Suppoting Information

In Situ Temperature-Dependent Transmission Electron Microscopy Studies of Pseudobinary *m*GeTe·Bi₂Te₃ Nanowires and First-Principles Calculations

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I. Materials and Methods

CVT Synthesis of *m*GeTe·Bi₂Te₃ NW. GeTe (99.999%, Alfa) and Bi₂Te₃ (99.999%, Alfa) powders were placed inside a quartz tube reactor. A silicon (Si) substrate, on which a 3 nm-thick Au film was deposited, was positioned at a distance of 10 cm away from the powder source. Argon gas was continuously flowed at a rate of 200 sccm under a pressure of 100 Torr. The temperature of the powder sources was set to 500-600 °C and that of the Si substrate was approximately 350 °C. The composition

was controlled using the temperature and ratio of the two source powders. The structure and composition of the products were analyzed by scanning electron microscopy (SEM, Hitachi S-4700), field-emission transmission electron microscopy (TEM, FEI TECNAI G² 200 kV), high-voltage TEM (HV-TEM, Jeol JEM ARM 1300S, 1.25 MV), and energy-dispersive X-ray fluorescence spectroscopy (EDX). Fast Fourier-transform (FFT) images were generated by the inversion of the TEM images using Digital Micrograph GMS1.4 software (Gatan Inc.). A tilt holder (Dual Orientation Tomography Holder 927, Gatan Co.) was used for the TEM measurements. High-resolution XRD patterns were obtained using the 9B and 3D beam lines of the Pohang Light Source (PLS) with monochromatic radiation.

In Situ **TEM** of NWs. *In Situ* **TEM** of NWs. The *in situ* temperature-dependent HRTEM studies were performed in a high-voltage electron microscope (HVEM, JEOL Ltd., JEM ARM1300S, LaB6 electron gun, Cs: 2.65 mm, Cc: 4.1 mm, point-to-point resolution: 1.2 A, operated at 1250kV) at the Korean Basic Science Institute. Both High-Voltage Gatan Image Filter (HV-GIF, Gatan Inc., SP-US1000HV, $2k \times 2k$, 16 bit) and side-mounted Top-TV (Gatan Inc., Orious SC200D) CCD cameras were used to record the HRTEM images and monitor the low magnification images, respectively. The HVEM direct magnification was enlarged 14.5 times by the HV-GIF camera. A double-tilt heating holder (Gatan Inc., 652) with programmable temperature controllers was used to heat the specimens (NWs) from room temperature (20 °C) to 400 °C (see Ref. S1 for details of the heating procedure). The NWs were loaded on a holey carbon-coated Mo grid (Pacific Grid-Tech, Mo-200HN) typically used for *in situ* heating TEM experiments. For each step, a holding time of 30 min was imposed to minimize the NW drift caused by thermal expansion. To avoid damaging the NW with the electron beam, the latter was turned off during heating and holding. The heating rate was 10 °C/min. The sample chambers of the HVEM, evacuated to 2×10^{-6} Pa were clean enough for these *in situ* heating experiments.

Measurement of I-V curves. The 4-point probe electrical transport measurements of NWs were performed using a nano-manipulator (Kleindeck MM3A) in a UHV-chamber focused ion beam (FIB) system (FEI Quanta 3D) and a semiconductor device analyzer (Agilent B1500A). The NWs were

dispersed in isopropyl alcohol and dropped on a 500-nm thick silicon dioxide (SiO₂) layer-deposited Si wafer. In the FIB chamber, careful switching was manipulated between the secondary electron imaging mode and ion-beam deposition mode in the dual-beam FIB system during the fabrication. By doing so, the Ga ion beam induced Pt deposition was limited only within the contact regions to avoid possible contamination over the entire NW. The NW length between the Pt electrode pads was approximately 20 µm in average. The thickness of Pt deposition pads was 500 nm. For I-V measurements, the standard 100 nm tungsten tips were used right after electrochemical etching at room temperature. We fabricated 3-5 NW electrodes, and measured the average value.

