SUPPORTING INFORMATION

Correlating Negative Thermal Expansion and Thermal Conductivity in Two-dimensional Carbon-based Materials

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Contents:

1. **Figure. S1.** Free energy-volume curve for the systems to obtain the equilibrium volume of a material.

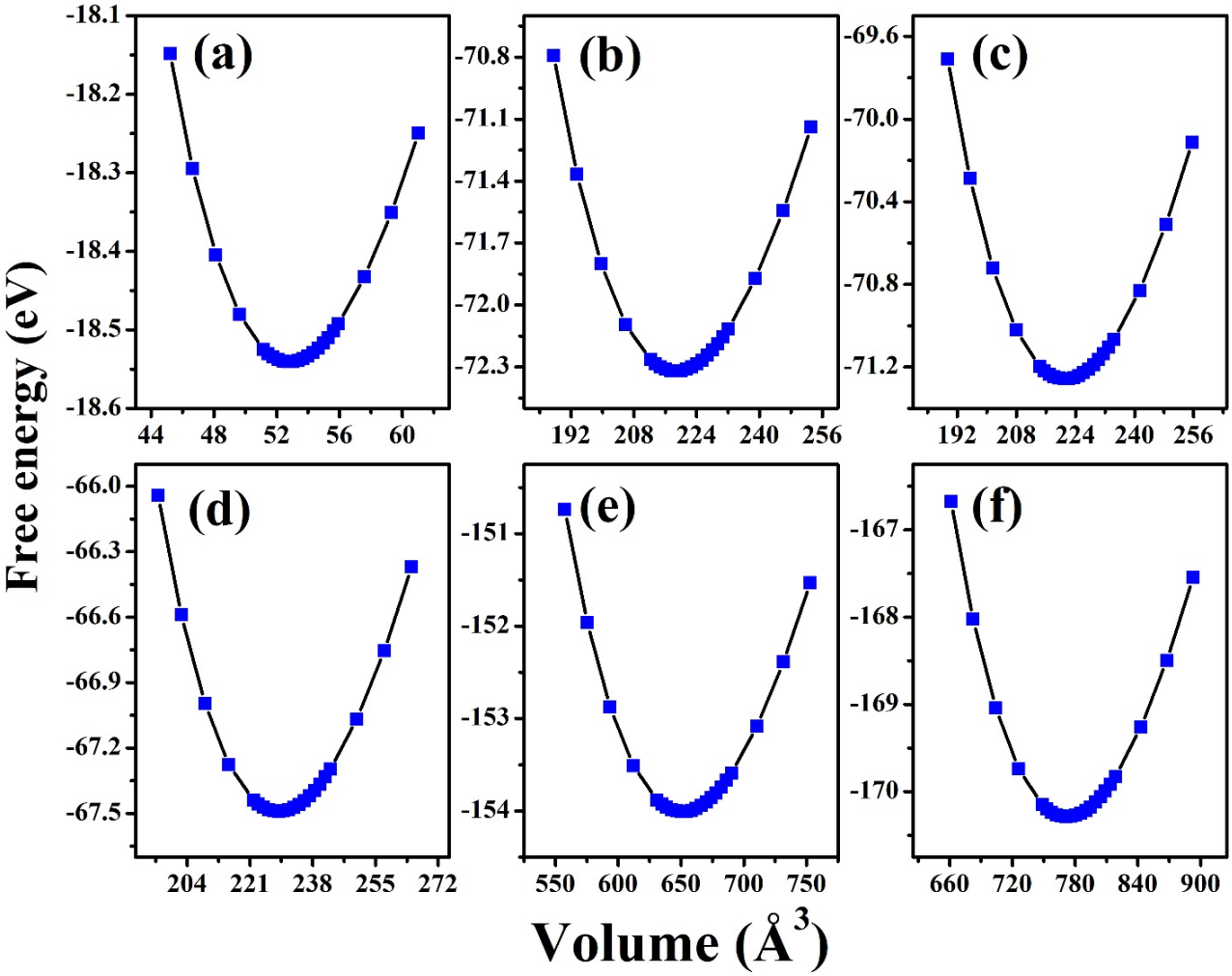

Figure S1: *Energy-volume plots for (a) graphene (b) haeckelite (c) pentahexoctite (d) s_graphene (e) 6.6.12-Gy and (f) delta-Gy.*

2. **Figure. S2.** Phonon band structure shows stability of the 2D systems.

