"The Next Generation Solid State Power Conversion Materials "
Terry M. Tritt (PI), Clemson University
DOE-EPSCoR Implementation Program

1.) DOE award # and name of the recipient (Institution)

DOE-EPSCoR Implementation Program: Phase II
DOE Grant (#DE-FG02-04ER -46139)
Clemson University, Clemson, SC

2.) Project Title and name of the PI

"The Next Generation Solid State Power Conversion Materials "
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3.) Report Date: Oct, 20, 2011

Period Covered: May 2007 to August 2011 Final Report:*

Including approved one-year extension (due primarily to achieve cost sharing Commitments and student support on DOE support)

* However, I will focus on the period May 2009 – Aug 2011 since 2 reports have been submitted for work between May 2007 and May 2009

4,) A brief description of accomplishments and final status of program:

The status of the program is very strong. The influx of money from this DOE/EPSCoR Implementation Program has allowed us to establish some excellent facilities and infrastructure within the Phase I and throughout the Phase II of this program. In addition, we have had some significant scientific findings resulting from this program. Each of these topics will be discussed in detail below and are highlighted within the publications list in the productivity section. *During this four-year review period we published 90 Journal Papers that have been published: 2007-09 (48 papers) and 2009-2011 (42 papers shown herein). In addition, there were 14 editorials or review chapters published. There were 59 Invited Talks given at National and International Meetings or University Colloquium and one (1) patent awarded.*

Our DOE/EPSCoR Implementation Program was renewed for August of 2007. The budget renewal in the original proposal was for $690K for the second year as reported in this project report. This was an increase over the previous funding and we have been able to resume the research on the skutterudites and the half Heusler alloys. We were also able to have a strong outreach program with visiting scientists. We are "grandfathered" into a 100% cost sharing level even though the current level is at 0% cost sharing. The University and SC EPSCoR is cost sharing this program at almost 18% higher than was required by the Implementation program. Thus the cost sharing was approximately $1.18 of cost share funds for each $1 of DOE funds.

Infrastructure: Space & Renovations:

- In year 3 of our Phase II grant, the University has renovated additional research laboratories and the newly acquired space for the DOE program. The funds for the renovations are not part of the cost sharing but are in addition to any cost sharing that was committed. These renovations and upgrades have totaled over $40,000. This new space houses the new spark plasma sintering system purchased at the end of last year under Phase II funds. This system is fully operational and functioning very impressively. In the last year (2011) we had to have further renovations in order to house the melt spinner and a specially vibration isolated room for the SEM.

- We renovated approximately 800 sq. ft. of additional laboratory space in Kinard Hall for the two new faculty members (Kang and He). This again is in addition to the already mentioned cost sharing.

Major Equipment Purchased: 2009-2011

- Significant equipment was purchased in Years 1-5 of this program since the goal of the program is to develop expertise, infrastructure and capabilities. Additional equipment was purchased in Year 6 and 7 due to some additional influx of stimulus money into the program. Some of this money was spent for the melt spinner and SEM. Of course, this extra stimulus money was cost shared by the University.

- *Spark Plasma Sintering (SPS) System:* ($220,000) from SPS Syntex which will allow us to grow highly densified polycrystalline materials, which can be grown to ≈ 99% of their theoretical density. The major piece of equipment purchased at the end of year one was a Spark Plasma Sintering (SPS) System. *We have grown over 600 samples this past year with this system.* (This was purchased in late 2008 but I include it here for reference.)

- *Optical Floating Zone Furnace:* ($190,000)
In spring of 2009 we submitted a purchase order for this furnace as part of the startup packages shared by two of the new faculty members, Dr.. He and Dr. Kang, for the growth of high quality oxide materials. The acquirement of optical floating zone system will significantly enhance the capability of synthesizing high temperature materials at Clemson University, such as the Oxide and half-Heusler materials with thermoelectric potential, and, the high T_c superconductors. The system can reach a maximum temperature ~ 2000-2200 °C to grow large size high quality single crystal without crucible, and it comes with a limited capability of synthesis under pressured gas.

- *Triple Grating Raman Spectrometer:* ($100,000)
  In spring of 2009 we submitted a purchase order for this equipment for Dr. Rao's group. The detection of low frequency Raman-active phonons or the rattler vibrational modes is challenging and warrants a triple grating Raman spectrometer. A comparative Raman study of low frequency rattling vibrations of the "guest" atoms inside the "cages" can help us identify which guest atom are more effective in reducing the lattice thermal conductivity. Total cost $105,000. It was installed and became functional in this reporting period.

- *Buhler Melt Spinner:* ($160,000)
  In January of 2010 we submitted a purchase order for this equipment for Dr. Tritt's group. It takes six months for the company to build the system. It will allow us to prepare melt-spun ribbons as precursor materials for the SPS. It will arrive at the end of June in Clemson. Dr. Tritt and a student are scheduled to go to Germany for training June 19-25, 2010.

- *Ball Mill Equipment:* ($50,000)
  In spring of 2010 we submitted a purchase order for this equipment for Dr. Tritt's group. This will allow us to ball mill powders and the melt spun ribbons as precursor materials for the SPS system and process. This was an addition due to the added increase we got last year.

- *Hitachi 3400 Scanning Electron Microscope* ($170K) with Composition Determination EDX Capabilities. This equipment was purchased primarily with University Cost Share funds. Our work was requiring us to spend a tremendous amount of time at the off campus SEM and Microscopy facilities at the (advanced Material Research Laboratory) AMRL, approximately 8 miles from the central campus. This Hitachi 3400 SEM system will greatly enhance our productivity and capabilities.

