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BULK NANOCARBON THERMOELECTRICS

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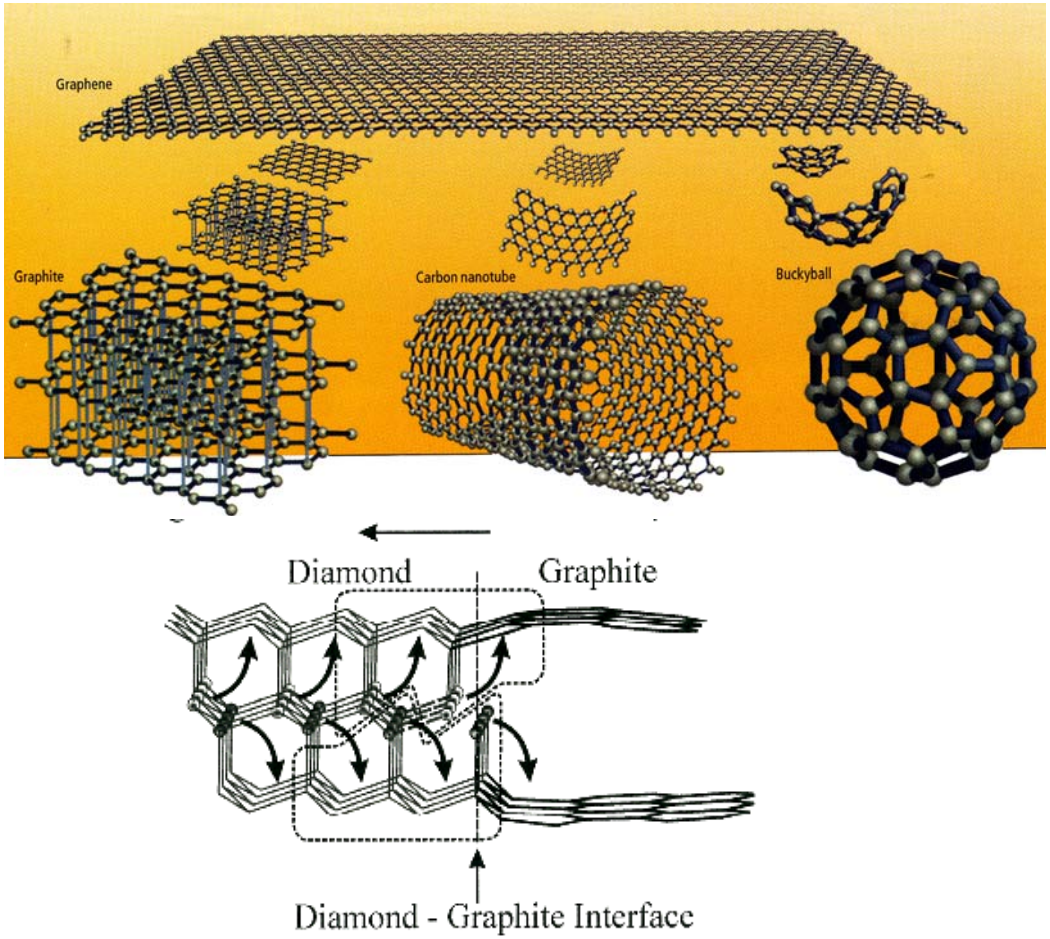
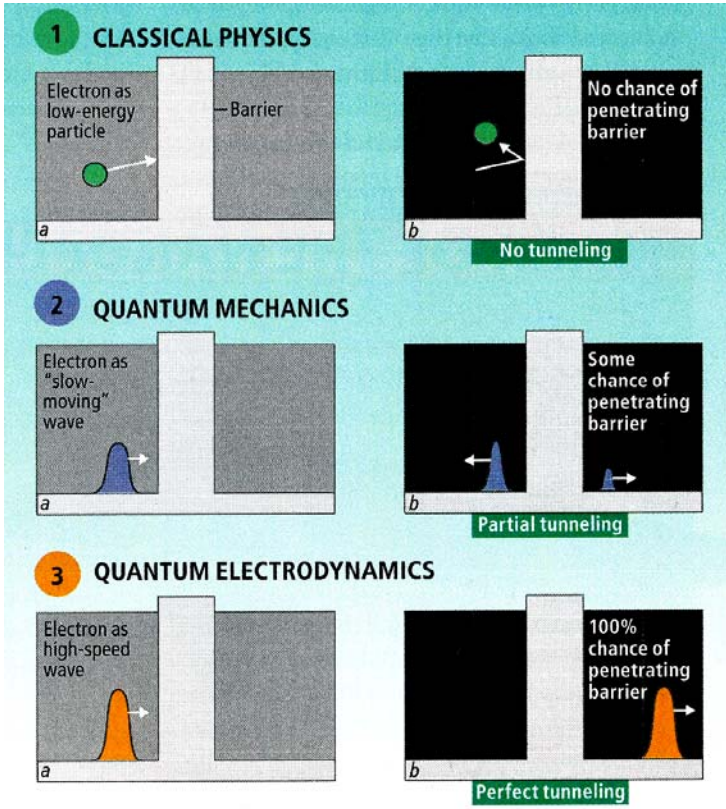
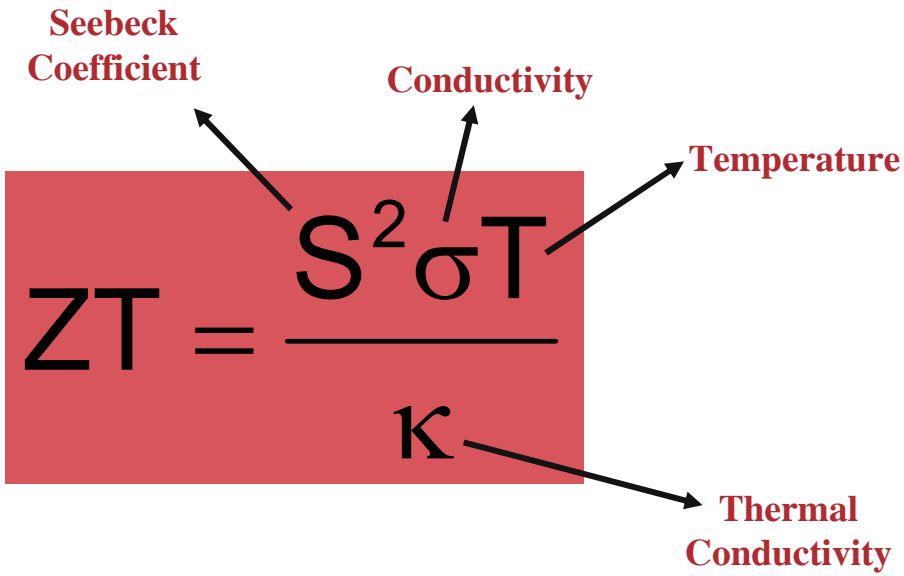
DO NANOCARBON ENSEMBLES PROVIDE AN OPPORTUNITY FOR THE SYNTHESIS OF A NEW CLASS OF HIGH EFFICIENCY THERMOELECTRICS?



Geim et al pg. 90, Scientific American, April 2008



*Kuznetsov et al, chap. 13, pg. 438, Ultrananocrystalline Diamond, Synthesis, Properties and Applications, Edited by O. Shenderova, D.M. Gruen 2006



The Coupling of ZT Parameters in bulk materials :

1) Increasing the electrical conductivity tends to decrease the Seebeck Coefficient.

