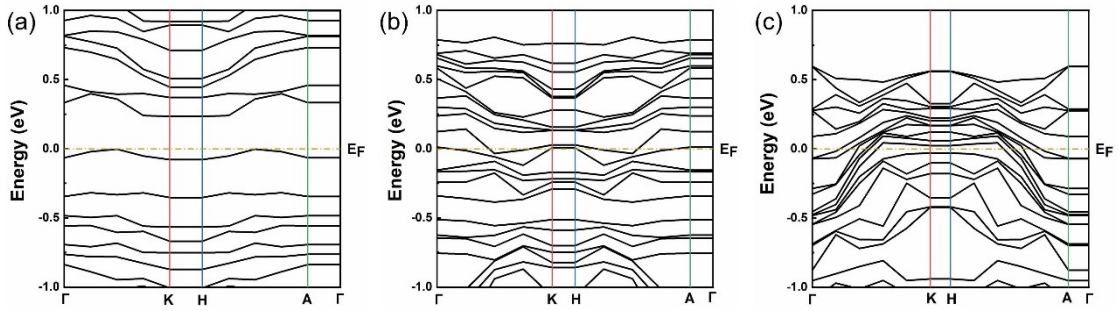
Figs. 6 The corresponding fitted curves and experimental data based on the trapping state model.

Tabs. 5 The parameters used for fitted curves based on the trapping state model.

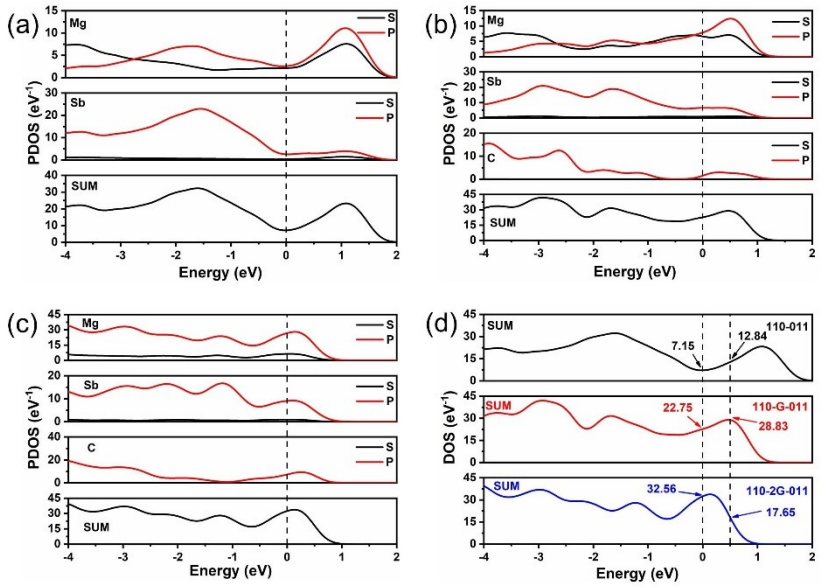
Sample	Temperature range /K	Elementary charge e/C	Grain size d/m	Carrier density n/m^{-3}	Effective mass m^*	Boltzmann constant k_B/JK^{-1}	Barrier height E_b /meV
x=0	300-525	1.60×10^{-19}	2.0×10^{-6}	2.0×10^{25}	1.2 m_e	1.38×10^{-23}	42
x=0.25	300-525	1.60×10^{-19}	2.0×10^{-6}	2.0×10^{25}	1.2 m_e	1.38×10^{-23}	32
x=0.5	300-525	1.60×10^{-19}	2.0×10^{-6}	2.0×10^{25}	1.2 m_e	1.38×10^{-23}	25
x=0.75	300-525	1.60×10^{-19}	2.0×10^{-6}	2.0×10^{25}	1.2 m_e	1.38×10^{-23}	26
x=1.0	300-525	1.60×10^{-19}	2.0×10^{-6}	2.0×10^{25}	1.2 m_e	1.38×10^{-23}	18