Calculations. First-principles calculation of the GBT and GST series was carried out using the Vienna *ab initio* simulation package (VASP).^{\$2} Since there are no comprehensive informations about lattice parameters, we have relaxed the structures. The projector augmented wave (PAW) method with the Perdew-Burke-Ernzerhof generalized gradient approximations (PBE-GGA) were used for the density functional theory (DFT) calculations.^{\$3} The cut-off energy in the plane-wave expansion of the valence states was set to 500 eV. To treat the interlayer Te-Te interactions more precisely, we employed the VdW-DF2 scheme (Grimmer's method) implemented in VASP.^{\$4} For GBT, spin-orbit coupling was considered for the Bi (or Sb) atoms. An $8 \times 8 \times 2$ k mesh was used in the full Brillouin zone. The calculated lattice parameters are summarized in Table S1. We calculated electrical conductivity from the structures using the BoltzTraP code^{\$55} implemented in the WIEN2k package, ^{\$6} wherein the semiclassical Boltzmann equation is solved using the rigid band approach. Boltzmann equation is solved using the rigid band approach. Boltzmann equation is solved using the rigid band approach. The scattering times was adjusted to fit the experimental conductivity of the bulk phase.^{\$7,\$8} We used the scattering time as $\tau = 2.5$ fs for *m*GeTe·Bi₂Te₃ (GBT) and $\tau = 5$ fs for *m*GeTe·Sb₂Te₃ (GST), and temperature is fixed to 300 K.

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II. Supporting Tables

Table S1. Lattice parameters for the H and C phase of mGeTe·Bi₂Te₃ (GBT), mGeTe·Sb₂Te₃ (GST), and GeTe. The experimental value (a_{exp} and c_{exp}) of H phase was obtained from the reference [S7: Shelimova, L. E.; Karpinsky, O. G.; Zemskov, V. S.; Konstantinov, P. Structural and Electrical Properties of Layered Tetradymite-like Componds in the GeTe-Bi₂Te₃ and GeTe-Sb₂Te₃ Systems. *Inorg. Mater.* **36**, 235, (2000)].

					С						
	т	Space group	C _{exp}	\mathcal{C}_{cal}	Δc (%)	a _{exp}	a_{cal}	Δ <i>a</i> (%)	Space group	С	а
	0	R3m	30.048	31.204	-3.846	4.384	4.345	0.881	R3m	10.826	4.420
	1	R3m	41.270	41.738	-1.133	4.322	4.289	0.753	R3m	42.765	4.365
	2	P3m1	17.320	17.407	-0.326	4.293	4.259	0.785	R3m	53.043	4.331
	3	R3m	62.590	62.526	0.102	4.268	4.243	0.578	P3m1	21.103	4.308
СРТ	4	R3m	73.130	72.827	0.415	4.259	4.233	0.605	R3m	73.576	4.291
UDI	5	P3m1	27.890	27.716	0.636	4.238	4.227	0.261	R3m	83.838	4.278
	6	R3m	94.322	93.749	0.607	4.235	4.219	0.368	P3m1	31.365	4.268
	7	R3m	104.903	104.230	0.641	4.228	4.214	0.329	R3m	104.346	4.260
	8	P3m1	38.493	37.990	1.308	4.222	4.212	0.230	R3m	114.603	4.253
	GeTe	R3m	10.657	10.591	0.617	4.164	4.172	-0.205	P3m1	10.242	4.181
	0	R3m	30.458	30.964	-1.562	4.191	4.2474	-1.345	R3m	10.560	4.181
	1	R3m	41.125	41.306	-0.441	4.24	4.226	0.329	R3m	41.912	4.278
	2	P3m1	17.229	17.229	0.011	4.224	4.215	0.220	R3m	52.158	4.259
	3	R3m	62.234	61.907	0.525	4.214	4.208	0.137	P3m1	20.804	4.248
GST	4	R3m	72.79	72.171	0.850	4.207	4.204	0.065	R3m	72.658	4.237
051	5	P3m1	27.754	27.478	0.995	4.202	4.201	0.018	R3m	82.906	4.231
	6	R3m	93.749	92.671	1.150	4.198	4.199	-0.022	P3m1	31.051	4.226
	7	R3m	104.23	102.92	1.260	4.194	4.197	-0.061	R3m	103.398	4.221
	8	P3m1	38.235	37.720	1.346	4.191	4.196	-0.135	R3m	113.644	4.218
	GeTe	R3m	10.657	10.591	0.617	4.164	4.172	-0.205	P3m1	10.242	4.181