  These last three pieces of equipment were delayed and this part of the reason we asked for and received a one year no-cost extension from the DOE.

Progress Against Schedule/Milestones stated in DOE/EPSCoR Proposal:

Significant Findings/Events/Accomplishments:

The DOE/EPSCoR Implementation Program at Clemson University has made significant progress with respect to our schedule for Phase II. Our most significant accomplishments had to do with the growth and synthesis of thermoelectric nano-materials and the incorporation of these nanostructures into a bulk composite using the spark plasma sintering (SPS) system. We have successfully grown state-of-the-art TE materials, Bi_2Te_3, using hydrothermal techniques, wherein we grow the materials directly onto the Bi_2Te_3powders and then they are compacted with the SPS. Thus, the nanolayers are at the grain boundaries. We call this technique grain boundary engineering. We have utilized hydrothermal synthesis in our labs in order to *in situ* synthesize initial bulk hybrid thermoelectric materials of PbTe and Bi_2Te_3. These are comprised of a matrix of bulk TE materials with nano-scale materials embedded within the composite. We have observed encouraging results with respect to the thermal conductivity, which showed reductions of ≈ 30% with the inclusion of the nano-particles. We have recently developed a nano-coating technique and have applied it to small particles of thermoelectric materials. We have resumed the work on the skutterdites and looked at a double and triple filled system with In and Yb. The results were very favorable and led to several publications. We have found that the inclusion of small amounts of selected secondary phases can be very beneficial to achieving higher performance materials.

We also are continuing a very active collaboration with Wuhan University of Technology, which has proven to be very fruitful. One of their students (Wenjie Xie) is working in Tritt's group the past two years. We have found that it is possible to nucleate samml nanocrystalline regions or nano-dots with Bi_2Te_3 materials via a melt spinning technique. These ribbons are then ground and re-solidified with the rapid (few minutes) SPS sintering system. Prof. Kang has performed some very nice neutron diffraction work in trying to resolve the phonon density of states in the p-type Bi_2Te_3 materials. We are also seeing some very promising properties in our work on multiple filled skutterudites.

Last year we set forward a list Plans and Timetable for Phase II. We have accomplished each of these in the past year. See Below.

Discussion of Plans/Timetable for 2009-10: *(Essentially all Accomplished*!!)*

The DOE/EPSCoR Implementation Program began its second year in September of 2005. During the thirdyear we planned to do the following and all were accomplished:

Year 3-4: 2009 –2011:

- Purchase Spark Plasma Sintering (SPS) System –*(Installed during Summer of 2008)*
- We have filled all three Faculty Hires in Physics (Materials Physicist-(Dr. He), Neutron Scattering Expertise, (Dr. Kang) and Theory (Dr. Tewari).
- Extensive Use of SPS System – *We synthesized over 600 samples using the SPS system since it was installed last in Summer of 2008*
- Integrate New Lab Space into Cluster for new equipment & new hires.
- We put out a bid for the melt spinning system and it will arrive in June 2010

Major Hurdles or Surprises: ***(For 2009-10)***

- Kinard Laboratory underwent a major HVAC upgrade, which has affected our progress on purchases and space, especially for the new faculty members, Dr. Jian He and Dr. Hye Jung Kang. This renovation closed our labs in Kinard from Sept. 30, 2008 until late March of 2009. We had to take some of our measurement equipment to Jordan Hall but were somewhat limited in our low temperature measurements. This will likely affect our publications and productivity next year. It also delayed the purchase of the optical furnace. It came in this reporting period and is fully operational.
  We had delays in the last two pieces of equipment (melt spinner and ball milling equipment) and this part of the reason we asked for and received a one year no-cost extension from the DOE. We needed to support students to get the systems operational and results forthcoming from this new equipment.

Significant Findings/Events/Accomplishments:

<u>Terry M. Tritt (PI) and Jian He (Co-PI)</u>

Prof. Tritt has served as the lead PI for the project. He worked with the other Co-PI's to identify additional systems of materials of interest to the project. He performed oversight and was responsible for the electrical and thermal transport measurements and other characterization of the materials synthesized for the project. He has coordinated the reporting and management of the team's efforts. He oversees the nanocomposite TE materials research effort along with that of other bulk materials: skutterudites, half-Heusler alloys and Zintl phase materials. Dr. Tritt works very closely with the new hire (Dr. Jian He) who is an expert in the synthesis of these materials. Dr. Tritt and Dr. Jian He are responsible for the spark plasma sintering that the group is doing.

- Prepared bulk samples using Spark Plasma Sintering (SPS). The SPS has become a centerpiece of our research over the last year and was a major equipment purchase.
- Perform hydrothermal synthesis of nanostructures of TE materials, specifically $CoSb_3$ and Bi_2Te_3, materials.
- Prepare composite samples of bulk TE materials with nanostructures incorporated into bulk composite.
- Fully evaluate the electrical and thermal transport properties of the materials that we have synthesized over a broad range of temperature, from 10 K up to temperatures as high as 1400 K, unless the materials decompose.
- Preparation and characterization of (Ce, In and Yb) multiple-filled $CoSb_3$-based skutterudite thermoelectric materials; resulting in a $ZT \approx 1.4$ at around 700K.
- Preparation and characterization of $FeSb_3$-based skutterudite thermoelectric materials;