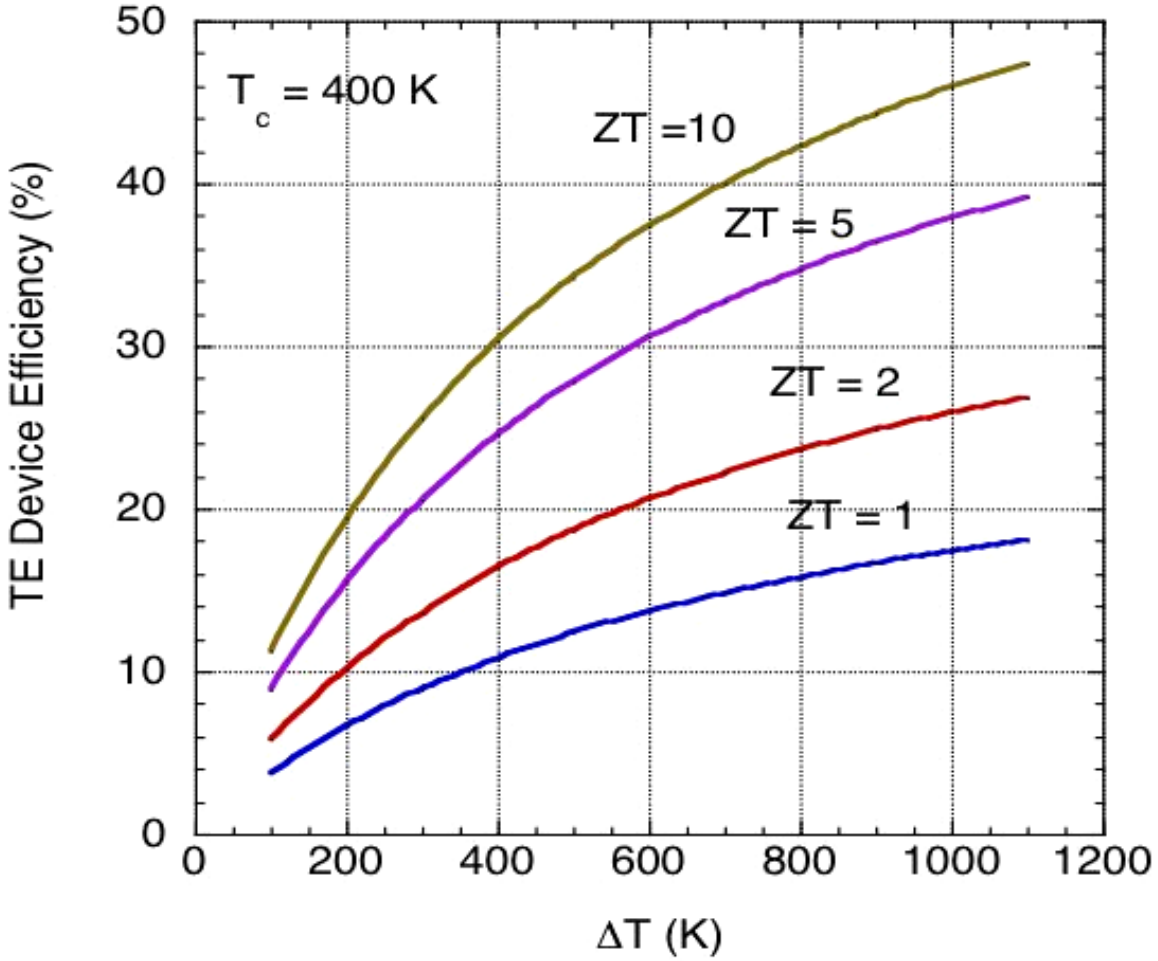
2) Increasing the electrical conductivity tends to increase the thermal conductivity.

Nanoensemble Design Considerations Intended to Decouple the ZT parameters:

1) Increased phonon scattering at grain boundaries reduces the thermal conductivity of nanomaterials.

2) One component of the nanoensemble is chosen to have a high electrical conducttivity without increasing the thermal conductivity of the nanoensemble.

3) Another component optimizes the configurational electronic entropy and produces a high density of states within thermal energies of the Fermi level without causing a decrease in electrical conductivity.



Efficiency vs. ΔT

$$\eta_{TE} = \eta_C \left(\frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+\frac{T_C}{T_H}} \right)$$

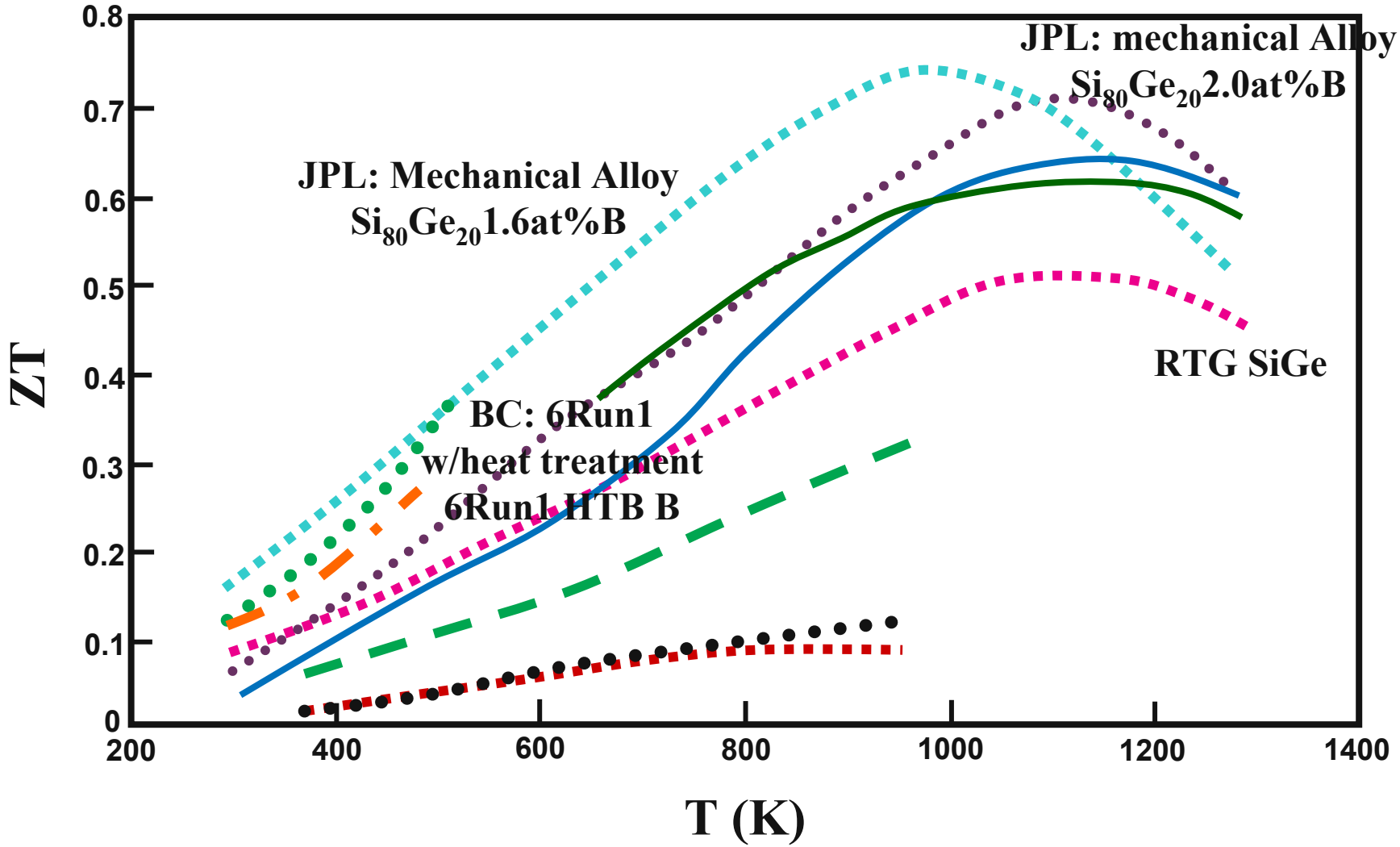
η_{TE}=thermoelectric efficiency

η_C=Carnot efficiency

- **Efficient conversion of heat to electricity requires large ΔT's and therefore high operating temperatures**