Table S2. Energy change (ΔE in a unit of eV) for the *m*GeTe insertion reaction into Bi₂Te₃ or Sb₂Te₃ unit cell; *m*GeTe + Bi₂Te₃ (or Sb₂Te₃) \rightarrow H (or C) phase *m*GeTe·Bi₂Te₃ (or *m*GeTe·Sb₂Te₃), where *m* = 1~8, energy change per GeTe ($\Delta E/m$), volume change (ΔV in Å³), volume change per GeTe change ($\Delta V/m$), and the energy difference between the H and C phase ΔE ($\Delta E_{H-C}/m$).

	m	Н					С				
	m	ΔΕ	$\Delta E/m$	ΔV	$\Delta V/m$	ΔΕ	$\Delta E/m$	ΔV	$\Delta V/m$	$\Delta L_{\rm H}$ -C/m	
	1	-2.322	-2.322	-1.600	-1.600	1.620	1.9620	0.337	0.337	-3.942	
	2	-2.269	-1.134	-3.032	-1.516	1.979	0.989	0.679	0.340	-2.123	
	3	-2.227	-0.742	-4.732	-1.577	2.262	0.754	1.025	0.342	-1.497	
CPT	4	-2.166	-0.542	-6.213	-1.553	2.484	0.621	1.234	0.309	-1.162	
UDI	5	-2.092	-0.418	-7.371	-1.474	2.668	0.533	1.400	0.280	-0.952	
	6	-2.052	-0.342	-9.182	-1.720	2.826	0.471	1.559	0.260	-0.813	
	7	-1.977	-0.282	-10.49	-1.444	2.963	0.423	1.665	0.238	-0.705	
	8	-1.942	-0.242	-12.09	-1.275	3.087	0.386	1.844	0.231	-0.034	
	1	-0.0265	-0.0265	-1.358	-1.358	0.912	0.912	-0.294	-0.294	-0.939	
	2	0.0096	0.0048	-2.519	-1.260	1.031	0.516	-0.292	-0.146	-0.512	
	3	0.0508	0.0169	-4.202	-1.401	1.163	0.388	-0.135	-0.045	-0.371	
CST	4	0.104	0.0260	-5.723	-1.431	1.254	0.314	-0.102	-0.172	-0.288	
051	5	0.160	0.0320	-7.190	-1.438	1.343	0.269	-0.034	-0.007	-0.237	
	6	0.208	0.0347	-8.771	-1.462	1.425	0.238	0.037	0.006	-0.203	
	7	0.274	0.0392	-10.44	-1.491	1.498	0.214	0.068	0.010	-0.175	
	8	0.312	0.0390	-11.82	-1.478	1.569	0.196	0.112	0.014	-0.116	

Phase	т	$n_{exp} (\times 10^{20} \text{ cm}^{-3})^a$	$ ho_{exp}$	
	2	0.992	1.429	Rerefence S7: Shelimova, L. E., Karpinskii, O.
	3	1.47	1.887	G., Zemskov, V. S.; Konstantinov, P. P. Structural
	4	1.54	1.724	
DorU	5	1.64	1.351	and electrical properties of layered tetradymite-
КОГП	6	2.29	1.333	like compounds in the GeTe-Bi ₂ Te ₃ and GeTe-
	7	2.61	1.389	SI T. S. Marco I. 16 (2000 26 225 242
	8	2.67	1.031	Sb ₂ 1e ₃ Systems. <i>Inorg. Mater.</i> 2000 , <i>30</i> , <i>235-242</i> .
	GeTe	3.4	0.150	

Table S3. Resistivity (ρ in a unit of m Ω ·cm) of *m*GeTe·Bi₂Te₃ (H-GBT and C-GBT), and GeTe, where the hole concentration *n*=0.5×10²⁰, 1×10²⁰, and 2×10²⁰ cm⁻³, and corresponding band gap (Eg).

^{*a*} Shelimova and coworkers reported *m*GeTe·Bi₂Te₃ (m = 2-8) (at $n = (1-3) \times 10^{20}$ cm⁻³) resistivities in the range 1.0–1.9 m Ω ·cm at 300 K. In the current study, the scattering time (2.5 fs) was adjusted to fit the value of ρ_{avg} to their experimental values (ρ_{exp}).