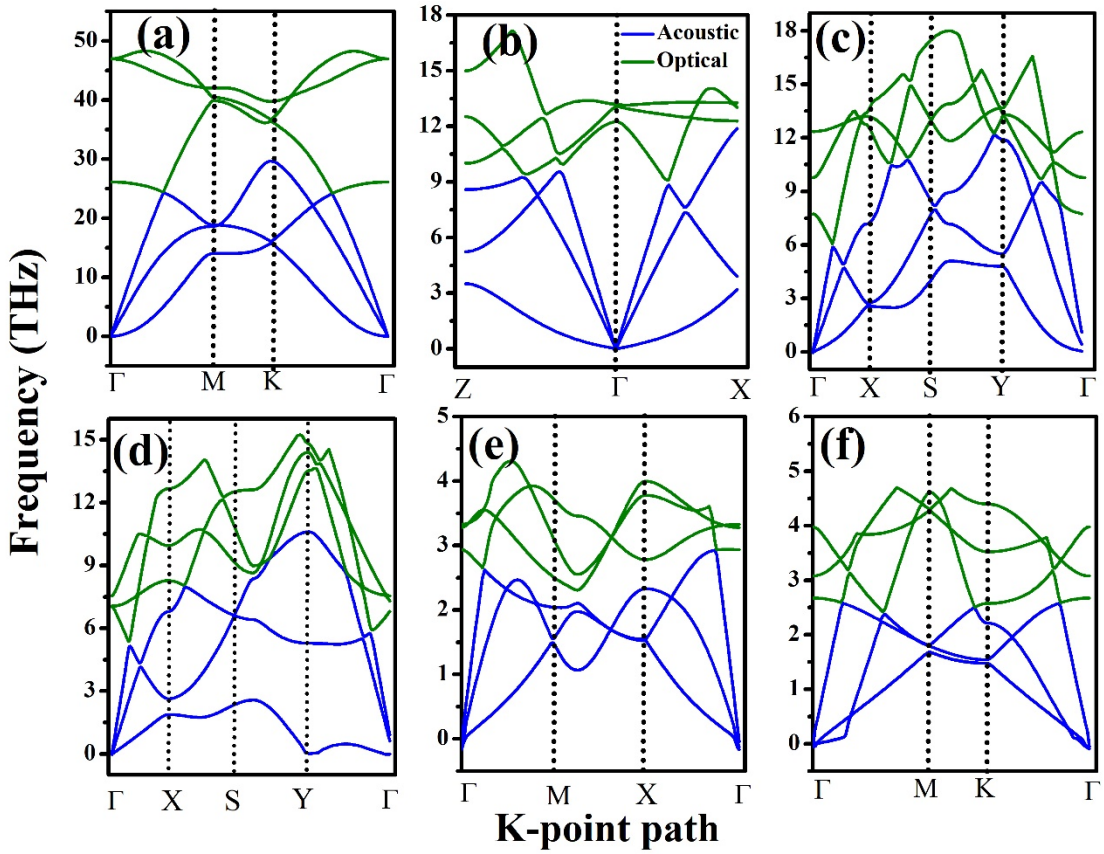

Figure. S2. (a) *First six phonon dispersion bands of the structure (a) graphene (b) haeckelite (c) pentahexoctite (d) s-graphene (e) 6.6.12-Gy and (f) delta-Gy. Blue and green lines indicate acoustic and optical phonons respectively.*

