Diamond Based TE Materials

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Project ID #

PM032

Overview

Timeline

- **Start- Oct 2007**
- **Continuing Development Program**
- **Progressive Series of Optimization Steps**

Budget

- **Funding received for FY08 500K**
- **Funding received for FY09 400K**
- **Funding received for FY10 100K**

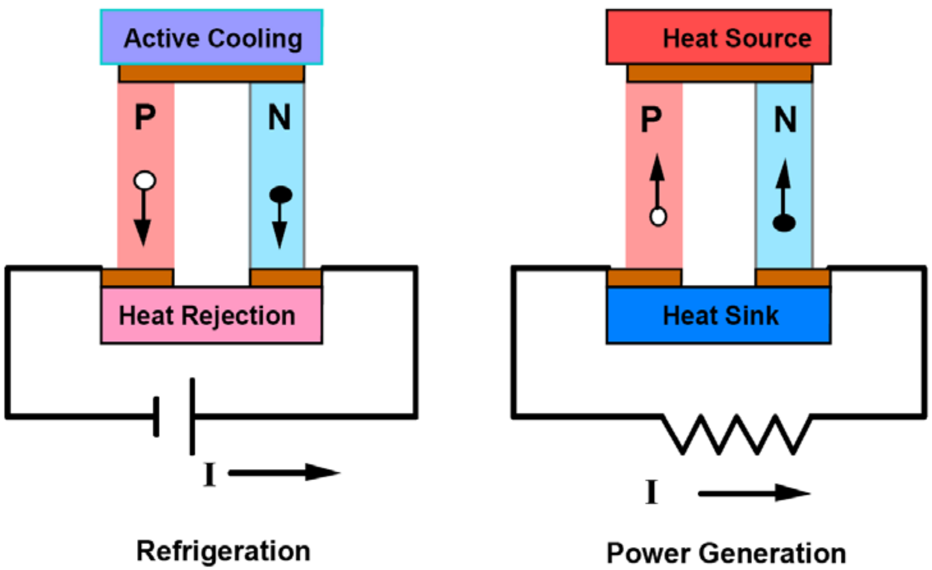
Partners

- **DOE/BES/Materials Science**
- **Michigan Technological University**
  (Dept. of Physics)
- **ONERA-CNRS, Paris, France**
  (HRTEM, HREELS, MWRaman)
- **ORNL**
  (Thermal Conductivity Measurements)
- **Naval Surface Weapon Research Center**
  (High Temperature Annealing)
- **Aegis Technology**
  (SBIR Pending)
- ***Laird Tech Center***

Barriers

- **Need higher ZT materials operating at high temperatures**
- **Must be cost effective**
- **Must be manufacturable in bulk amounts and durable**
- **Must be mechanically and thermally stable**

$$ZT=\sigma S^2 T/\kappa$$



Relevance

- High-efficiency thermoelectrics can be used to recover 3-10% of the waste heat from vehicles, thereby increasing fuel efficiency.
- If substantial increases in ZT can be achieved these materials would also lend themselves to applications such solar thermal energy conversion

Objective

- Create a new class of high-efficiency, high–temperature bulk, environmentally friendly, thermoelectric materials based on highly entropic nanocarbon ensembles.

Milestones

- **2008 - Proof of Principle**

  Bulk, thermally and mechanically stable p-type nanocarbon ensembles were successfully synthetized

  (D. Gruen, P. Bruno, M. Xie, APL 2008, 92 (143118))

- **2009 – 20 to 40 fold increase of Power Factor to 1 $\mu W/K^2cm$ after equilibrium annealing at 2500K**

  (D. Gruen, P. Bruno, R. Arenal, J. Routbort, D. Singh, M. Xie, J. Appl. Phys. 2009, 105, 7, (073710))

Milestones cont.

- **2009 – Density functional calculations show that boron doping creates a high density of states within thermal energies of the Fermi level**

  (P. Redfern, D. Gruen, L. Curtiss, Chem. Phys. Lett., Volume 471, Issues 4-6, March 2009, Pages 264-268)

- **2010 – Further increase in Power Factor by quench annealing**

  (M. Xie, C.H. Lee, J.Wang, Y.K.Yap, P.Bruno, D. Gruen, D. Singh, J. Routbort in press on Review of Scientific Instruments 2010)