Phase	Eg (eV)	т	$n=0.5\times10^{20} \text{ cm}^{-3}$		$n=1\times10^{20} \text{ cm}^{-3}$			$n=2\times10^{20} \text{ cm}^{-3}$			
			$ ho_a$	$ ho_c$	$ ho_{avg}$	$ ho_a$	$ ho_c$	$ ho_{avg}$	$ ho_a$	$ ho_c$	$ ho_{avg}$
	0.126	0	3.081	9.445	3.974	1.766	5.320	2.272	1.107	3.170	1.414
	0.062	1	3.986	14.790	5.268	2.157	6.529	2.777	1.253	3.203	1.572
	0.032	2	4.076	12.143	5.236	2.292	5.346	2.832	1.341	2.621	1.602
	0.014	3	3.966	10.324	4.991	2.991	4.604	2.752	1.353	2.243	1.559
п	0.018	4	4.001	8.481	4.856	2.281	3.932	2.652	1.336	1.968	1.496
п	0.033	5	4.012	7.539	4.753	2.253	3.670	2.585	1.301	1.897	1.453
	0.042	6	3.931	6.934	4.595	2.198	3.472	2.504	1.288	1.886	1.440
	0.041	7	3.863	7.170	4.595	2.159	3.693	2.506	1.264	2.062	1.451
	0.053	8	3.988	7.382	4.709	2.197	3.931	2.576	1.270	2.273	1.489
	0.372	GeTe	4.782	6.688	5.284	2.258	3.508	2.562	1.102	1.915	1.282
	0.046	0	16.07	25.26	18.29	8.443	12.79	9.521	4.507	6.712	5.061
	0.190	1	15.07	15.54	15.22	7.608	8.032	7.744	3.947	4.338	4.070
	0.250	2	11.50	16.42	12.78	5.919	8.275	6.540	3.176	4.320	3.484
	0.243	3	8.898	16.05	10.45	4.731	8.235	5.513	2.643	4.358	3.042
C	0.219	4	7.228	15.82	8.825	3.927	8.223	4.755	2.259	4.428	2.700
C	0.193	5	6.066	16.50	7.686	3.381	8.551	4.234	1.994	4.650	2.463
	0.165	6	5.123	18.00	6.727	2.878	9.405	3.745	1.711	5.180	2.203
	0.145	7	4.742	19.82	6.353	2.711	10.39	3.597	1.629	5.710	2.148
	0.125	8	4.387	22.36	5.992	2.504	11.64	3.391	1.504	6.352	2.017
	0.066	GeTe	1.924	2.018	1.995	1.047	1.084	1.059	0.592	0.606	0.597

Phase	т	$n_{exp} (\times 10^{20} \text{ cm}^{-3})^a$	$ ho_{exp}$	Rerefence S8: Shelimova I. F.: Karninsky, O. G.:
	0	3.4	0.20	Konstantinov P. P.: Kretova M. A.: Avilov F. S.:
	1	2.6	0.444	Zemskov V S Composition and Properties of
R or H	2	2.9	0.417	Lavorad Compounds in the CoTe Sh.Te. System
	3	1.64	0.345	Layered Compounds in the Gene-So ₂ Te ₃ System.
	4	4.3	0.617	<i>Inorg. Maler.</i> 2001 , <i>37</i> , 342-348.

Table S4. Resistivities (ρ , m Ω cm) of *m*GeTe·Sb₂Te₃ (H-GST and C-GST) and GeTe, at hole concentrations $n = 2 \times 10^{19}$, 5×10^{19} , 1×10^{20} , 2×10^{20} , and 3×10^{20} cm⁻³, and band gaps (E_g).

^{*a*} Shelimova and coworkers reported *m*GeTe·Sb₂Te₃ (m = 0–4) resistivies at 300 K. The scattering time

(5 fs) was adjusted to fit the value of ρ_{avg} to their experimental values.

