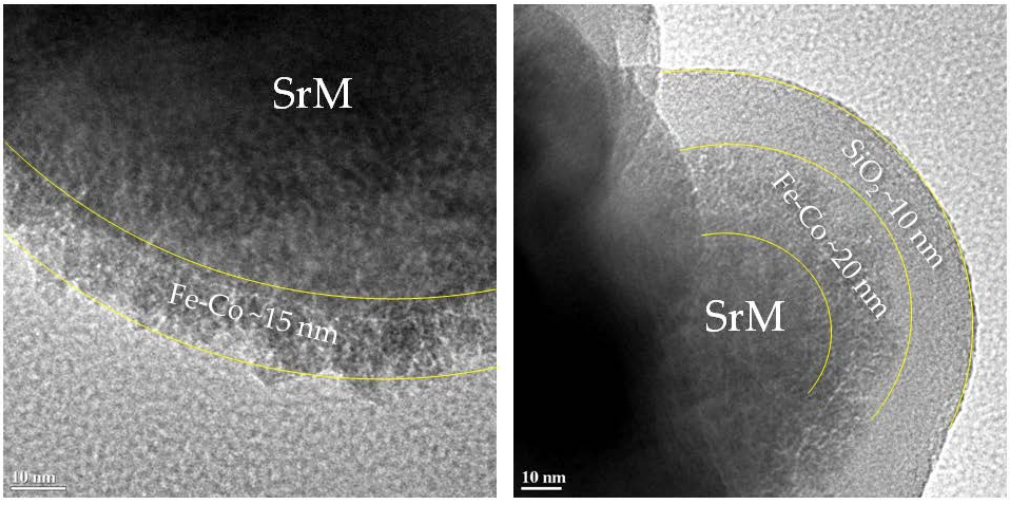
Final Scientific/Technical Report

Title: Rare-Earth-Free Permanent Magnets for Electrical Vehicle Motors and Wind Turbine Generators: Hexagonal Symmetry Based Materials Systems Mn-Bi and M-type Hexaferrite

Contract Number: DE-AR0000189



Core(SrM)-Shell(Fe-Co) Core(SrM)-Shell(Fe-Co)-Shell(SiO_2)

Award:	DE-AR0000189
Lead Recipient:	The University of Alabama
Project Title:	Rare-Earth-Free Permanent Magnets for Electrical Vehicle Motors and Wind Turbine Generators: Hexagonal Symmetry Based Materials Systems Mn-Bi and M-type Hexaferrite
Program Director:	Dr. Mark Johnson
Principal Investigator:	Dr. Yang-Ki Hong
Contract Administrator:	Lisa Joiner
Date of Report:	June 5, 2014
Reporting Period:	January 1, 2012 – September 30, 2013

╬Public Executive Summary

1) How the research adds to the understanding of the area investigated?

The research we conducted focuses on the rare-earth (RE)-free permanent magnet by modeling, simulating, and synthesizing exchange coupled two-phase (hard/soft) RE-free core-shell nano-structured magnet. The RE-free magnets are made of magnetically hard core materials (high anisotropy materials including Mn-Bi-X and M-type hexaferrite) coated by soft shell materials (high magnetization materials including Fe-Co or Co).

Therefore, our research helps understand the exchange coupling conditions of the core/shell magnets, interface exchange behavior between core and shell materials, formation mechanism of core/shell structures, stability conditions of core and shell materials, etc.

2) The technical effectiveness and economic feasibility of the methods or techniques investigated or demonstrated.

We have developed new iron- and manganese-based composite materials for use in the electric motors of EVs and renewable power generators. For the iron-based composite materials, we have synthesied exchange coupled hard/soft core-shell particles by remanent magnetization assisted self-assembly. By assembling the magnetically hard and soft particles in this way, the lattice mismatch between hard and soft phases is overcome and core/shell structured particles are produced. This synthetic method for core-shell structured particles shows a great potential to combine wide variety of magnetically hard and soft materials in nano scale for exchange coupling. Furthermore, the magnetic self-assembly is a fully in-situ synthesic method that does not include further treatments of ball milling or other mixing processes, therefore, cost-effective.