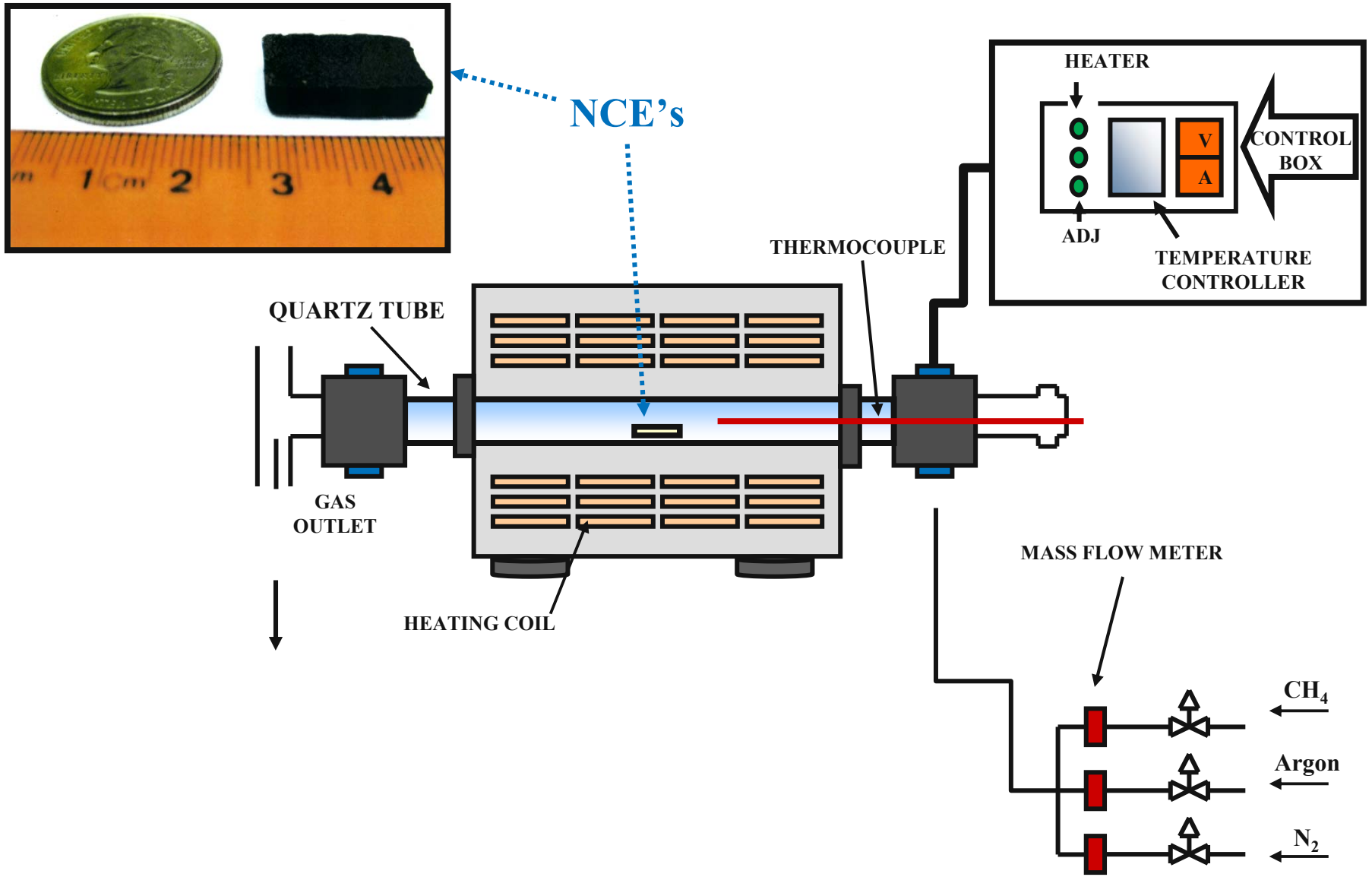
- **Carbon Nanoensembles are among the very few materials that, because of their high Debye temperatures, maintain their nanocrystallinity at high temperatures.**

State of the art performance of SiGe alloys in space thermoelectric applications



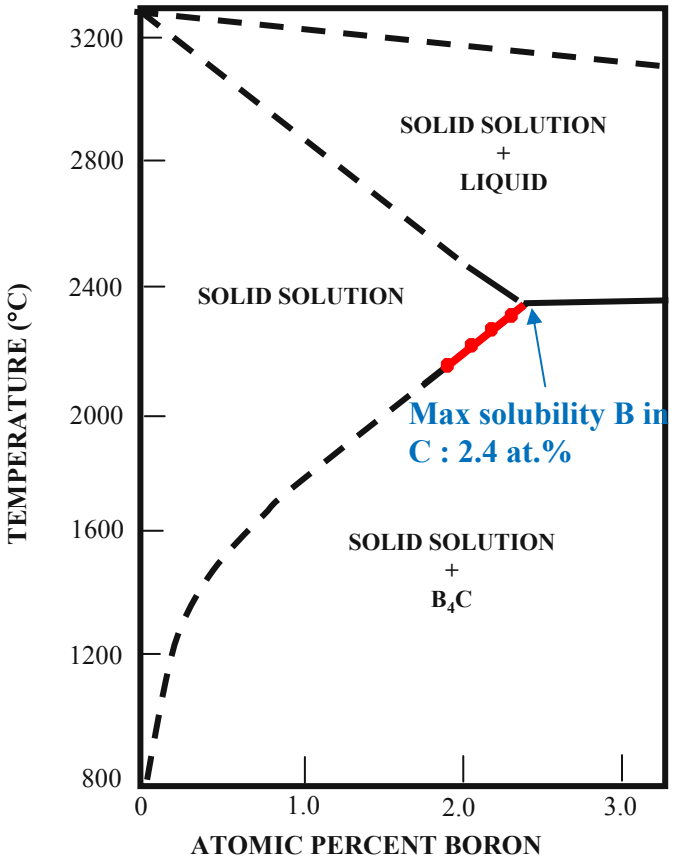
M.S. Dresselhaus et al. , *Advanced Materials*, 19, 1043 (2007)