Phase	F (eV)	m	$n=2\times10^{19} \text{ cm}^{-3}$			n	$n=5\times10^{19} \text{ cm}^{-3}$			$1 \times 10^{20} \text{ cm}^{-3}$		
	$L_g(UV)$	m	ρ_a	$ ho_c$	$ ho_{avg}$	$ ho_a$	$ ho_c$	$ ho_{avg}$	$ ho_a$	$ ho_c$	$ ho_{avg}$	
	0.148	0	7.543	13.996	8.913	3.198	5.992	3.786	1.750	2.290	2.073	
	0.025	1	7.333	38.455	10.041	3.570	13.088	4.693	2.018	5.702	2.572	
	0.023	2	7.831	50.756	10.905	3.631	14.614	4.845	1.998	5.911	2.563	
	0.041	3	7.735	46.421	10.710	3.592	12.724	4.722	1.979	5.442	2.512	
ц	0.057	4	7.566	37.795	10.317	3.461	10.816	4.475	1.898	4.786	2.376	
11	0.068	5	7.713	31.338	10.302	3.411	9.789	4.357	1.851	4.492	2.302	
	0.072	6	7.217	26.446	9.525	3.209	8.549	4.053	1.779	4.040	2.187	
	0.076	7	6.937	23.955	9.089	3.129	8.283	3.947	1.746	4.011	2.151	
	0.075	8	6.898	22.537	8.974	3.040	8.256	3.851	1.680	4.124	2.093	
	0.372	GeTe	6.177	7.892	6.659	2.391	3.344	2.642	1.129	1.754	1.281	
	0.050	0	11.080	25.208	13.626	4.805	10.336	5.848	2.478	5.201	3.002	
	0.170	1	8.562	19.436	10.525	3.537	7.933	4.338	1.816	4.016	2.222	
	0.195	2	6.398	23.625	8.452	2.727	9.358	3.578	1.458	4.723	1.895	
	0.197	3	6.202	20.505	8.081	2.687	8.441	3.477	1.450	4.304	1.861	
C	0.188	4	5.517	18.756	7.215	2.484	7.721	3.210	1.389	3.985	1.775	
C	0.178	5	4.948	18.388	6.542	2.228	7.548	2.981	1.308	3.881	1.679	
	0.165	6	4.534	18.325	6.052	2.096	7.621	2.763	1.191	3.940	1.552	
	0.156	7	4.402	18.660	5.952	2.031	7.508	2.683	1.177	3.950	1.536	
	0.146	8	4.143	18.992	5.604	1.945	7.726	2.592	1.114	4.014	1.468	
	0.066	GeTe	2.155	2.320	2.200	0.962	1.009	0.997	0.524	0.542	0.530	

	100		$2 \times 10^{20} \text{ cm}^{-3}$			$3 \times 10^{20} \text{ cm}^{-3}$	3
	m	$ ho_a$	$ ho_c$	$ ho_{avg}$	$ ho_a$	$ ho_c$	$ ho_{avg}$
	0	1.039	1.918	1.226	0.432	0.832	0.562
	1	1.174	2.605	1.437	0.444	0.869	0.530
	2	1.179	2.679	1.450	0.452	0.888	0.541
	3	1.154	2.540	1.411	0.434	0.833	0.516
TT	4	1.103	2.285	1.333	0.415	0.751	0.487
п	5	1.063	2.176	1.281	0.397	0.730	0.468
	6	1.044	2.061	1.249	0.394	0.717	0.463
	7	1.036	2.120	1.248	0.392	0.755	0.467
	8	0.989	1.224	1.214	0.374	0.797	0.454
	GeTe	0.551	0.958	0.641	1.102	1.915	1.282
C	0	1.296	2.652	1.562	0.805	1.449	0.945
C	1	0.972	2.108	1.185	0.680	1.453	0.827

2	0.820	2.365	1.049	0.597	1.576	0.753
3	0.823	2.244	1.043	0.606	1.541	0.756
4	0.809	2.109	1.018	0.603	1.471	0.751
5	0.780	2.059	0.984	0.591	1.446	0.736
6	0.712	2.112	0.914	0.537	1.482	0.682
7	0.708	2.153	0.912	0.540	1.540	0.689
8	0.670	2.209	0.873	0.511	1.595	0.660
GeTe	0.296	0.303	0.298	0.213	0.217	0.215

III. Supporting Figures



Figure S1. SEM EDX spectrum of GBT-1–5, using the Ge L-shell, Bi M-shell, and Te L-shell peaks.