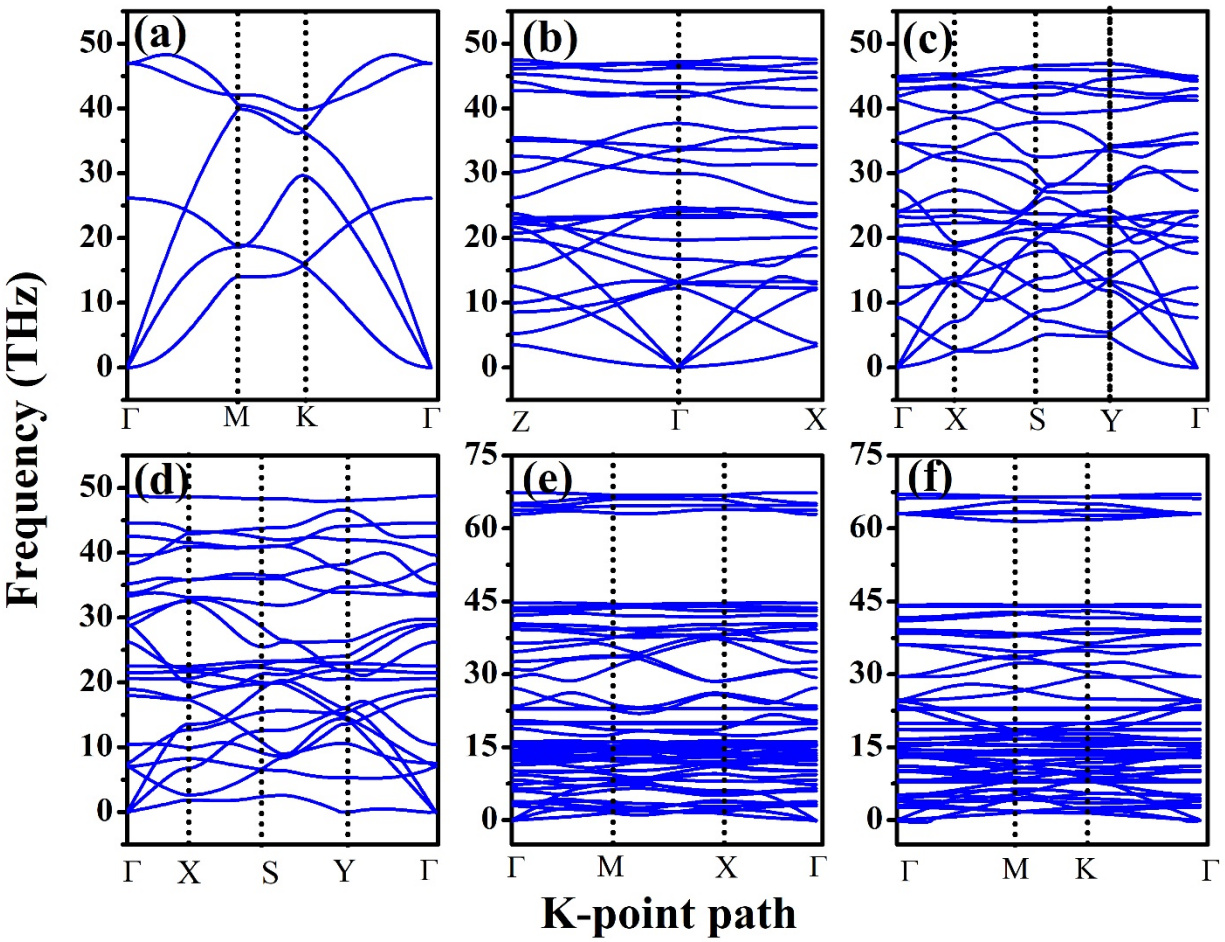

Figure S2. **(b)** *Phonon dispersion bands show stability of the structure (a) graphene (b) haeckelite (c) pentahexoctite (d) s-graphene (e) 6.6.12-Gy and (f) delta-Gy.*