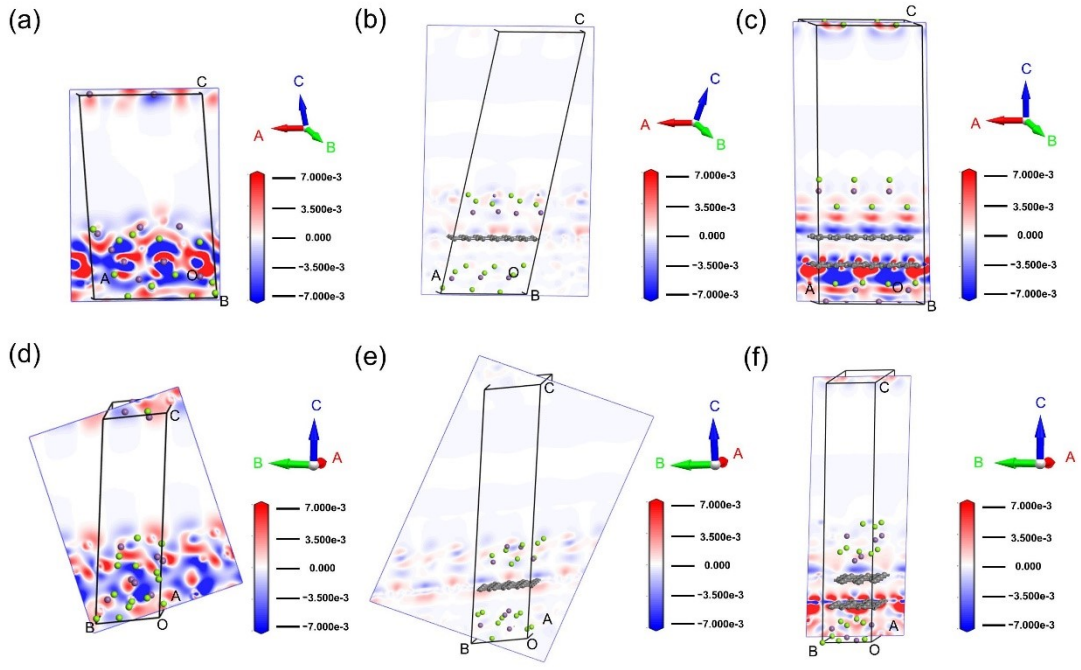
Figs. 7 Energy band structures of the three interface structures: (a) Mg_3Sb_2(110)|Mg_3Sb_2(111), (b) Mg_3Sb_2(110)|G(1layer)|Mg_3Sb_2(111), (c) Mg_3Sb_2(110)|G(2layers)|Mg_3Sb_2(111).



Figs. 8 Energy band structures of the three interface structures: (a) Mg_3Sb_2(110)|Mg_3Sb_2(011), (b) Mg_3Sb_2(110)|G(1layer)|Mg_3Sb_2(011), (c) Mg_3Sb_2(110)|G(2layers)|Mg_3Sb_2(011).



Figs. 9 Electronic DOS of three interface structures: (a) Mg_3Sb_2(110)|Mg_3Sb_2(111), (b) Mg_3Sb_2(110)|G(1layer)|Mg_3Sb_2(111), (c) Mg_3Sb_2(110)|G(2layers)|Mg_3Sb_2(111) and (d) the contrast of the total DOS of the three interface structures.



Figs. 10 Charge density difference maps of three interface structures: (a), (d) Mg_3Sb_2(110)|Mg_3Sb_2(011); (b), (e) Mg_3Sb_2(110)|G(1layer)|Mg_3Sb_2(011); (c), (f) Mg_3Sb_2(110)|G(2layers)|Mg_3Sb_2(011) with (a),(b), (c)//(A,C) plane and (d), (e), (f)//(B,C) plane.