Figure S2. (a) Full-range XRD patterns taken from GeTe and Ge₉Bi₁Te₁₀ (x = 0.1, GBT-1), Ge₈Bi₂Te₁₁ (x = 0.2, GBT-2), Ge₆Bi₂Te₉ (x = 0.25, GBT-3), Ge₅Bi₂Te₈/Ge₄Bi₂Te₇ (x = 0.3, GBT-4), and Ge₃Bi₂Te₆ (x = 0.4, GBT-5), (b) a magnified view of the $2\theta = 28$ –30° region showing the R GeTe (202), C GeTe (200), R Ge₃Bi₂Te₅ (0 1 11), and R Bi₂Te₃ (015) peaks. The peaks of rhombohedral (R) phase GeTe (JCPDS No. 47-1079; R3m, a = 8.642 Å, c = 10.668 Å), rock-salt type cubic (C) phase GeTe (JCPDS No. 03-065-0415; a = 6.024 Å), R phase Ge₃Bi₂Te₆ (JCPDS No. 50-0735; R3m, a = 4.261 Å, c = 62.56 Å), and Bi₂Te₃ (JCPDS No. 82-0358; R $\bar{3}$ m, a = 4.395 c = 30.440 Å) are shown for referencing purposes. The peaks for H phase GBT (GBT-3–5) were all tentatively indexed to those of Ge₃Bi₂Te₆.

The peak position of GeTe NW matched exactly to that of bulk R GeTe. The 10 % Bi doped GeTe (GBT-1) induced the slight red shift peak of $\Delta 2\theta = 0.08$ degrees from that of the R GeTe, which is due to the large difference in the radii of Ge²⁺ (87 pm) and Bi³⁺ (117 pm). The 20 % incorporation of Bi produced only the C GeTe phase (GBT-2), whose peaks are exacly matched with those of the reference.

GBT-3 –5 showed the coexistence of the C GeTe and H GBT phases, and the fraction of the H GBT phase increased with the Bi content. The R (0 1 11) peak of GBT-3 ~ GBT-5 showed a broadening, which is probably correlated with the distribution of the period of superlattice structures. We estimated the raio of C and H phases by the integration of C (200) and R (0 1 11) peaks; 1:1, 1.2, and 1:4 for GBT-3, -4, and -5, respectively.



(c) Full-rage XRD patterns taken from GeTe, Ge₉Sb₁Te₁₀ (x = 0.1, GST-1), Ge₈Sb₂Te₁₁ (x = 0.2, GST-2), and Ge₃Sb₂Te₆ (x = 0.4, GST-4), (d) the magnified scaled R (202), C (200), and R (103) peaks. The peaks of the H phase GST were all tentatively assigned to that of R Ge₂Sb₂Te₅, since the XRD patterns of the R phase GST homologous series were very close to each other. The incorporation of 10 % of Sb (GST-1) induced the formation of the metastable NaCl structure, resulting in the coexistence of R and C phases. As the Sb content increased to x = 0.2 (GST-2), the C phase became dominant. GST-4 showed the coexistence of the C and H phases. The R (103) peak of GST-4 sample showed significant broadening, which is correlated with the defects of the short period superlattice structures. We estimated the raio of C and H phases by the integration of C (200) and R (103) peaks; 1:4 for GST-4. Furthermore we estimated the raio of C and R GeTe phases by the integration of C (220) and R (220) peaks; 1:3 for GST-1.



Figure S3. Schematic models for the helical NW; (a) side view and (b) top view, based on the TEM images of Ge₅Bi₂Te₈ NW at the zone axis of [001], [011], [$\bar{1}12$], and [$1\bar{1}2$], as shown on the right. The top-view model shows that the blocks have four equivalent $\langle 110 \rangle$ directions: [$1\bar{1}0$], [$10\bar{1}$], [110], and [101], and there is a 90° rotation between two adjacent blocks. These building blocks stack with an inclined angle of 45°, along the [100] axial direction of the square pillar. At the zone axis (ZA) of [001], two [$1\bar{1}0$] and [110] blocks are zigzagged with an angle of 90°. When the NW is rotated by 45°, the zone axis becomes [011]. The [$10\bar{1}$]/[110] and [101]/[$\bar{1}10$] blocks are zigzagged with an angle of 91°. When the NW is rotated by 45°, the zone axis becomes [011]. The [$10\bar{1}$]/[110] and [101]/[$\bar{1}10$] blocks are zigzagged with an angle of 91°. When the NW is rotated by 45°, the zone axis becomes [011]. The [$10\bar{1}$]/[110] and [101]/[$\bar{1}10$] blocks are zigzagged with an angle of 91°. When the NW is rotated by 45°, the zone axis becomes [011]. The [$10\bar{1}$]/[110] and [101]/[$\bar{1}10$] blocks are zigzagged with an angle of 110° at the zone axis of [011].