3. **Figure S3.** Phonon lifetime vs frequency plots for the systems

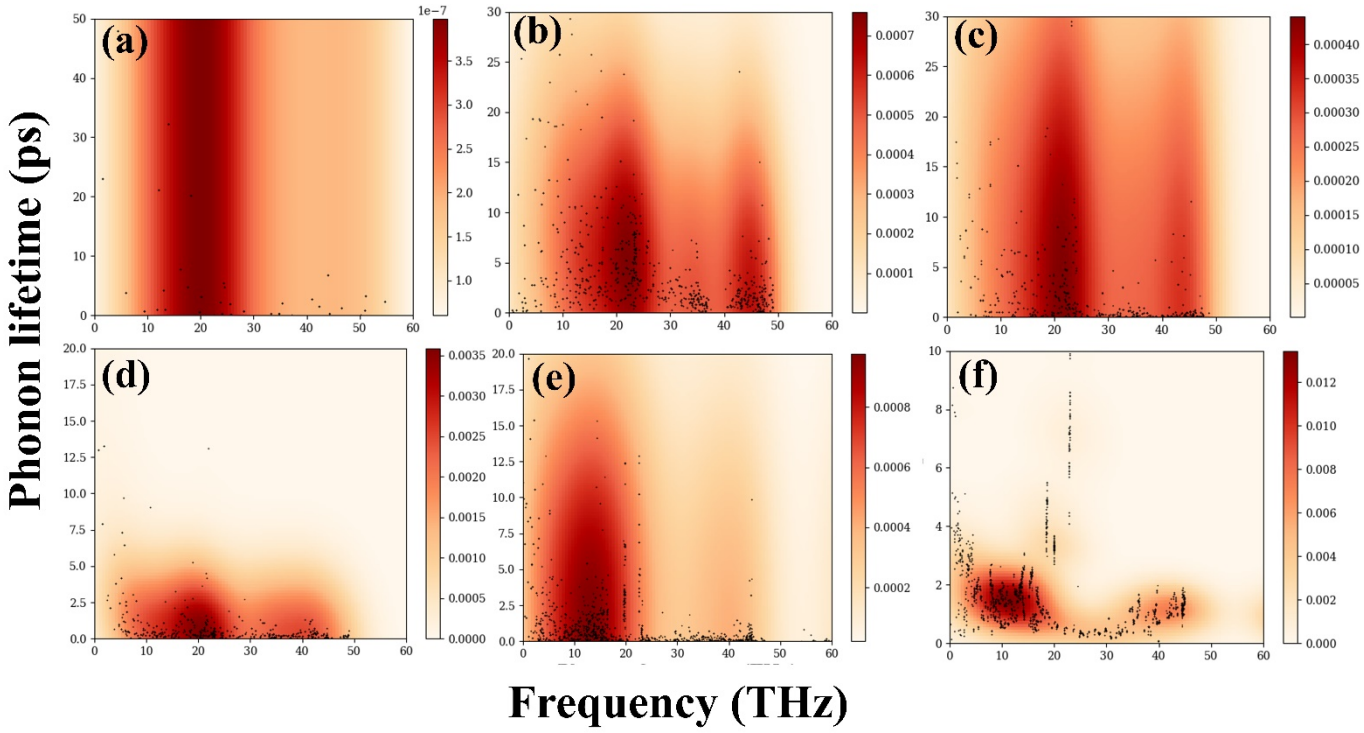

Figure S3: *Phonon lifetime vs frequency plots for (a) graphene (b) haeckelite (c) pentahexoctite (d) s-graphene (e) 6.6.12-Gy and (f) delta-Gy at 300K.*

The plot draws density of phonon modes in the frequency-lifetime plane. The black dots show original data points. More density (Red colour) indicates more phonon lifetime. Highest density of phonon lifetime can be observed for graphene and the lowest is observed for delta-*Gy*. High phonon lifetime indicates that the phonons which are heat carriers remain stable for a long period and carry heat in a crystal. Hence, they are directly proportional to the thermal conductivity of a system.