- Preparation and characterization of both p-type and n-type Bi_2Te_3 nanocomposties by incorporating carbon nanostructures.
- Our collaboration with Wuhan University of Technology in Wuhan China: p-type $Bi_{0.5}Sb_{1.5}Te_3$ samples were made by ZM (zone melted) and MS (melt spinning) methods are densified using the Spark Plasma Sintering (SPS) process for bulk samples, ZM-SPS and MS-SPS, respectively. The rapid SPS process largely preserves the multiscale structures in the ribbon of MS sample, especially those at the nanometer scale. Physical property measurements show that the sample made by MS-SPS has substantially lower thermal conductivity compared to the sample made by traditional ZM-SPS, while it has little effect on the electrical conductivity. As a result, it raised the ZT value to 1.56 at room temperature, a ~ 40 % improvement.
- Attended various national and international meetings and presented scientific results and exchange at these meetings.
- Conference Organizer for PACRIM 8 Symposium in May 2009 focused on New Thermoelectric Materials and Processing.
- Conference Organizer for 2011 E-MRS Symposium on Energy with a Thermoelectrics Symposium (4 full days) in Nice, France.
- Dr. Tritt gave an extensive number of Invited talks at Universities and Conferences this year. He wrote several review articles over the last two years. (See Productivity at the end of report)
- Participated in Student Exchange program and collaboration with Wuhan University of Technology.

<u>Prof. Apparao Rao (co-PI)</u>:

Bi Nanowires

During Phase I, we had developed a pulsed laser vaporization technique to prepare small diameter (~ 10 nm) bismuth nanowires. The high resolution transmission electron microscopy (HRTEM) studies of our nanorods showed crystalline Bi core oriented along <012> direction. The HRTEM images also showed evidence for the presence of a thin native Bi_2O_3 layer around individual nanorods. Room temperature Fourier Transform Infrared (FTIR) spectroscopy showed clear signature for quantum confinement in our bismuth nanowires since the infrared absorption peaks (assigned to the electronic transition from the L point to the T point in the bismuth Brillouin zone) exhibited a $1/d^2$ dependence where d is the dominant nanowire diameter [1].

In Phase II, as a further check on the assignment of the FTIR absorption peaks to the L-T point transitions, we have conducted detailed low temperature FTIR absorption studies (77 K) of bismuth nanowires with different dominant diameters. We find a discrepancy between our temperature dependent FTIR absorption data and the expected dependence of the $E_{L\text{-}T}$ transition energies [2]. In this model of the L-T transition [2], the L-point band structure, in contrast to the T-point, has strong temperature dependence above 80 K due to the coupling between the non-parabolic L-point valence and conduction bands. The L-point bandgap and L-T band overlap have shown significant temperature dependence in bulk Bismuth [3]. Using the empirical relationships determined for these parameters as a function of temperature, we can expand on the model presented in Levin *et al.* [2] and predict the energy of the transition over a range of temperatures from room temperature down to 80 K. For transitions from any of the three L-points, three distinct peaks have been observed at room temperature and attributed to this indirect transition. The transition energy,, should have magnitude in the bulk equal to the bulk Bismuth L-point bandgap, E_{gL}, plus the overlap between the L-point conduction band and the T-point valence band, E_0. Quantum confinement will change the band edge as a function of wire diameter parabolically for the T-point and non-parabolically for the L-point, as is described in Ref 2. The result is the following expression for the transition energy as a function of diameter,

$$E_{L-T}(d) = E_{gL} + E_0 - \frac{E_{gL}}{2}\left(1 - \sqrt{1 + \frac{h^2}{E_{gL} m_L m_0 d^2}}\right) - \frac{h^2}{4 m_T m_0 d^2} \qquad (1)$$

with E_{gL}, E_0, and m_L, are the L-point bandgap, L-T band overlap, and L-point effective mass, respectively. m_0 and m_T are the electron mass and T-point effective mass respectively, where $m_T = 0.0835\ m_0$. For the $L(A)$-T transition, we expect a downshift of the transition frequency on the order of several hundred wavenumbers for nanowires with diameter ~10 nm as temperature decreases from 300 K to 80 K.

CdS Nanowires

There has been a considerable interest in semiconducting nanowires in recent years due to their importance in the development of electronic and photonic devices. The increased interest in such materials arises mainly from their bandgap tunability; the bandgap increases upon decreasing the size as a result of quantum confinement. Development of such materials with confined dimensions having desired optical and electronic properties is always a challenging issue in making nanoscale devices. One of the extensively investigated materials in this regard is the wide direct bandgap II–VI semiconductor, cadmium sulfide (CdS). While the thermoelectric properties of bulk CdS resemble that of pristine multi-walled carbon nanotubes, the thermoelectric properties of nanoscale CdS have not been reported in the literature. We have used the pulsed laser vaporization method developed in Phase 1 for Bi nanorods to prepare CdS nanowires with diameters in the range from 50 to 100 nm and have studied their optical properties using photoacoustic, UV-Vis, Raman, and photoluminescence spectroscopy. The photoacoustic (PA) technique yielded clean spectra with a steeper absorption edge for as-prepared opaque semiconducting CdS nanowires when compared to the corresponding conventional optical absorption spectra. The PA signal intensity was also significantly higher for nanowires. The Raman spectrum using an ecitation wavelength λ_{ex} = 514.5 nm revealed increased exciton–longitudinal-optical-phonon coupling. The appearance of a narrow photoluminescence peak at 491nm (FWHM ~9 nm) and the absence of emission above 500 nm demonstrate the high quality of nanowires. High-resolution transmission electron microscopy showed excellent ordering of the atoms in the [001] planes perpendicular to the growth direction. These results have been published in [4, 5].