2.3 Thermal transport properties of $Mg_{3.24}Sb_{1.5}Bi_{0.49}Te_{0.01}$/x vol% G (x=0-1.25) samples

To illustrate the effects of G on phonon scattering processes, we employed the Debye-Callaway model to quantitatively differentiate the respective contributions from different phonon scattering mechanisms, and the related equations are given below[1-3]:

$$\kappa_L = \frac{4\pi k_B}{v_s}\left(\frac{k_B T}{h}\right)^3 \int_0^{\theta_D/T} \tau_{tot} \frac{y^4 e^y}{(e^y-1)^2} dy \quad (1)$$

$$\tau_{tot}^{-1} = \tau_B^{-1} + \tau_{PD}^{-1} + \tau_U^{-1} + \tau_{NP}^{-1} \quad (2)$$

$$\tau_B^{-1} = \frac{v_s}{d_{avg}} \quad (3)$$

$$\tau_{PD}^{-1} = A\omega^4 = \frac{\bar{V}\Gamma}{4\pi v_s^3}\omega^4 \quad (4)$$

$$\tau_U^{-1} = B\omega^2 T exp\left(-\frac{\theta_D}{3T}\right) = \frac{h\gamma^2}{2\pi M_{avg} v_s^2 \theta_D}\omega^2 T exp\left(-\frac{\theta_D}{3T}\right)$$

(5)

$$\tau_{NP}^{-1} = v_s V_{NP}\left[\left(2\pi R^2\right)^{-1} + \left(\frac{4}{9}\pi R^2 \left(\Delta\rho/\rho_0\right)^2 \left(\omega R/v_s\right)^4\right)^{-1}\right]^{-1} \quad (6)$$

$$\theta_D = \frac{h}{k_B}\left(\frac{3N}{4\pi V}\right)^{1/3} v_s \quad (7)$$

$$\Gamma = \Gamma_m + \Gamma_s \quad (8)$$

$$\Gamma_m = \frac{\sum_{i=1}^{n} c_i \left(\frac{\bar{M}}{\bar{\bar{M}}}\right)^2 f_1 f_2 \left(\frac{M_1 - M_2}{\bar{M}}\right)^2}{\sum_{i=1}^{n} c_i}$$

(9)

$$\Gamma_s = \frac{\sum_{i=1}^{n} c_i \left(\frac{\bar{M}}{\bar{\bar{M}}}\right)^2 f_1 f_2 \varepsilon \left(\frac{r_1 - r_2}{\bar{r}}\right)^2}{\sum_{i=1}^{n} c_i}$$

(10)

$$\bar{M} = f_1 M_1 + f_2 M_2 \quad (11)$$

$$\bar{\bar{M}} = \left(\frac{\sum_{i=1}^{n} c_i \bar{M}}{\sum_{i=1}^{n} c_i}\right) \quad (12)$$

$$\bar{r} = f_1 r_1 + f_2 r_2 \quad (13)$$

$$\varepsilon = \frac{2}{9}\left(\frac{6.4 \times \gamma(1+\nu)}{1-\nu}\right)^2$$

(14)

Where $y=\hbar\omega/k_B T$, τ, d_{avg}, θ_D, $\bar{V}$, γ, N, $\hbar$, ω, ν, ε are the reduced phonon energy, the phonon relaxation

time, the average grain size, the Debye temperature, the average atomic volume, the Grüneisen parameter, and the number of atoms in a primitive unit cell, the reduced Planck constant, the phonon frequency, Poisson's ratio, strain field-related adjustable parameter, respectively.