Approach

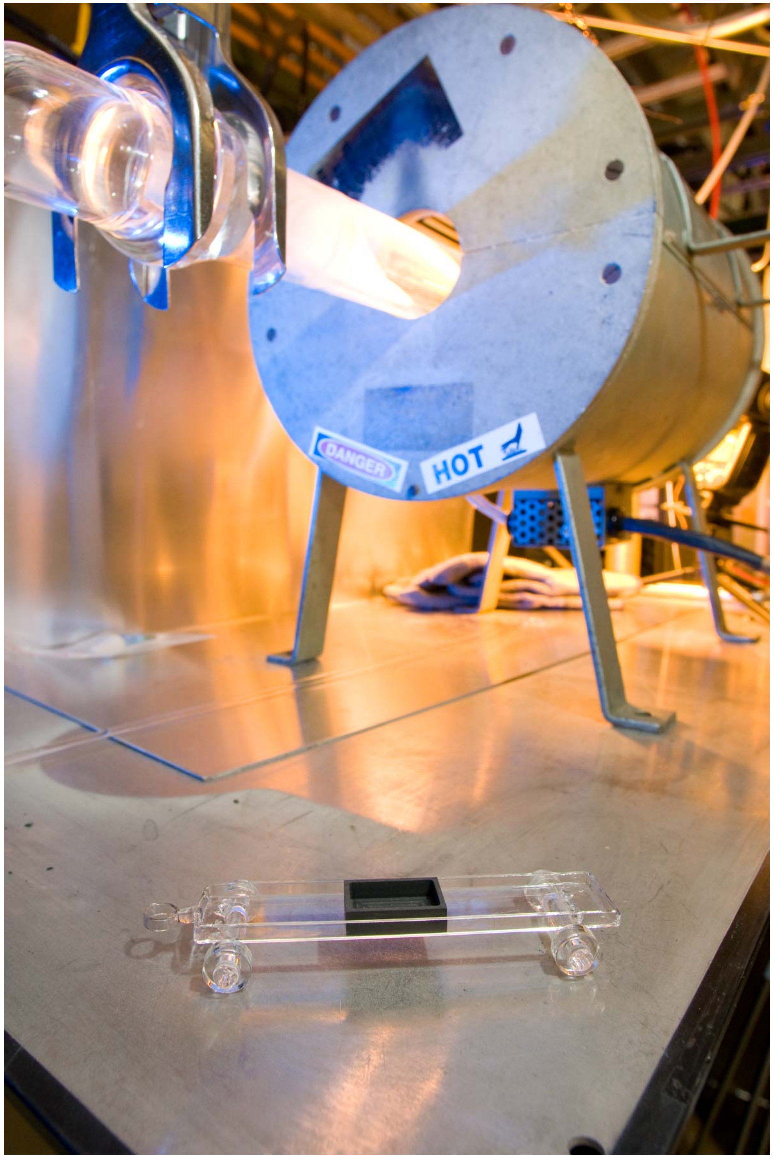
The search for a new class of potentially high ZT materials focuses on the following characteristics:

- **Preservation of nano-crystallinity at high temperatures**
- **Potential for high electronic entropy**
- **Potential for p and n-type doping**
- **Not resource limited**
- **Environmentally benign**
- **Scalable fabrication, low cost production**

Nanocarbons have been found to possess all the above properties **and have been chosen as a model system on which to study thermoelectric performance. In addition they lend themselves to**

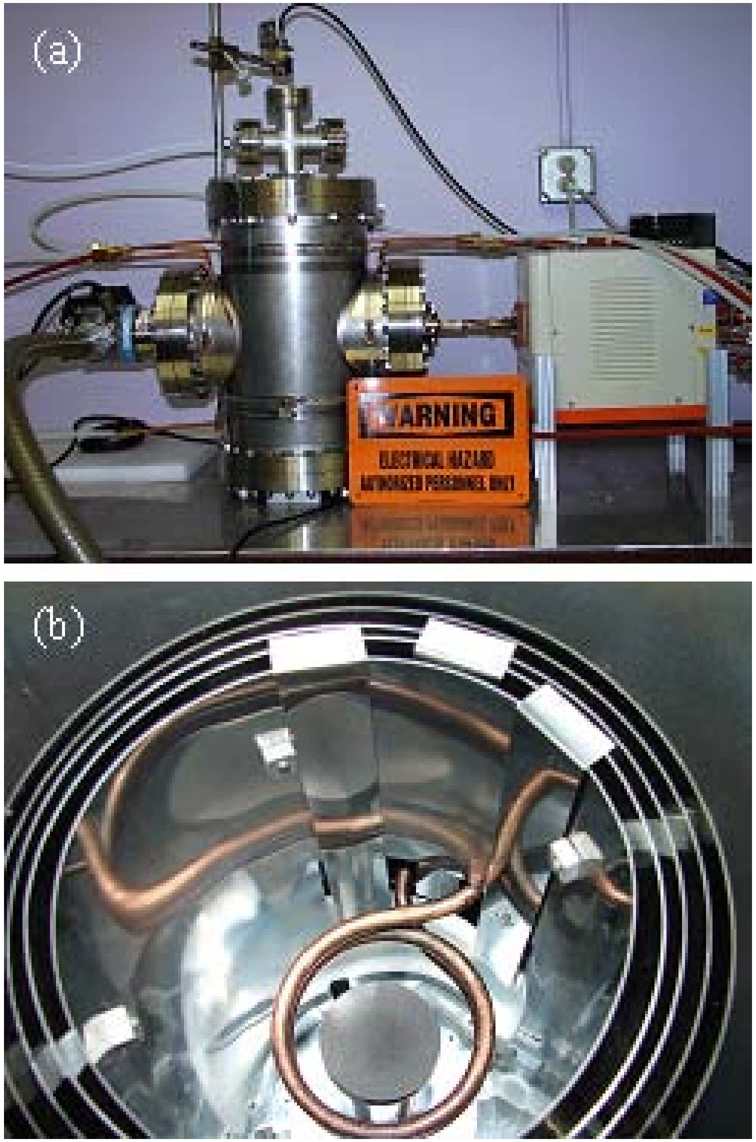
- **Rigorous density functional theoretical calculations.**