Tuning the Electrical and Thermal Properties of Carbon Nanotubes using Spark Plasma Sintering method

Millimeter long, vertically oriented, multiwall carbon nanotube (MWCNT) arrays were pre-aligned and densified using a spark plasma sintering (SPS) technique to form aligned MWCNT bulk samples. The combined results of x-ray powder diffraction, Raman spectroscopy, scanning electron microscopy and high resolution transmission electron microscopy show that the MWCNTs largely retain their orientation and individual tubular morphology in the aligned MWCNT bulk samples, and that the SPS process induces inter- and intra-tubular bonding as well as graphene formation. In view of the one-dimensional nature of individual MWCNTs, it is particularly noteworthy that the transverse electrical resistivity ρ_T is slightly lower than the longitudinal resistivity ρ_L, whereas the transverse thermal conductivity κ_T is ~ 50% of κ_L. The room temperature κ_L is ~ 31 W/(m-K), one of the highest reported in MWCNT bulk samples. In addition, the thermopower measurements show anisotropy and features of phonon drag. These results have been published in [6].

We also find that the electrical and thermal connectivity in multiwalled carbon nanotube buckypaper can be tuned using a spark plasma sintering (SPS) technique. It is found that elevated SPS temperatures promote the formation of inter-tube connections and consequently impact the electrical resistivity, thermoelectric power and thermal conductivity of the buckypaper. In particular, the magnitude of the electrical resistivity as a function of SPS temperature exhibits a percolative behavior while the low temperature lattice thermal conductivity shows a crossover in the sample dimensionality. The results are discussed in terms of the quasi-one-dimensional metallic nature of multiwalled carbon nanotubes, the packing density and the electron-phonon coupling in [7].

REFERENCES:

1) "Laser-assisted Synthesis and Optical Properties of Bi nanorods", Jason Reppert, Rahul Rao, Malcolm Skove, Jian He, Matthew Craps, Terry M. Tritt and A.M. Rao, *Chem. Phys. Lett.* 442, 334-338 (2007).

2) A. J. Levin *et al*., Phys. Rev. B **79**, 165117 (2009).

3) M. P. Vecchi and M. S. Dresselhaus, Phys. Rev. B **10**, 771 (1974).

4) N. Kuthirummal, J. Reppert, B. Diehl, and A. M. Rao, *Applied Optics* **48**, 2842 (2009).

5) V. S. Muthukumar, J. Reppert, C. S Sandeep, S. Sivaramakrishnan, N. Kuthirummal, S.Siva Sankara Sai, K. Venataramaniah, R. Philip, and A. M. Rao, *Optics Commun.* (in press).
6) K. Yang, J. He, Z. Su, J. B. Reppert, M. J. Skove, T. M. Tritt, and A. M. Rao, *Carbon* **48**, 756 (2010).
7) Keqin Yang, Jian He, Pooja Puneet, Zhe Su, Malcolm J Skove, Jay Gaillard, Terry M Tritt and Apparao M Rao, Journal of Physics: Condensed Matter (in press).

Prof. Murray Daw (co-PI): (Theory)

Prof. Daw leads the computational and modeling efforts of the project at Clemson. He will be responsible for identifying many of the materials as potential TE materials and perform the subsequent theoretical modeling and band structure calculations for these materials. Important progress has been made in the development of the theory of vibrational mode lifetimes and lattice thermal conductivity. The theory has been applied successfully to a simple model of anharmonic lattice vibrations. The early results indicate that an economical, low-order treatment of the theory is sufficient to obtain reliable results on mode lifetimes for the model.

Asst. Prof. Fivos Drymiotis (co-PI):

During the past year major emphasis was placed on the LAST compounds. Dr. Drymiotis and his students synthesized $(PbTe)_m(AgSbTe_2)$ for a large range of m in an effort to understand how the structure and thermoelectric behavior evolve as a function relative concentration.

The subject of the proposal emerged from results that were obtained while investigating techniques to lower the thermal conductivity of PbTe and LAST. Dr. Drymiotis discovered that solid solutions of Pb, Te, Ag and Se in a 1:1:1.9:1 molar ratio, give rise to what appears to be a single phase alloy which crystallizes in an fcc structure and have very low thermal conductivity. Recent investigation of the structure, using EDX, reveals the coexistence of two-phases (doped-PbTe and doped –β-Ag_2Te) with identical lattice parameters. The total thermal conductivity of the formed compound is remarkably low for a crystalline material, $\kappa_T < 0.6$ W/m-K at 675K, it is reproducible and in addition, the compound has good mechanical properties.

Dr Drymiotis is transferring most of his work to the NSF grant he received and he is transitioning off of the DOE EPSCoR grant and in fact received little support from the DOE grant this past year, except for the extensive use of the equipment and facilities developed under the DOE grant.

Assoc. Prof. Catalina Marinescu (co-PI): (Theory)

- We calculated the thermoelectric coefficients of a nanoparticle-doped semiconductor superlattice and studies their dependence on the nanoparticle parameters: width, barrier height, concentration. Based on the mechanism of selective scattering, we identified the most effective nanoparticle characteristics for improving the figure of merit of the superlattice in the transport regime parallel to the superlattice axis.
- We analyzed the existence of spin-dependent density fluctuations in semiconductor superlattices with spin-orbit interaction and analyzed their behavior under an applied temperature gradient, with an eye on obtaining spin-dependent thermoelectric phenomena.
- We are currently developing a Kubo-Green formalism for the study of electron transport under temperature gradients in semiconductor superlattice.

In a different research project, we focused on developing a Kubo-Green's function formalism of calculating the thermoelectric transport properties in systems with strong electron-electron interactions, such as the 2D layers involved in the superlattices discussed above.