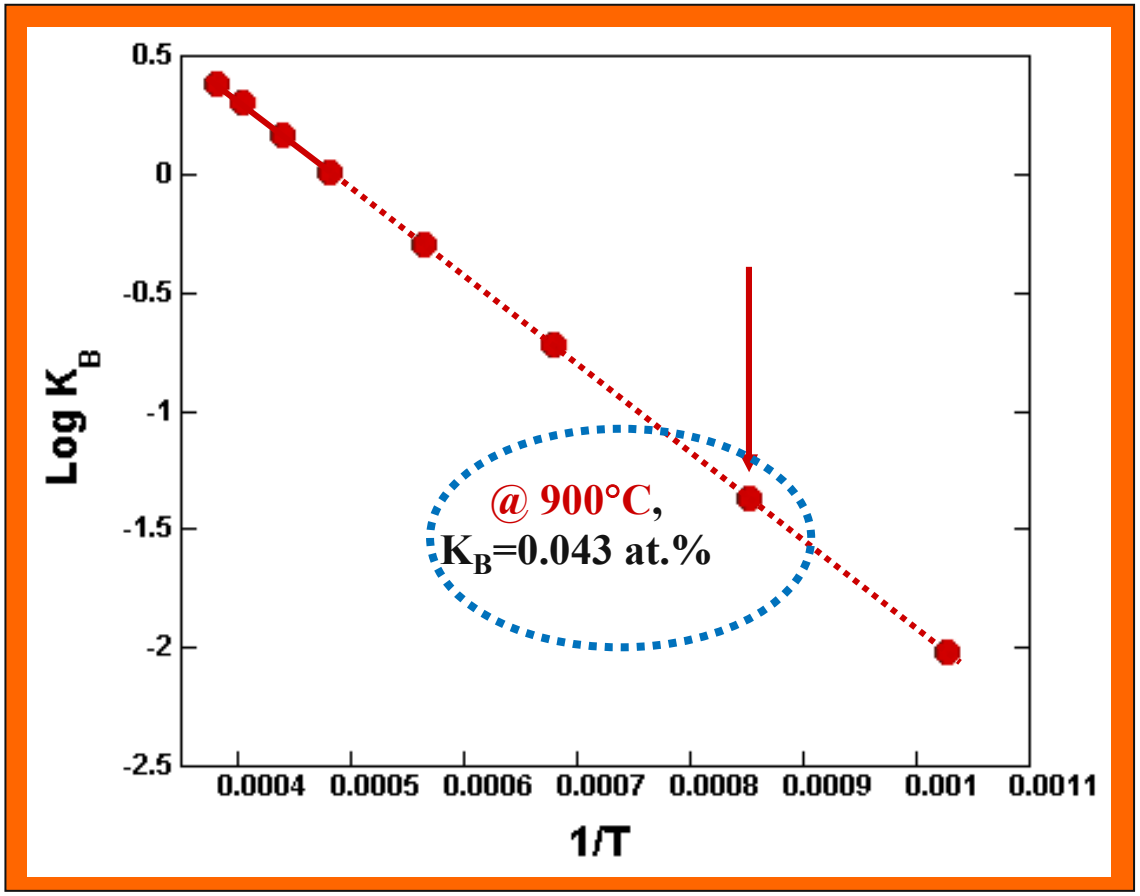
Apparatus for the synthesis of Nanocarbon Ensembles



Boron substitutional solid solutions in graphite

The system Boron- Carbon

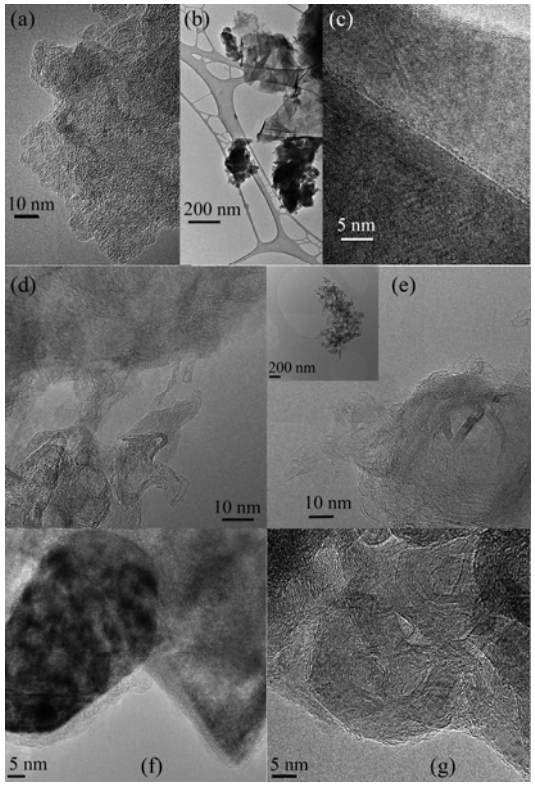




C.E. Lowell, *J. Am. Ceramic Soc.* 50, 142 (1967)