4. **Figure. S4.** Cumulative phonon lifetime vs frequency plots for the systems.

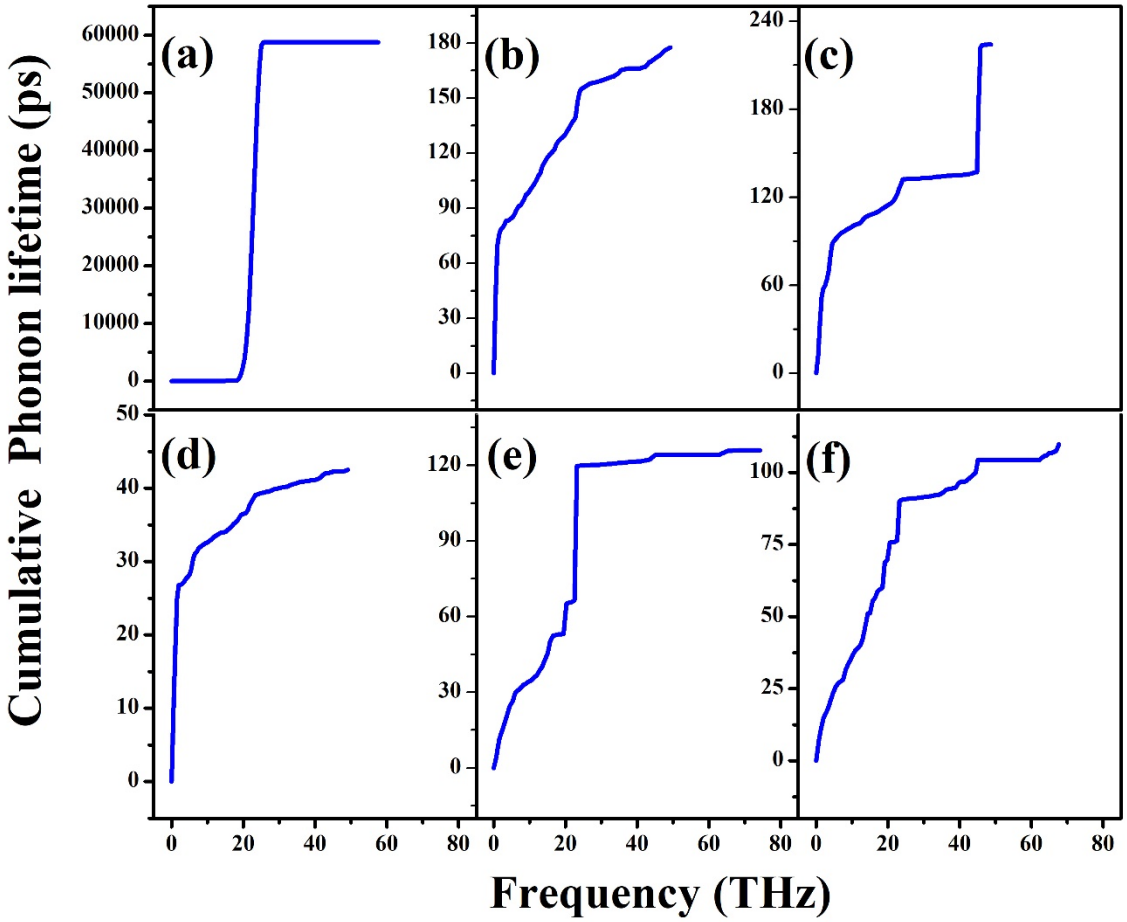

Figure S4. *Cumulative phonon lifetime vs frequency plots for (a) graphene (b) haeckelite (c) pentahexoctite (d) s-graphene (e) 6.6.12-Gy and (f) delta-Gy.*