Asst. Prof. Hye Jung Kang (co-PI): (Neutron Diffraction – New Hire: 9-08)

- Inelastic neutron scattering study on Phonon density of states of *p*-type thermoelectric material $Bi_{0.48}Sb_{1.52}Te_3$.
- Small angle neutron scattering on multiscale microstructures in melt spun $Bi_{0.48}Sb_{1.52}Te_3$.
- Inelastic neutron scattering study on Phonon density of states of dual element filled $CoSb_3$ skutterudite.
- Successful installation and test of optical image furnace at the Physic department
- Synthesis of powder samples of dual charge doped high T_c cuprate $Nd_{2-x-y}Sr_xCe_yCuO_4$ and neutron diffraction to study the crystal structure as a function of doping.
- Synthesis of powder samples of electron doped high T_c cuprate $Pr_{1-x}LaCe_xCuO_4$ for the study of high pressure effect on superconductivity.

Asst. Prof. Sumanta Tewari (co-PI): (Theory – New Hire: 8-08)

Dr. Tewari looked into the possible origin of an anomalously large Nernst signal in the so-called pseudo-gap phase of the cuprate high temperature superconductors. The pseudo-gap phase is the phase of the cuprates above their superconducting critical temperature Tc. Understanding this phase, from which the superconductivity arises by lowering the temperature, is thought to hold the key to the physics of the cuprate superconductors.

He studied the possibility of a remarkable, spontaneous, thermoelectric effect in single and bilayer grapheme. Graphene is just a single, isolated, carbon layer of graphite and a strictly two-dimensional material. Because of the hexagonal crystal lattice, the tight binding Hamiltonian of grapheme has two Dirac points, that is, points in the Brillouin zone where the valence and the conduction bands touch. Graphene quasiparticles, therefore, realize the theorists' dream of 2D Dirac quasiparticles in the laboratory. It has some of the largest mobilities of the quasiparticles ever realized, and hence, is potentially extremely important for semiconductor applications. We showed that the graphene quasiparticles, in the case when the sample is artificially gapped (which is necessary for device applications), acquire a non-trivial Berry curvature.

5.) **A list of Papers:** (already published, in press, submitted) in which DOE support is acknowledged. These include 2009, 2010 and 2011 papers since our last review.

DOE Implementation Program
Productivity 2009-2010
(Since Last Review: May 15, 2009 to Aug. 15, 2011)

2009-2011 Editorials: (1 this period)

Journal of Materials Research: Special Focused Issue:
Advances in Thermoelectric Materials
Terry M. Tritt and Harold Boettner (Guest Editors)
Volume **26**, Issue (15), pp 1743-2006, August 2011

2009-2011 Review Chapters: (9 this period)

Thermal-to-Electrical Energy Conversion from the Nanotechnology Perspective,
J. He and Terry M. Tritt, Chapter **3**, 47-77,
"Nanotechnology for the Energy Challenge"
edited by Javier Garcia Martinez, Wiley-VCH,
ISBN 978-3-527-32401-9 (2010).

HIGH TEMPERATURE SEEBECK COEFFICIENT METROLOGY
J. Martin, T. Tritt and C. Uher
Applied Physics Reviews, Jour. Appl. Phys. **108**, 121101 (2010)

Thermoelectric Applications in the United States:
K. Koumoto, R. Funahashi and T. M. Tritt
Japanese Handbook of Thermoelectrics, Invited Review Chapter
NTS Inc., 2-16-16, Yushima, Bunkyo-ku, Tokyo, Japan (http://www.nts-book.co.jp/)

"Oxide Thermoelectrics: the Challenges, Progress and Outlook", J. He, Y. Liu and R. Funahashi, J. Mater. Res. **26**, 1762 (2011).

Improving Thermoelectric Performance of Pulverized p-type Bi_2Te_3 via a Grain Boundary Engineering Approach
Zhe Su, Jian He, Xiaohua Ji, Nick Gothard, and Terry M. Tritt
Science of Advanced Materials. *A Special Issue on Advanced Thermoelectric Materials and Devices*, Sci. Adv. Mater. 3, 596-601 (2011)

Terry M. Tritt, Xinfeng Tang, Q. Zhang and Wenjie Xie
MRS and Cambridge University Press (CUP) Chapter 22,
Textbook: *Fundamentals of Materials for Energy and Environmental Sustainability*.
Edited by David Ginley and Daven Cahen
Accepted and in press

Thermoelectric Materials Phenomena, Applications and Measurements
Annual Rev. Mats Research (July 2011) Vol. **41,** pp. 433-448**,** Terry M. Tritt,

"Tuning electrical properties of Carbon Nanotubes via Spark Plasma Sintering", Keqin Yang, Dale Hitchcock, Jian He and A. M. Rao, book chapter for Springer titled Encyclopedia of Nanotechnology (in press).

"Nonlinear Optical Absorption and Scattering Studies in Organic and Inorganic Nanostructures", Sai Muthukumar V, Ramakrishna Podila, Benoy Anand, S. Siva Sankara Sai, K. Venkataramaniah, Reji Philip, and Apparao M. Rao, book chapter for Springer titled Encyclopedia of Nanotechnology (in press).