Results

TEM micrographs of boron doped NCE

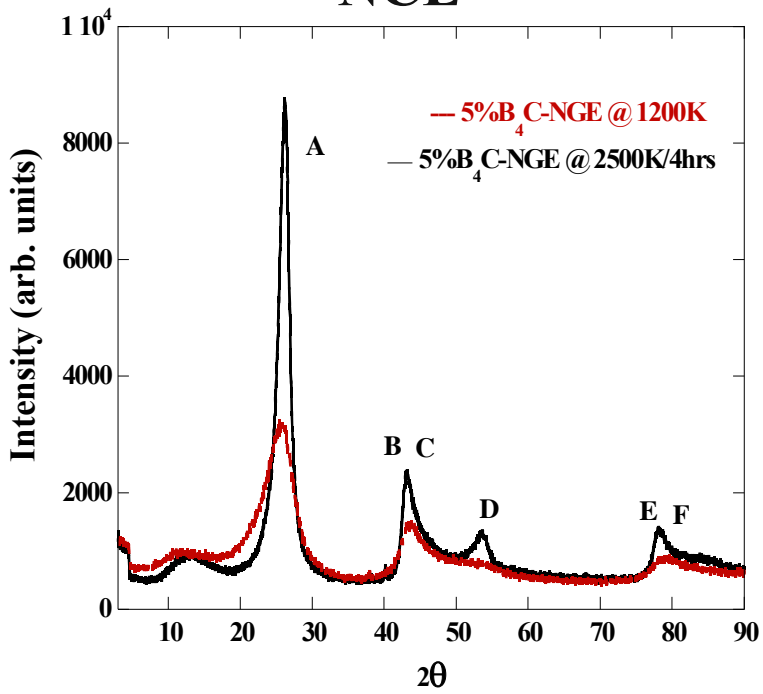


As- fabricated

Annealed at 1700K

Annealed at 2100K

XRD spectra of boron doped NCE

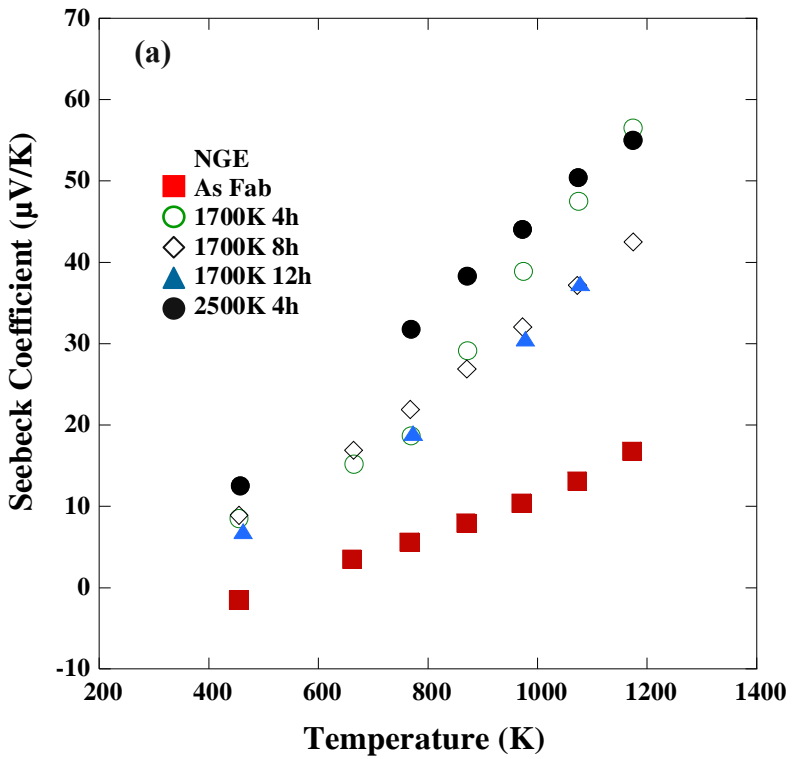


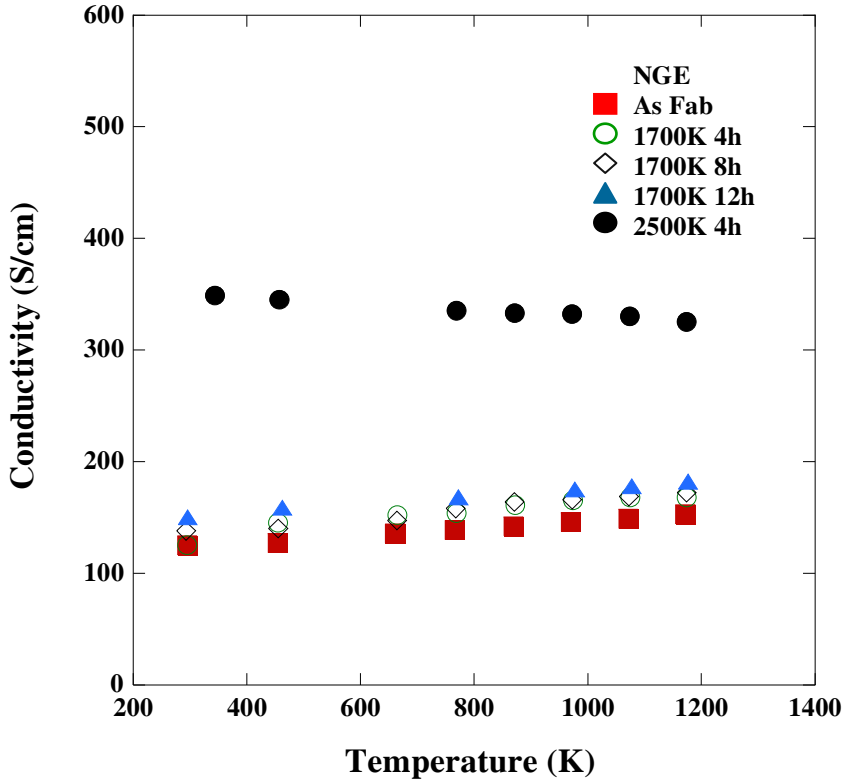
as fabricated and after annealing at 2500K

- the thermal treatment reduces the amount of unorganized (disordered) carbon in the material

Results

Seebeck coefficient (left) and Electrical conductivity (right) results for a boron doped sample as a function of temperature and annealing times.



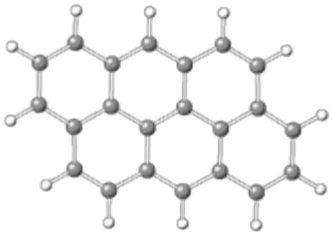


- **Seebeck coeff. and electrical conductivity increase with the annealing temperature and time**

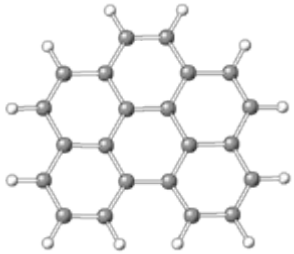
AN INTERESTING INSIGHT TO THE PHYSICAL MEANING OF THE ABSOLUTE THERMOELECTRIC POWER CAN BE OBTAINED BY (CONSIDERING THAT) EACH ELECTRON INVOLVED IN THE ELECTRIC CURRENT CARRIES WITH IT AN ENTROPY. THE THERMOELECTRIC POWER CAN BE LOOKED ON AS THE ENTROPY TRANSPORTED PER COULOMB BY THE ELECTRON FLOW.

H.B Callen, "THERMODYNAMICS", John Wiley and Sons, 1960.

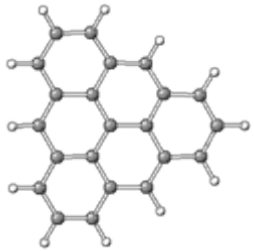
Structures of molecular analogs of graphene.



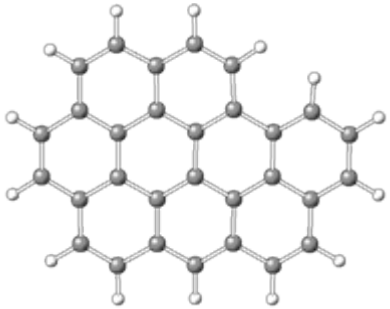
$C_{22}H_{12}$ (K1)



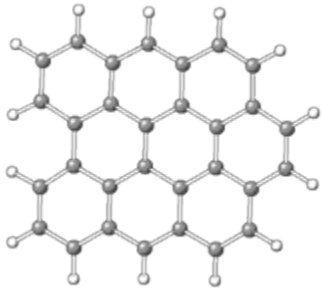
$C_{22}H_{12}$ (K2)



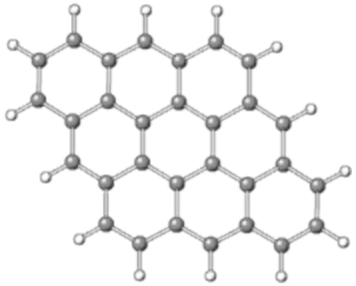
$C_{22}H_{12}$ (NK)



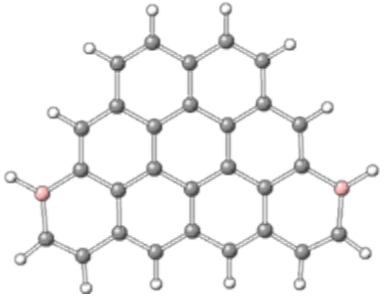
$C_{30}H_{14}$(K1)



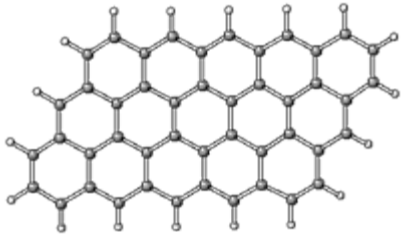
$C_{30}H_{14}$(K2)



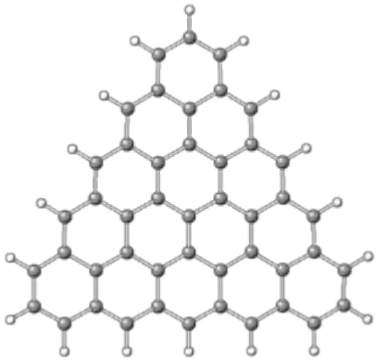
$C_{30}H_{14}$(K3)



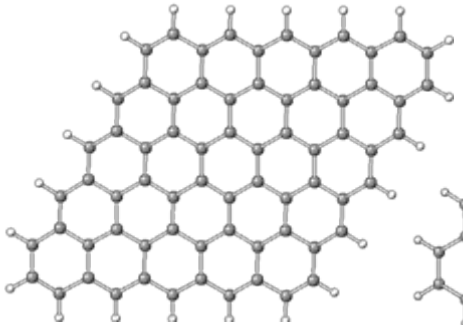
$C_{30}H_{14}$(NK)



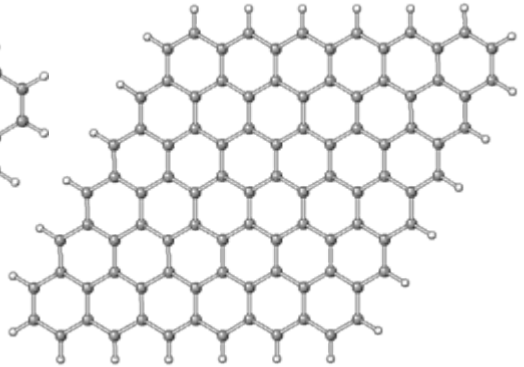
$C_{46}H_{18}$(K)



$C_{46}H_{18}$(NK)