5. **Table ST1:** Maximum and minimum phonon group velocity (v_g) and the corresponding frequency for the materials

		ZA		TA		LA	
		Frequency	**GV**	**Frequency**	**GV**	**Frequency**	**GV**
graphene	**Max**	9.28	9.48	6.79	14.14	3.13	21.49
	Min	14.07	0.04	18.82	0.71	18.98	2.51
haeckelite	**Max**	2.97	5.67	1.10	13.20	2.22	20.79
	Min	3.52	0.12	6.42	0.81	8.60	0.45
pentahexoctite	**Max**	3.40	6.34	1.11	13.64	5.19	20.71
	Min	0.22	1.45	7.29	3.71	8.83	3.30
s-graphene	**Max**	0.13	6.64	2.80	12.72	1.87	19.66
	Min	1.73	0.79	5.28	0.18	6.94	0.71
6.6.12-Gy	**Max**	1.43	4.07	0.66	9.74	1.83	17.01
	Min	1.11	1.55	2.18	0.75	2.31	0.72
delta-Gy	**Max**	1.31	2.46	0.96	10.85	1.79	15.72
	Min	1.36	0.47	1.42	0.50	2.45	0.93

6. **Table ST2.** Comparison of experimental and theoretical TEC, TC (300 K) values with the present work

TEC and TC values of graphene at 300K

	Experimental	Theoretical	Present work
TEC	= (−8.0 ± 0.7) × 10^{-6} K^{-1} (*ref.* 1)	= −6 ×10^{-6} K^{-1} (*ref.* 2)	= -6.85 ×10^{-6} K^{-1}
TC	= (3.1 ± 1.0) × 10^{3} Wm^{-1} K^{-1} (*ref.* 3)	= 3.00 × 10^{3} Wm^{-1} K^{-1} (*ref.* 4)	= 3.01 × 10^{3} Wm^{-1} K^{-1}

References

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2. Demiroglu, I.; Sevik, C. Extraordinary Negative Thermal Expansion of Two-Dimensional Nitrides: A Comparative Ab Initio Study of Quasiharmonic Approximation and Molecular Dynamics Simulations. *Phys. Rev. B Condens. Matter* 2021, *103* (8), 085430.
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4. Das, G. P.; Raghuvanshi, P. R.; Bhattacharya, A. Phonons and Lattice Thermal Conductivities of Graphene Family. *Procedia Structural Integrity* **2019**, *23*, 334–341.

7. Unit cell structures (POSCAR format) of the studied systems.

(a) graphene
```
  1.00000000000000
    2.4672320370031575   -0.0000000004273772   -0.0000000000000000
   -1.2336163892563132    2.1366854086995160    0.0000000000000000
    0.0000000000000000    0.0000000000000000   15.000000000000000
   C
    2
Direct
 0.3333333347903888  0.1666666682283378  0.5000000000000000
 0.6666666652096112  0.8333333317716622  0.5000000000000000
```

(b) haeckelite
```
 1.0000000000000
    4.7422514835752541   -0.1772202470086433    0.0000000000000000
    1.3029163726511479    4.5631986420385013    0.0000000000000000
```

0.0000000000000000 0.0000000000000000 15.000000000000000
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0.5930754441466526 0.5930753639475739 0.5000000000000000

(c) Pentahexoctite
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0.0000000000000000 0.0000000000000000 15.000000000000000
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0.0000000000000000 0.0000000000000000 15.0000000000000000
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0.2582557220486377 0.8034085195930204 0.5000000000000000
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(e) 6,6,12-graphyne
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C
18
Direct

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(f) delta-graphyne
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0.0000000000000000 0.0000000000000000 15.000000000000000
C
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