2009-11 Journal Publications**: (42 Total published in this period)**

Thermoelectric properties of (In,Yb) double-filled $CoSb_3$ Skutterudite
J.Y. Peng, P.N. Alboni, J. He, B. Zhang, T. Holgate, Z. Su, N. Gothard
and T.M. Tritt
Proceedings of ICT 2008 Corvalis Oregon, Aug, 3-7, 2008, (July 2009 Special Issue)
Journal of Elec. Mats., **38**, 981 (2009)

New Arsenides for High Temperature Thermoelectric Applications
Hong Xu[1], Tim Holgate[2], Terry M. Tritt[2], and Holger Kleinke[1]
Proceedings of ICT 2008 Corvalis Oregon, Aug, 3-7, 2008, (July 2009 Special Issue)
Journal of Elec. Mats., **38**, 1030 (2009)

Thermoelectric Properties Of Zintl Compound $YbZn_2Sb_2$ With Mn Substitution In Anionic Framework
T.J. Zhu, C. Yu, J. He, S.N. Zhang, X.B. Zhao and Terry M. Tritt
Proceedings of ICT 2008 Corvalis Oregon, Aug, 3-7, 2008, (July 2009 Special Issue)
Journal of Elec. Mats., **38**, 1068 (2009)

Thermoelectric properties and the microstructure study of TAGS-x
S.N. Zhang, J. He, X.H. Ji, Z. Su, S.H. Yang, T.J. Zhu, X.B. Zhao and T.M. Tritt
Proceedings of ICT 2008 Corvalis Oregon, Aug, 3-7, 2008, (July 2009 Special Issue)
Journal of Elec. Mats., **7**, 1142 (2009)

Thermoelectric properties and electronic structure calculations of low thermal conductivity Zintl phase series $M_{16}X_{11}$ (M=Ca and Yb; X= Sb and Bi)
V. Ponnambalam, X. Gao, S. Lindsey, P. Alboni, S. Zhe, B, Zhang, F. Drymiotis, M. S. Daw and Terry M. Tritt
Jour. of Alloys and Compounds, **484**, 80-85 **(2009)**

High Thermoelectric Performance BiSbTe Alloy with Unique Low-Dimensional Structure
Wenjie Xie, Xinfeng Tang, Yonggao Yan, Qingjie Zhang, and Terry M. Tritt
Jour. of Appl. Phys., **105**, 113713, (2009)

Synthesis and thermoelectric properties of (Ti,Zr,Hf)(Co,Pd)Sb half-Heusler compounds
Wenjie Xie, Song Zhu, Jian He, Shanyu Wang, Yonggao Yan, V. Ponnambalam, Xinfeng Tang, Qingjie Zhang, S. Joseph Poon and Terry Tritt
Journal of Physics D, **23**, 235407- (2009)

Glassy Thermal Conductivity in the 2-phase $Cu_xAg_{3-x}SbSeTe_2$ alloy and High-Temperature Thermoelectric Behavior.
F. Drymiotis, T. Drye, D. Rhodes, Q. Zhang, J. Lashey[*], Y. Wang, S. Cawthorne, B. Ma, S. Lindsey and T. Tritt.
Journal of Physics: Condensed Matter, **22,** 035801 (2010)

**Thermal conductivity reduction in fullerene-enriched p-type bismuth telluride composites*
N. Gothard, J.E. Spowart and T.M. Tritt,
Phys. Stat. Sol. A, **207**, No. 1, 157-162 (2010)
Editor's Feature Article, PSS-a Issue Cover

Effect of Processing Route on the Microstructure and Thermoelectric Properties of Bismuth Telluride-Based Alloys
N. Gothard, G. Wilks, T.M. Tritt, And J.E. Spowart
2009 ICT Meeting, Freiburg, Germany (April 24-30th, 2009)
Journal of Elec. Mats., **39,** p1909 (2010)

Tuning electrical and thermal connectivity in multiwalled carbon nanotube buckypaper
Keqin Yang, Jian He, Pooja Puneet, Zhe Su, Malcolm J. Skove, Jay Gaillard, Terry. M. Tritt and Apparao. M. Rao
Special Edition, Jour. of Cond. Matt. Physics **, 22,** 334215 (6pp) **(2010)**

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Probing lattice dynamics of $Cd_2Re_2O_7$ pyrochlore: Thermal transport and thermodynamics study
J. He*, D. Hitchcock, I. Bredeson, N. Hickman, Terry M. Tritt, and S. N. Zhang
Physical Review B (Condensed Matter and Materials Physics) Volume: 81 Issue: 13 Pages: 134302 (7 pp.) Published: 2 April 2010

Thermoelectric properties of $A_{0.05}Mo_3Sb_{5.4}Te_{1.6}$ (A = Mn, Fe, Co, Ni),
H. Xu, K. M. Kleinke, T. Holgate, D. Rossouw, G. Botton, T. M. Tritt, H. Kleinke,
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"Soft phonons and structural phase transition in superconducting Ba0.59K0.41BiO3," Kang, H. J., Lee, Y. S., Lynn, J. W., Shiryaev, S.V., and Barilo, S. N., *Physica C* **471**, 303 (2011).

Low Phonon Thermal Conductivity of layered $(Bi_2)_m$-$(Bi_2Te_3)_n$ Thermoelectric Alloys
P. A. Sharma, A. L. Lima Sharma, D. L. Medlin, A. M. Morales, N. Yang, M. Barney, J. He, F. Drymiotis, J. Turner, T. M. Tritt
Physical Review B, **83**, 235209 (**2011**)

Introduction to Advances in Thermoelectric Materials
Terry M. Tritt and Harold Boettner
Journal of Materials Research, **26**, (15) 1743 (2011)

Tuning the Thermoelectric Properties of Polycrystalline $FeSb_2$ by the In-situ Formation of InSb nanoinclusions
Song Zhu, Wenjie Xie, Jian He and Daniel Thompson, Yonggao Yan, Menghan Zhou and Terry M. Tritt [a)]
Journal of Materials Research: Special Focused Issue: Advances in Thermoelectric Materials, Journal of Materials Research, **26**, (15) 1894 (2011)