Tabs. 6 Parameters related to the Debye-Callaway model calculation

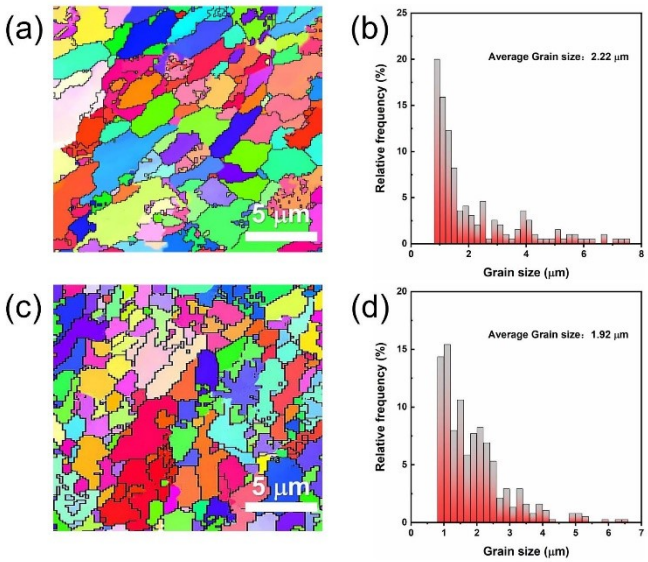
Parameters	Symbol	Value	
Average sound velocity	v_s	2155 ms^{-1} [4]	
Debye temperature	θ_D	215 K [5]	
Debye frequency	ω_D	2.81×10^{13} s^{-1} [Cal. from θ_D]	
Grüneisen parameter	γ	1.87 [6]	
Poisson's ratio	ν	0.34 [5]	
Average atomic mass	$\bar{\bar{M}}$	1.20×10^{-25} kg [Cal.]	
Average atomic volume	$\bar{V}$	2.62×10^{-29} m^3 [Cal.]	
Average grain size	d_{avg}	2.20 μm [Cal.]	
		2.22 μm [Exp.] (**Figs. 11(a), (b)**)	
		1.92 μm [Exp.] (**Figs. 11(c), (d)**)	
Density of graphene	ρ_G	2.20×10^{3} kgm^{-3} [7]	
Density of matrix	ρ	4.40×10^{3} kgm^{-3} [Exp.]	
Mass fluctuation parameter	Γ_m	0.110 [Cal.]	
Strain fluctuation parameter	Γ_s	0.426 [Cal.]	
strain field-related adjustable parameter	ε	134.21 [Cal.]	
Point-defect phonon scattering factor	A	1.15×10^{-40} s^3 [Cal.]	
U-process phonon scattering factor	B	3.08×10^{-18} sK^{-1} [Cal.]	
Equivalent size	R	68 nm (x=0.25)	[Cal.]
		69 nm (x=0.50)	
		75 nm (x=0.75)	
		89 nm (x=0.10)	
Number density of graphene	V_{NP}	6.05×10^{18} m^{-3} (x=0.25)	[Cal.]
		1.21×10^{19} m^{-3} (x=0.50)	
		1.81×10^{19} m^{-3} (x=0.75)	
		2.42×10^{19} m^{-3} (x=0.10)	

Footnote: (1) [*No.*]-From reference; (2) [Cal.]-From calculation; (3) [Exp.]-From experiment.

Tabs. 7 τ_{tot}^{-1} in κ_s as a function of the reduced phonon energy y

Sample	τ_B^{-1} (s^{-1})	τ_{PD}^{-1} (s^{-1})	τ_U^{-1} (s^{-1})	τ_{NP}^{-1} (s^{-1})
x=0	9.80×10^{8}	2.74×10^{14} y^4	1.12×10^{12} y^2	--
x=0.25	9.80×10^{8}	2.74×10^{14} y^4	1.12×10^{12} y^2	$1.30\times10^{22}/(3.44\times10^{13}+262\ y^4)$
x=0.50	9.80×10^{8}	2.74×10^{14} y^4	1.12×10^{12} y^2	$2.61\times10^{22}/(3.34\times10^{13}+240\ y^4)$
x=0.75	9.80×10^{8}	2.74×10^{14} y^4	1.12×10^{12} y^2	$3.90\times10^{22}/(2.83\times10^{13}+146\ y^4)$

x=1.0	9.80×10^{8}	$2.74\times10^{14}\ y^{4}$	$1.12\times10^{12}\ y^{2}$	$5.22\times10^{22}/(2.01\times10^{13}+52.3\ y^{-4})$



Figs. 11 $Mg_{3.24}Sb_{1.5}Bi_{0.49}Te_{0.01}$/0 vol% G (a) EBSD map, (b) grain size；$Mg_{3.24}Sb_{1.5}Bi_{0.49}Te_{0.01}$/1.0 vol% G (c) EBSD map, (d) grain size

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