Figure S4. TEM EDX spectrum, line-scanning profile, and elemental mapping of indivual GeTe, and Ge₉Bi₁Te₁₀ (GBT-1), Ge₈Bi₂Te₁₁ (GBT-2), Ge₆Bi₂Te₉ (GBT-3), Ge₅Bi₂Te₈/Ge₄Bi₂Te₇ (GBT-4), and Ge₃Bi₂Te₆ NWs (GBT-5). NW, using the Ge K-shell, Bi M-shell, and Te L-shell peaks.



Figure S5. TEM images of (a) as grown Ge₃Bi₂Te₆ NW and after heating at (b) 350 °C, and (c) 400 °C. As the superlattice structures transform into single-crystalline C phase, the end of the NW becomes round with a wrinkled surface.



Figure S6. (a) HRTEM images of a Ge4Bi₂Te₇ NW after heating at 400 °C. The NW is ruptured and an amorphous sheath (probably GeO_x) is formed around the residual NW. The NW part ((i) apart from the edge) still retains a 2.6-nm-period superlattice Ge4Bi₂Te₇ structure, but the ruptured edge (ii) has a superlattice structure with a shorter period. (b), (c) HRTEM images and intensity line profile (iii) for the crystalline residue (as shown in Figure 2b of the text), revealing 2.1-nm-period Ge₂Bi₄Te₅ superlattice structures. The ED pattern (zone axis = $[2\overline{1}\overline{1}0]$) shows approximately 11 spots between the brighter ED spots corresponding to adjacent atomic layers (1.9 Å), confirming the R phase of the Ge₂Bi₄Te₅ structure in which one Bi₂ layer is intercalated in the Ge₂Bi₂Te₅. (d) The EDX line scan (along the axial direction) confirms that the Bi content is significantly higher in the edge region, *ca.* Ge:Bi:Te = 2:4:5. The region of inhomogeneous elemental distribution is ~100 nm wide, which is narrower than for Ge₈Bi₂Te₁₁ (Figure 3). (e) The elemental maps of helical Ge₅Bi₂Te₈ NWs after heating at 400 °C also highlight Bi-rich regions in the vicinity (~100 nm) of the fractured edge. These results indicate that GeTe evaporation is less efficient than in Ge₈Bi₂Te₁₁.



Figure S7. HRTEM images of (a) Ge₈Sb₂Te₁₁ and (b) Ge₃Sb₂Te₆ NWs after heating at 400 °C. The Ge₈Sb₂Te₁₁ NWs are ruptured slightly, but the Ge₃Sb₂Te₆ NWs are not damaged. The 3.8 nm and 2.2 nm periodic superlattice structures of Ge₈Sb₂Te₁₁ and Ge₃Sb₂Te₆ NWs, respectively, remains the same upon the heating.



Figure S8. Crystal structures of the H phase GeTe, Bi_2Te_3 , and $mGeTe \cdot Bi_2Te_3$ (*mGeTe* layer at the center and one Bi_2Te_3 layer at the edge) in the conventional hexagonal unit cells. The Ge (pink balls), Bi (green balls), and Te (grey balls) are labeled.



Figure S9. Atomic arrangement of cubic (C) and hexagonal (H) phase Ge₃Bi₂Te₆. The lattice parameters are a = 4.308 Å and c = 21.103 Å for the C phase, and a = 4.243 Å ($a_{exp} = 4.268$ Å) and c = 62.526 Å ($c_{exp} = 62.590$ Å) for the H phase. Both phases can be represented using hexagonal lattices ($P\bar{3}$ m1 or R3m) and intrinsic vacancies (red color) stacked along the c axis. The stacking sequence of C phase is -Te-Ge-Te-Bi-Te-V-Te-Bi-Te-Ge- along the [111] direction (V represents one vacancy layer), which is the same as its stable hexagonal counterpart. It consists of two well-defined highly ordered three-dimensional repeat units; -Te-Ge-Te-Bi-Te- and -Te-Bi-Te-Ge-, that repeat units are bonded alternatively in space consistent with a rock-salt structure. In the H phase, the intrinsic vacancies do not occupy the high-symmetry sites but only separate the building blocks, as in the R Bi₂Te₃ structure. The debate is ongoing regarding the atomic arrangement, *i.e.*, whether it is a mixed- or single-species layer, particularly for GST (m = 1-3). Herein, we only consider the stacking sequence of single-species layers for each structure. It should also be pointed out that the calculated C phase is not the single-crystalline C phase observed at high temperatures using *in situ* TEM. For all the simulations, the lattice parameters a and c were relaxed independently.