Investigation of the Sintering Pressure and Thermal Conductivity Anisotropy of Melt-spun Spark-plasma-sintered $(Bi,Sb)_2Te_3$ Thermoelectric Materials
Wenjie Xie, Jian He, Song Zhu, Tim Holgate[2], Shanyu Wang, Xinfeng Tang. Qingjie Zhang and Terry M. Tritt
Journal of Materials Research: Special Focused Issue: Advances in Thermoelectric Materials, Journal of Materials Research, **26**, (15) 1836 (2011)

Introduction of resonant states and enhancement of thermoelectric properties in half-Heusler alloys
J.W. Simonson, D. Wu, W. Xie T.M. Tritt, and S.J. Poon
Physical Review B, **83**, 235211 (2011)

Figure of Merit Enhancement in Nanocomposites formed via C_{60} Incorporation into Bismuth Telluride Alloys
N. Gothard, T.M. Tritt, and J.E. Spowart
Journal of Applied Physics, **110**, 021101 (2011)
Virtual Journal of Nanoscience

Enhanced Thermoelectric Figure-of-Merit of p-Type Half-Heuslers
Xiao Yan[†], Giri Joshi[†,‡], Weishu Liu[†], Yucheng Lan[†], Xiaowei Wang[‡], Hui Wang[†], Bed Poudel[‡], Jack William Simonson[§], Joseph Poon[§], Gang Chen[*], Z. F. Ren[*,†] and T.M. Tritt
Nano Lett., **2011**, *11* (2), pp 556–560 (2011)

High Seebeck coefficient $AMXP_2$ (A = Ca and Yb; M, X = Zn, Cu and Mn) Zintl Phosphides as high temperature thermoelectric materials
V. Ponnambalam, S. Lindsey, W. Xie, D. Thompson, F. Drymiotis, and Terry M. Tritt
Jour. Phys. D*: Appl. Phys.,* **44,** 155406 **(2011)**

High Temperature Thermoelectric Properties of Co_4Sb_{12} Based Skutterudites with Multiple Filler Atoms: $Ce_{0.1}In_xYb_yCo_4Sb_{12}$
Jennifer Graff, Song Zhu, Tim Holgate, Jiangying Peng, Jian He and Terry M. Tritt
Journal of Electronic Materials, Vol. 40, p.696 (**2011**)

2007-11 Patent Applications: (1 this period)

Patents

Convective Flow Chemical Vapor Deposition Growth Of Nanostructures

Terry M. Tritt, Bo Zhang and Jian He

US Pub. # 7,871,668 issued date January 18, 2011

2007-11 Invited Presentations: (59 Total)

Including National and International Symposia, University Colloquia and Special Workshops on Thermoelectric Materials Research

2007 (11 Invited Talks)
2009 (6 Invited Talks)
2009 (12 Invited Talks)
2010 (16 Invited Talks)
2011 (14 Invited Talks)

2009-11 Conference Presentations (Numerous Unpublished Conference Presentations):

6. A list of people working on the project: (2009 – 2011)
Graduate students, postdocs, visitors, etc.

Graduate Students, Support and Project Description,

Jason Reppert, (Full RA Support-100%): Graduated Ph.D.Fall of 2009
We will be synthesizing and measuring the TE properties of graphene. We will also by combining two synthesis techniques (PLD and CVD) to grow different heterostructured 1D materials (i.e. Si/SiGe and Bi/BiSb).
Jason Reppert selected as a Fellow of the Department of Energy for the 58th Lindau Meeting of Nobel Laureates and Students in Physics, Lindau, Germany, *June 2008*.

Sloan Lindsey, (Full RA Support-100%): Graduated MS Summer of 2011
Begin a study on Zintl phase materials, $Yb_{14}MnSb_{11}$ and its alloys using the newly acquired SPS system and Scanning Electron Microscopy. Participated in research studies as an exchange student at ZheJiang University in China exploring powder processing and sintering conditions on final thermoelectric properties. Addition of both insulating and conducting low solubility to insoluble nano inclusions may be examined.

Daniel Thompson, (Partial RA Support, $3000, 15%):
Has been helping some on measuring R&S for Dr. Drymiotis LAST-m and PbTeAgSe systems. This summer he plans to begin to study high density nanocomposites of the SiGe system synthesized using the SPS. He just passed the oral part of his Ph.D. qualifying exam.

Song Zhu, (Partial RA Support, $3000, 15%):
Last summer he learned the basic laboratory technology of sample mount & measurement, such as RS & TC. This past year he has worked extensively with the student from Wuhan on

the TE properties of BiSbTe nanocomposites. Meanwhile he is also studying the principles of thermoelectricity.

Tim Holgate, (Full RA Support, 100%): Graduated Ph.D. Summer of 2011
Working on the TE Properties of Chalcogenide materials in collaboration with Prof. Holger Kleinke of Waterloo University in Canada. Part of Outreach Program.

Jennifer Hubbard (F) (Full RA Support, 100%):
Continuing the work of Dr. Peng – our collaborator
Indium and Ytterbium double-filled Skutterudites $In_{0.1}Yb_yCo_4Sb_{12}$ (y = 0.0 ~ 0.2) have been synthesized by melting method, with single phase structure and good thermal stability. A state-of-the-art *ZT* value ~ 1.4 has been attained in $Ce_{0.1}In_{0.2}Yb_{0.1}Co_4Sb_{12}$ at 750 K, with *ZT* > 1.2 from 600 K to 900 K. Jennifer's recent work focused on further decrease the lattice thermal conductivity via tuning the filling component (adding a third filler Ce) and/or filling fraction. She will also look at TE nanocompsoites of these materials.