Technical Accomplishments



In-house furnace equipped with quartz tube + trolley for the preparation of the nanocarbon ensembles

Technical Accomplishments



Induction furnace

- Annealing up to 2400K
- Helium Quenching capabilities
- Highly reliable over prolonged periods of heating.
- Less than 1/3 the cost of commercial graphite or induction furnaces.

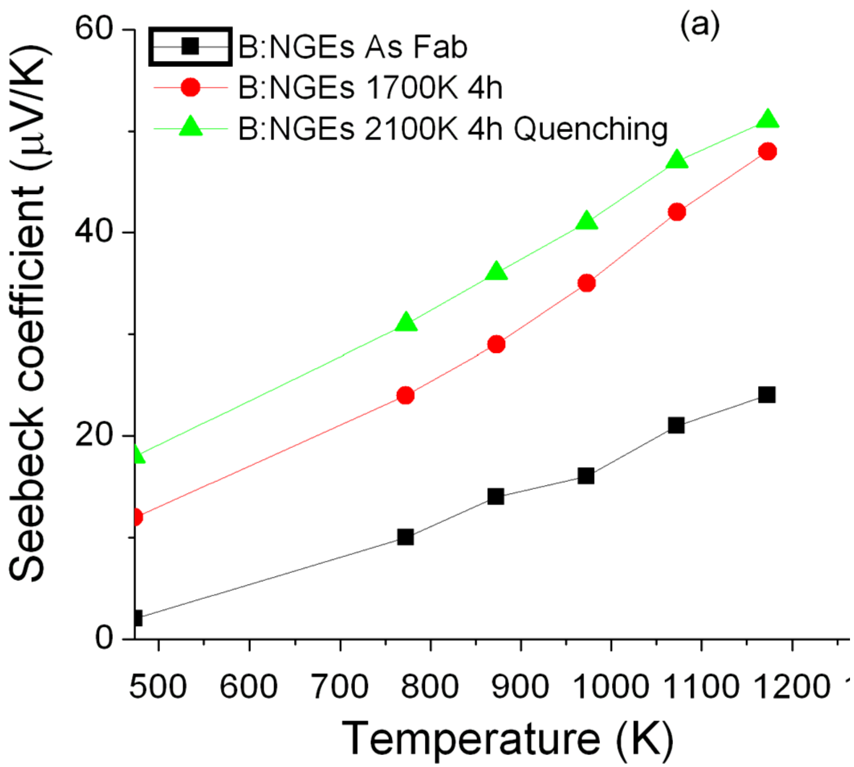
Technical Accomplishments

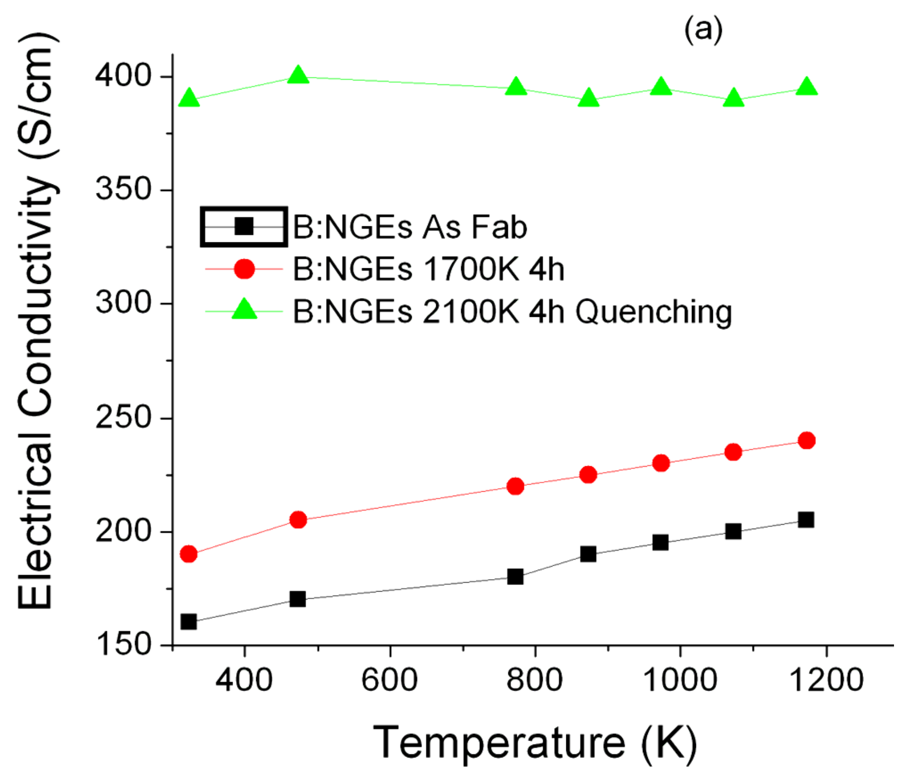
In-house apparatus for measuring Seebeck coefficient and electrical conductivity on the nano-ensembles