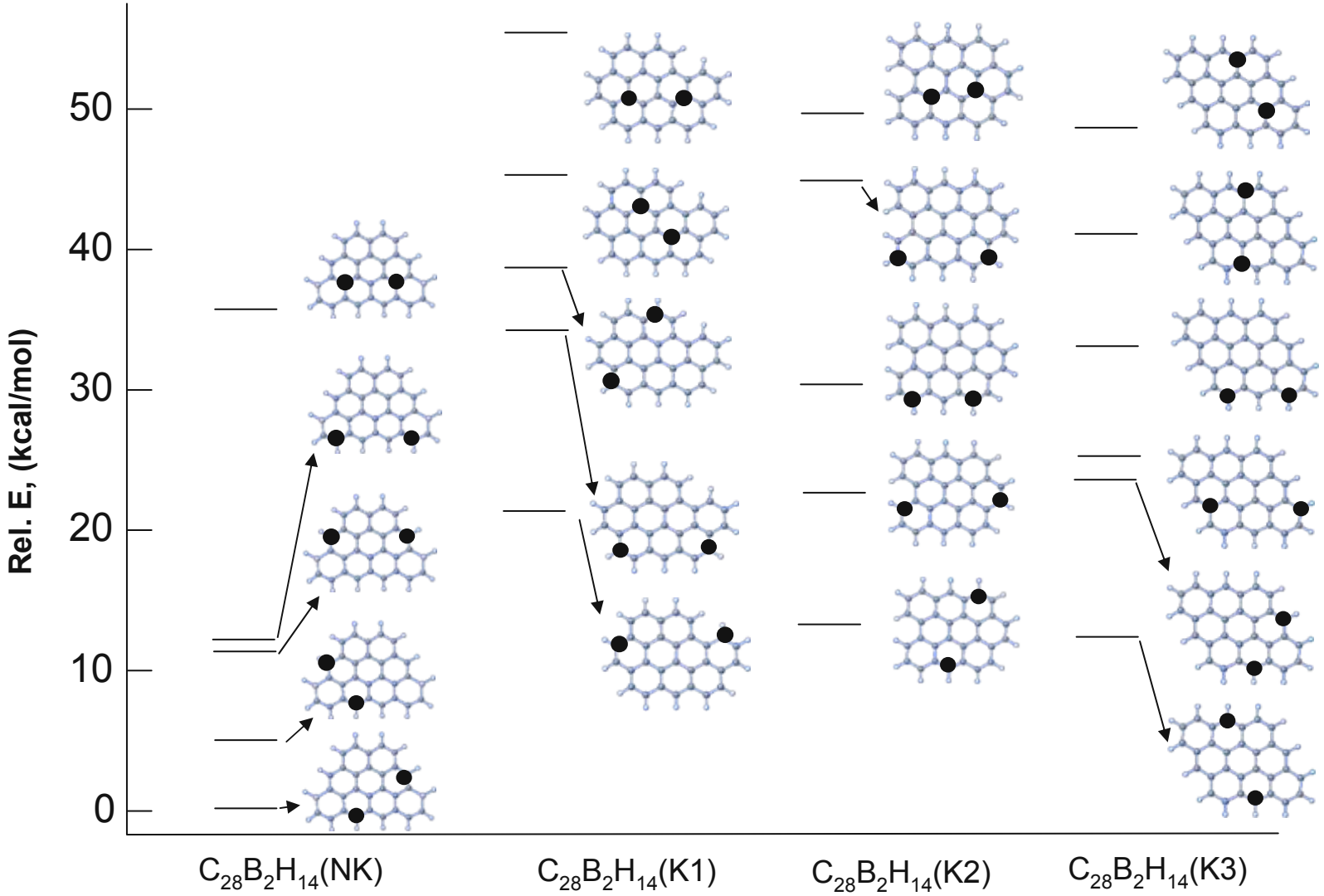


$C_{70}H_{22}$(K)



$C_{96}H_{26}$(K)

B3LYP/6-31G* relative energies of boron disubstituted C30 graphene sheets.



Solid circles indicate where boron substitutions are located.

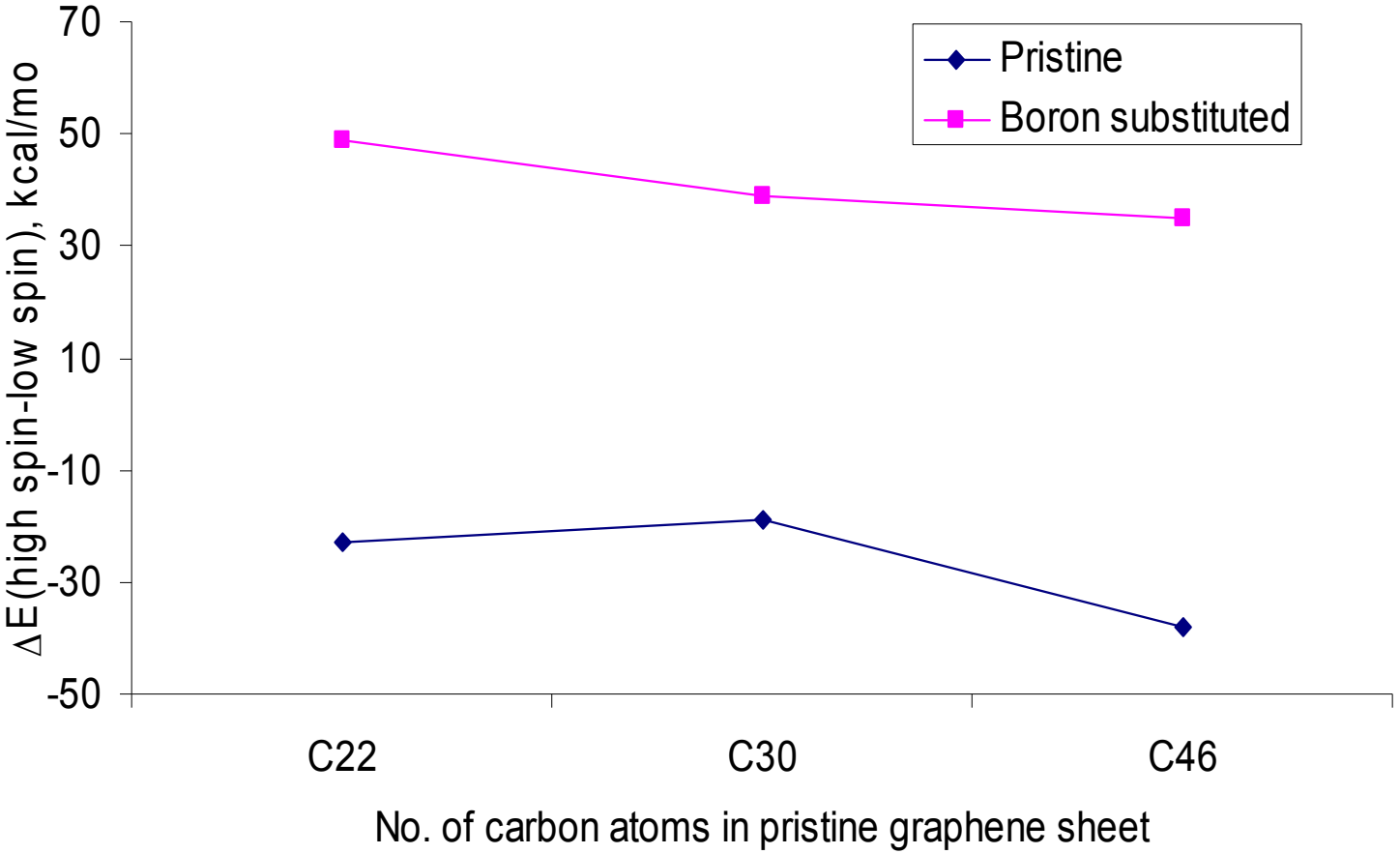
B3LYP/6-31G* relative energies of molecular analogs of graphene and of different electronic states

Graphene sheet stochiometry	Structure	Relative energy, kcal/mol for different isomers	Energy relative to singlet (kcal/mol)		
			Singlet	Triplet	Quintet
$C_{22}H_{12}$	K1 (3x2)	5.9	0.0	32.1	103.3
	K2	0.0	0.0	47.3	120.7
	NK	26.7	0.0	-23.4	62.7
$C_{30}H_{14}$	K1	0.0	0.0	44.3	109.0
	K2	8.6	0.0	26.0	102.5
	K3 (3x3)	13.7	0.0	20.6	73.9
	NK	25.7	0.0	-19.4	47.5
$C_{46}H_{18}$	K (5x3)	0.0	0.0	3.0	31.8
	NK	17.1	0.0	-28.9	-38.2
$C_{70}H_{22}$	K (5x5)	===	0.0	-7.1	0.4
$C_{96}H_{26}$	K (6x6)	===	0.0	-12.8	-17.9

B3LYP/6-31G* relative energies of different electronic states of boron-substituted molecular analogs of graphene.