Wenjie (Michael) Xie, (Full RA Support, DOE Support $6,500, China Scholarship, $10,000):
Michael is the student who is working on a project as part of our collaboration with Prof. X. Tang of Wuhan University of Technology. He is working on melt spinning of TE materials, specifically p-type $Bi_{0.5}Sb_{1.5}Te_3$ materials. The materials are then processing using our spark plasma sintering system. The materials show nanodots, which exist in the material due to the melt spinning and are preserved through the SPS process.

Ted Dickel is a third-year grad student who is working part time on this project. The only support he received was travel expenses to attend the APS March meeting.

Keqin Yang – Graduate student (Ph.D) *graduated Fall 2009*
Yang was working on the carbon nanotube materials that were densified with the SPS and this work is highlighted in the Carbon paper published in 2010.

Postdoctoral Associates, Support and Project Description,

Dr. V. Ponns, (100% DOE Support):
Exploring new thermoelectric materials including p-type half Heusler materials and new Zintl phase materials. He is responsible for high temperature resistivity and Seebeck measurement systems and measurements. He left Clemson in October of 2009 to join Dr. Morelli's group at Mich. St. Univ. under a DOE-EFRC program.

Undergraduate Students and Admin. Asst.,

Several undergraduate students:
Several undergraduate students receive various levels of support for their research under this project. These include: Matthew Hendrix, Mark Harmon and Mercy Lard who received support from this program. They all conducted research of either synthesis or characterization of thermoelectric materials.

Administrative Assistant: Lisa Lawson:

Supported by DOE Funds: Lisa Lawson (in charge of budgets, reporting, purchases, scheduling etc.). She had two undergraduate students who helped her in her duties. Anil Jian is a graduate student who is supported to maintain and develop our group web site, ($4000 a year).

8. An update list of other support:

TERRY M. TRITT (PI)

Current Support

"ONR-HEL-MURI – Eye Safe Polycrystalline Lasers"

Through 9/30/2012

Proposal to KAUST in Saudi Arabia as part of a faculty initiated collaboration
($600 K over 3 years) began March 2011

DOE-STTR Subcontract w/Nanosonic and UVa ($250 K over 2 years, beginning Sept 2011)

NSF-Materials World Network (along with Dr. He) with Zhejiang Univ. in China
(Partially funded for travel $45K over 3 years)

Proposal Processing: (Tritt)

Submitted numerous proposals;

- Lead a team on a DOE –EFRC proposal. Not Funded
- Lead a team on a DOD-MURI proposal (Not Funded)
- Submitting a proposal (in June) to the NSF-DOE Vehicles Program.
  A team of 4 universities and Research Triangle Institute in NC.

MURRAY DAW (CO-PI)

The only current support that Dr. Daw has is the DOE-EPSCoR grant herein

Pending Support

"*Improved Calculation of Intrinsic Lattice Thermal Conductivity*",
proposal submitted to NSF. Ideas developed under support of this DOE grant are seminal to the further work proposed to NSF.

APPARAO RAO (CO-PI)

Proposal Processing:
Secured DARPA funding in conjunction with the Univ. of Texas at Dallas

Microstructural Analysis and Micromechanical Testing of Novel Hybrid Fibers
Army Research Office (Pending)

CATALINA MARINESCU (CO-PI)

The only current support that Dr. Marinescu has is the DOE-EPSCoR grant herein

Proposal Processing:

"Thermoelectric spin and charge transport in semiconductor superlattices".
To be submitted to DOE, in progress

“Spin-dependent Thermoelectric Phenomena in Semiconductor Superlattices with Spin-Orbit Interaction”, D. C. Marinescu and S. Tewari, to be submitted.

JIAN HE (CO-PI-NEW HIRE JANUARY 2008)

Pending Support

The following proposals are in progress and will submitted in the fall of 2010
to either NSF or DOE

“Pursuing Thermoelectricity in the Electron-Ion Mixed Conductor Chalcogenide”

“The Percolative Behavior and its Effects on the Thermoelectric Performance in a Metal-Oxide Composite System”

SUMANTA TEWARI (CO-PI-NEW HIRE, AUG. 2008)

Pending Support

Title: Topological Quantum Computation in Superconductors, Superfluids, and Cold Atom Optical Lattices (Collaborative Research with Chuanwei Zhang at Washington State University)
Amount: $221,558 for three years at Washington State University
Agency: National Science Foundation (Physics at the Information Frontier)
Period: 06/01/2009 -- 05/31/2012

Title: Fundamental Questions For Magnetoelectric Phenomena In Magnetically-Driven Multiferroics, (Collaborative Research with Chuanwei Zhang at Washington State University)
Amount: $218,568 for three years at Washington State University
Agency: National Science Foundation (Condensed Matter and Materials Theory)
Period: 06/01/2009 -- 05/31/2012

HYE JUNG KANG (CO-PI-NEW HIRE, AUG. 2008)

Proposal Processing:

"Multigrain phases in thermoelectric materials and its effects to the physical properties"
to NSF in Fall of 2011

DOE EPSCoR, "Magnetism-Superconductivity Phase Diagram of High T_c Cuprate Superconductor $Nd_{2-x-y}Sr_xCe_yCuO_4$: Single Crystal Growth and Neutron Scattering Study", Co-PI, 2010-2013 (Pending)

9. Cost status:

We currently have $0 balance in the DOE grant and $0 balance in the SC EPSCoR and Cost Sharing Commitment as of August 14, 2011.