Results & Progress

Seebeck Coeff and Electrical cond.: effect of quenching on the doped NCE's

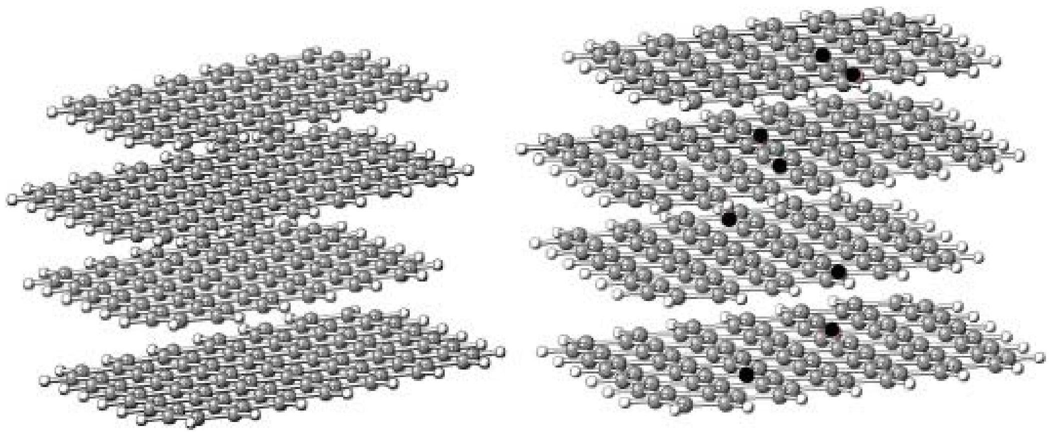
FY10





- **Both Seebeck coefficients and electrical conductivities of boron doped NCE increase monotonically temperature after induction annealing followed by quenching.**

Results/Theory



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

Results from DFTB calculations.

- DF calculations indicate that boron substitution leads to low spin nanographene sheets, unlike the all carbon systems. This implies that boron substitution in nanographite lowers the Fermi level and creates holes in the valence band.
- Boron Substitution on the 4-layer NG structure results in the creation of ‘holes’ at the top of the valence band by the electron deficient borons. The large number of empty states as compared to nanographite may account for the good thermoelectric properties that have been observed in boron-doped nanographite.

Future Work

- **Increase Seebeck Coefficient**

✓ **Modification of nano-ensemble composition by inclusion of high Seebeck coefficient nano-materials**

- **Increase the electrical conductivity**

✓ **Addition of small percentage of high electrical conductivity nano-materials (eg. metal nanostructured materials) to the NCE chemical composition**

- **Decrease the thermal conductivity**

✓ **Control of density and porosity of the compacts through variations in the synthesis process (i.e. exploring the SPS sintering process)**

- **Extend theoretical calculations**

✓ **Development of transport theory of nanoporous thermoelectric nano-ensembles**

Summary

- **Bulk boron doped nanocarbon ensembles based on the concept of strongly enhanced electronic configurational entropy have been shown to exhibit promising TE properties.**
- **Power factors, already increased in the last 2 years of 20 to 40 fold over previous results primarily by simply high temperature annealing procedures, got comparable values after 2100K anneals in the induction furnace followed by quenching.**
- **The thermal conductivity of the nanoensembles has been kept in the 10^{-2} W/cmK range.**
- **Both Seebeck coefficients and electrical conductivities of boron doped nanocarbon ensembles increase monotonically with temperature after induction annealing followed by quenching.**
- **Future work is primarily aimed at increasing the Seebeck coefficient by the exploitation of compositional changes augmented by new sintering/annealing techniques.**

Acknowledgements

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Collaborators

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