Figure S10. Band gap of the H and C phase (a) mGeTe·Bi₂Te₃ and (b) mGeTe·Sb₂Te₃, where m = 1-8.



Figure S11. (a) SEM image showing NW between Pt electrode pads with four-probe tungsten (W) tips and typical cross-sectional image of NW–Pt electrodes. (b) I–V characteristics of Ge₉Bi₁Te₁₀ (GBT-1), Ge₈Bi₂Te₁₁ (GBT-2), Ge₆Bi₂Te₉ (GBT-3), Ge₅Bi₂Te₈ (GBT-4), Ge₄Bi₂Te₇ (GBT-4), and Ge₃Bi₂Te₆ (GBT-5).

A typical cross-sectional image of a NW-Pt electrode is shown in the lower part of (a). The currentvoltage (*I*-*V*) curves were monitored using four-probe tungsten (W) tips. The voltage was applied between two outer electrodes (distance = $50-60 \mu$ m), and the *I*-*V* data was measured using the inner electrodes. The *I*-*V* plots for Ge₉Bi₁Te₁₀, Ge₈Bi₂Te₁₁, Ge₆Bi₂Te₉, Ge₅Bi₂Te₈, Ge₄Bi₂Te₇, and Ge₃Bi₂Te₆ NW electrodes are linear, indicating good ohmic contact. The resistances (R) of three to five NW electrodes with well-defined cross-sections (A = πr^2 , where *r* is the radius of NW) and lengths (*L*) between the Pt electrodes provided reliable values of resistivity ($\rho = RA/L$).



Figure S12. Calculated resistivities of *m*GeTe·Bi₂Te₃ (GBT) at $n = 0.5 \times 10^{20}$, 1×10^{20} , and 2×10^{20} cm⁻³: (a) ρ_a and ρ_c versus *m* for H-GBT, (b) ρ_a and ρ_c versus *m* for C-GBT, (c) ρ_{avg} versus *m* for H-GBT and C-GBT, and (d) ρ_{avg} as a function of *n*, for m = 1-8. The log values were plotted. The results show that (1) ρ_c is two to three times higher than ρ_a ; (2) ρ_{avg} of the H phase is lower than that of the C phase; (3) ρ_{avg} of the H phase is nearly the same for all values of *m*, whereas that of the C phase decreases significantly with increasing *m*.



Figure S13. Calculated resistivities of mGeTe·Sb₂Te₃ (GST) at $n = 0.2 \times 10^{20}$, 0.5×10^{20} , 1×10^{20} , 2×10^{20} , and 3×10^{20} cm⁻³: (a) ρ_a and ρ_c versus *m* for H-GST, (b) ρ_a and ρ_c versus *m* for C-GST, (c) ρ_{avg} versus m for H-GST and C-GST, and (d) ρ_{avg} as function of *n*, for m = 1-8.

Both H- and C-GST consistently exhibit anisotropic resistivity, *i.e.*, $\rho_c > \rho_a$. The ρ_{avg} of the H and C phases is nearly the same for all values of *m*. In the range $n = (0.2-2) \times 10^{20}$ cm⁻³, the ρ_{avg} value of the C-phase is slightly lower than that of the H phase; this is different from the case for GBT. However, as *n* increases to 3×10^{20} cm⁻³, the resistivity of the H phase becomes lower than that of the C phase. It is worth noting that there are large differences between the GBT and GST.

IV. High Resolution Movies

Movie S1: Destruction of Ge₄Bi₂Te₇ NW at 400 °C: the first part (×300k magnification) and the second part (×500k magnification) show the layer-by-layer peeling processes.