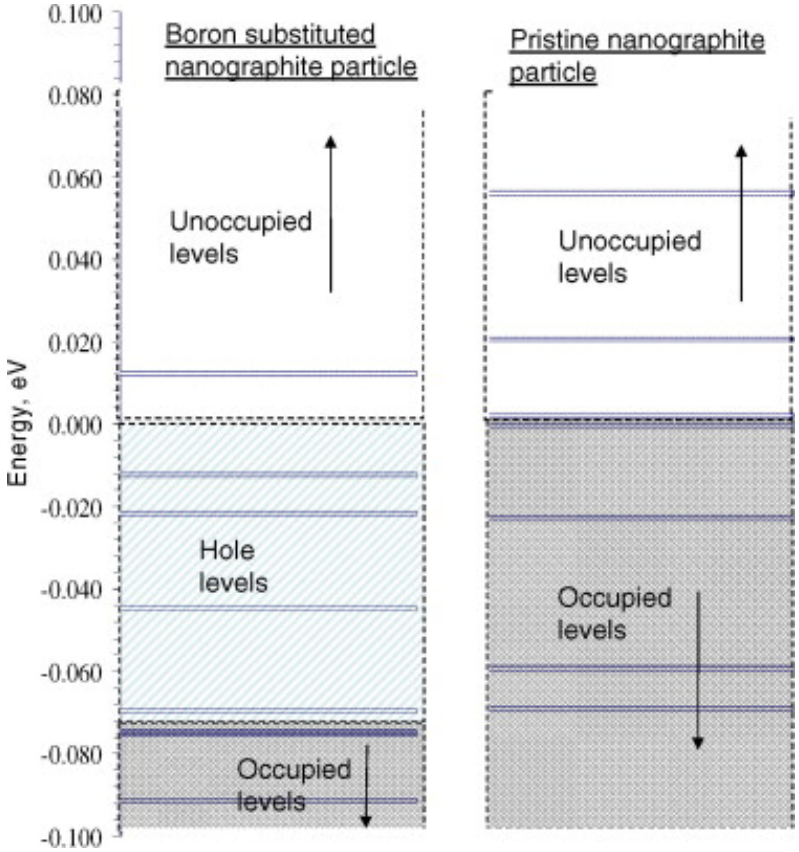
Graphene sheet stochiometry	Structure	Energy relative to singlet (kcal/mol)		
		Singlet	Triplet	Quintet
$C_{20}B_2H_{12}$	K1 (3x2)	0.0	37.4	107.7
	NK	0.0	49.8	
$C_{28}B_{214}$	K3 (3x3)	0.0	16.5	77.3
	NK	0.0	39.1	91.7
$C_{44}B_2H_{18}$	K (5x3)	0.0	33.9	84.3
	NK	0.0	-17.4	19.8
$C_{42}B_4H_{18}$	NK	0.0	35.8	84.7
$C_{70}H_{22}$	K (5x5)	0.0	3.0	41.2
$C_{96}H_{26}$	K (6x6)	0.0	-13.5	2.1

B3LYP/6-31G* energy difference between high spin and low spin states of pristine and boron substituted molecular analogs of graphene.



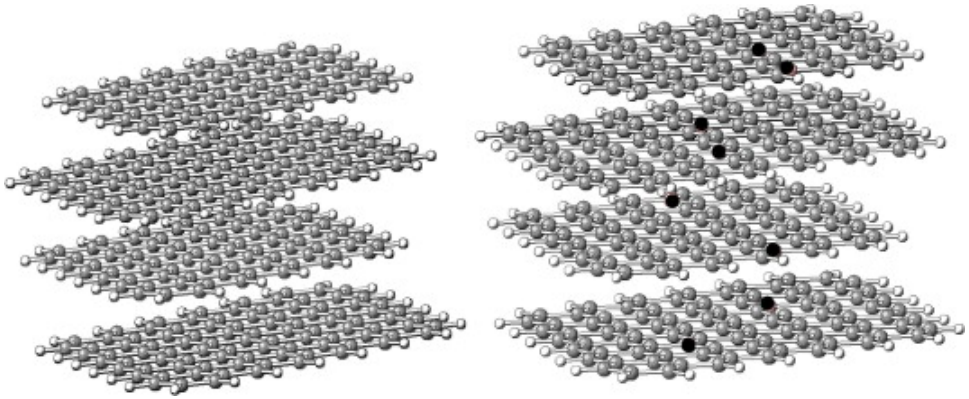
For C22 and C30 the results are for 2 borons and for C46 it is for 4 borons.

Results/Theory



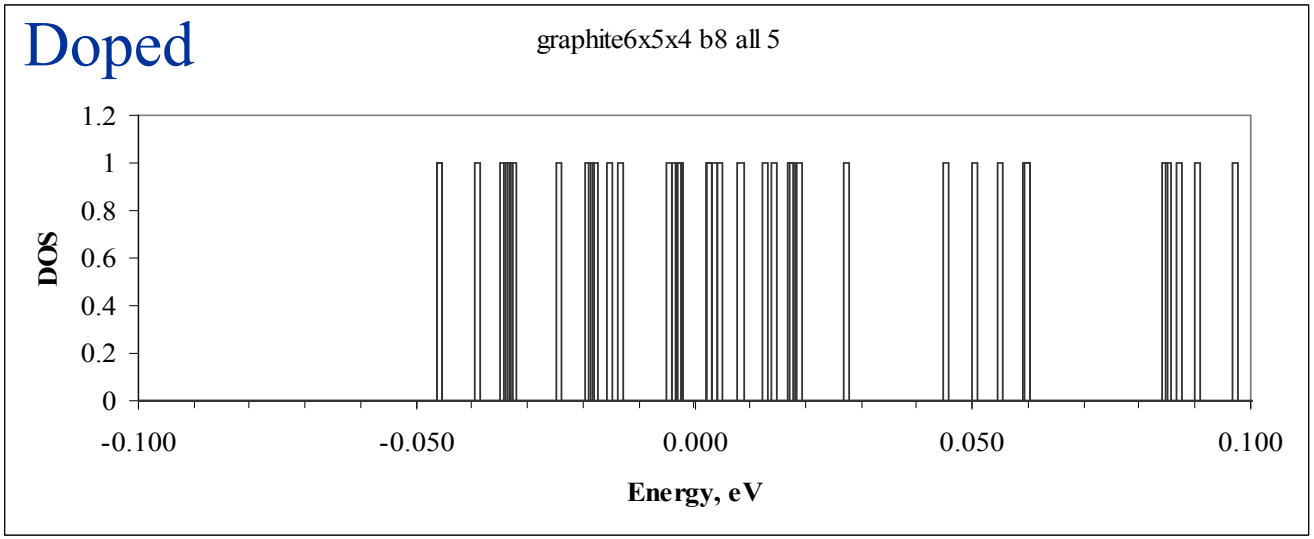
Results from DFTB calculations.

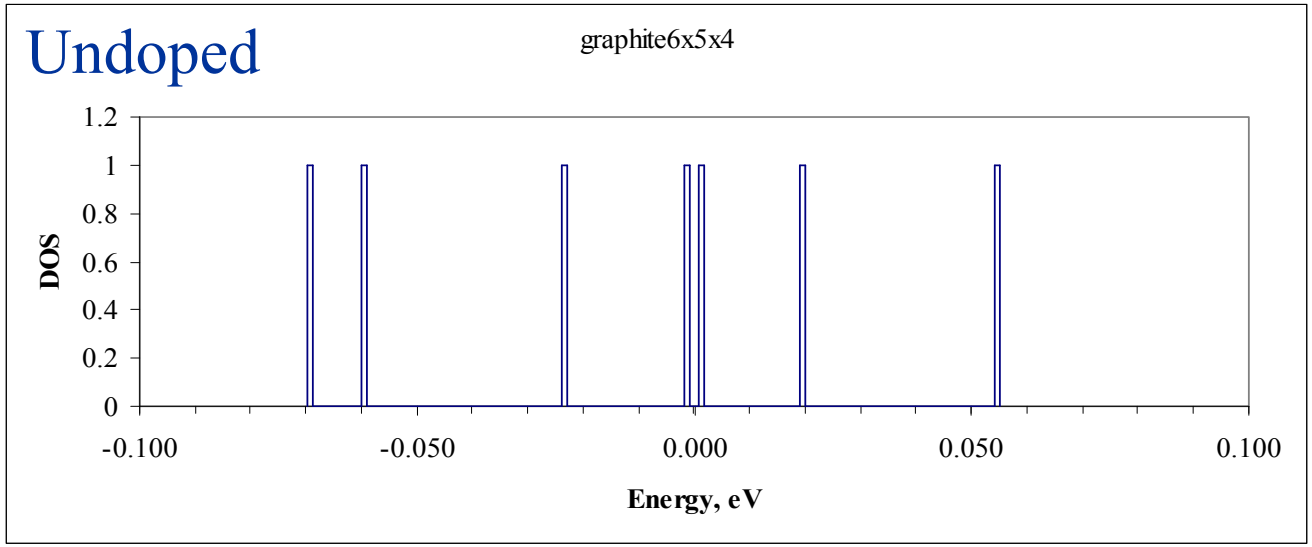
Energy levels for pristine and boron substituted nanographite particles with four layers of graphene sheets.



Structure of 4-layer nanographite particles with and without boron substitutions (filled black circles).

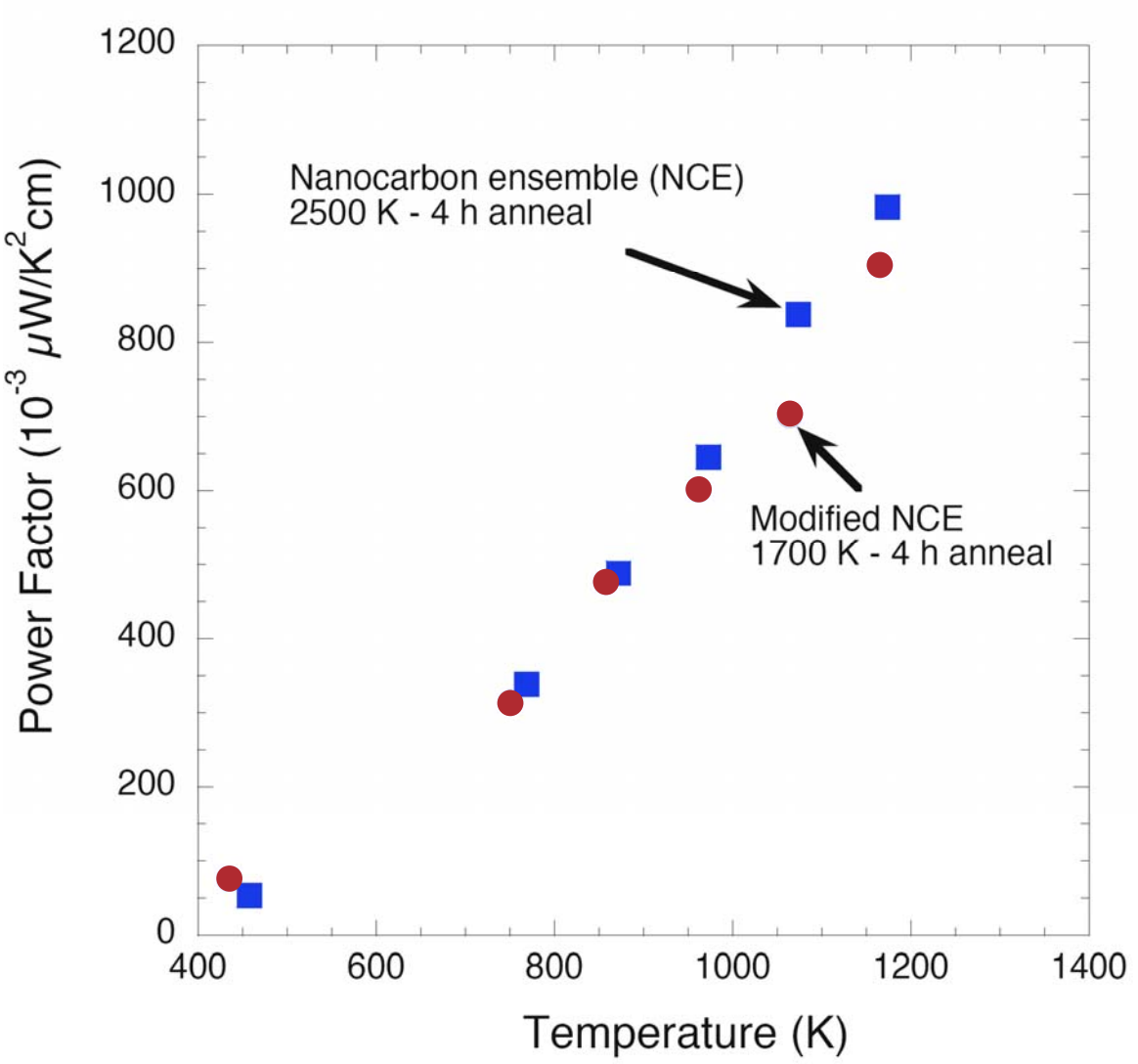
The effect of Boron Substitution on the DOS near the Fermi level of Nanographite Crystallites of Four Stacked Graphene Sheets.





Superposition of Five Crystallites each with a different configuration of two boron atoms substituted for two carbon atoms in a 96 carbon atoms graphene sheets.

Results & Progress



- **Modified NCE has the same PF after 1700K anneal as the NCE after 2500K.**

- **We expect that the PF of the modified NCE will be strongly enhanced after 2500K anneal.**

Summary

- **Bulk boron doped nanocarbon ensembles based on the concept of strongly enhanced electronic configurational entropy have been shown to exhibit promising TE properties.**

- **During the last year, power factors have been increased 20 to 40 fold over previous results primarily by high temperature annealing procedures which increases both the Seebeck coefficient and the electrical conductivity.**

Summary (2)

- The thermal conductivity of the nanoensembles is in the 10^{-2} W/cmK range.

- Future work is primarily aimed at increasing the Seebeck coefficient by the exploitation of compositional changes augmented by new annealing/quench techniques.

Acknowledgements

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M. Xie

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