3) How the project is otherwise of benefit to the public?

Developing alternatives to the magnets based on rare earth elements has a potential to reduce our dependence on these critical materials and will have a positive impact on our national economic and energy security. The transportation and electric power sectors account for nearly 75% of U.S. greenhouse gas emissions each year. Better magnets would support the widespread use of EVs and wind power, significantly reducing these emissions. The U.S. spends nearly $1 billion per day on imported petroleum. Improvements in magnet technology would enable a broader use of EVs, which would help insulate our economy from unexpected spikes in the price of oil.

Acknowledgements

This work was supported by the U.S. Department of Energy ARPA-E REACT Program under Award number DE-AR0000189. The Co-PIs [Dr. Sungho Jin (UCSD), Dr. Ami Berkowitz (UCSD), Dr. Seong-Gon Kim (MSU), Dr. Oleg Mryasov (UA) and Dr. Timothy Haskew (UA)] are greatly appreciated for their expert contributions. The UA, USCD, and MSU are acknowledged for their cost-share. Dr. Lane (UA) is also appreciated for valuable discussions.

Table of Contents

Table of Figures/Tables

Accomplishments and Objectives

Table 1. Key Milestones and Deliverables.

Tasks	Milestones and Deliverables
Task 1: Development of Core-shell Magnet with Mn-Bi Core: Sungho Jin (UCSD) and Ami Berkowitz (UCSD)	
1.1 Synthesis of MnBi core nanoparticles	**Q2 Milestones:** Produce MnBi nanoparticles: (a) particle size: > 50 wt% in 10 - 100 nm (b) purity: > 30 v.% in ferromagnetic phase (c) production rate: > 0.8 g/h (d) oxygen content: < 10 % **Actual Performance: All milestones for Q2 are met.** (a) ~50% in the as-sparked state and >~70% in sieved state (b) >~60 % ferromagnetic phase (c) ~40 g/hr production rate (d) 3.23 % oxygen content
	Q4 Milestones: Produce MnBi nanoparticles: (a) particle size: > 60 wt.% in 10 - 100 nm (b) purity: > 40 v.% in ferromagnetic phase (c) production rate: > 1.0 g/h (d) oxygen content: < 5% **Actual Performance: All milestones for Q4 are met.** (a) particle size: > ~70 wt.% in sieved state (b) purity: ~77 v.% in ferromagnetic phase (c) production rate: ~40 g/h (d) oxygen content: 3.23 % oxygen content
	Q6 Milestone: Synthesis of MnBi core nanoparticles (a) particle size: > 60 wt.% in 30 - 70 nm (b) purity: > 60 v.% in ferromagnetic phase (c) production rate: > 4.0 g/h (d) oxygen content: < 2% **Actual Performance: All milestones for Q6 are met.** (a) particle size: ~70 wt.% in 30 - 70 nm (b) purity: 93 v.% in ferromagnetic phase (c) production rate: ~70 g/h (d) oxygen content: ~1.5 wt.%

Tasks	Milestones and Deliverables
1.2 Synthesis of MnBi core-shell nanoparticles	**Q4 Milestones**: Produce MnBi core/Fe-Co shell nanoparticles: (a) core size: < 80 nm (b) shell thickness: 15 ± 5 nm (c) saturation magnetization (σ_s): > 30 emu/g (d) coercivity (H_c) : > 5 KOe (e) production rate: > 0.5 g/h **Actual Performance: All milestones for Q4 are met.** (a) core size: ~30 nm diameter (b) shell thickness: ~10 nm diameter (c) saturation magnetization (σ_s): ~57 emu/g (d) coercivity (H_c) : ~10-20 kOe at RT and > 25 kOe at 200 ^{o}C (e) production rate: > 0.5 g/h
	Q6 Milestone: Synthesis of MnBi core-shell nanoparticles (a) core size: < 70 nm (b) shell thickness: 15 ± 5 nm (c) saturation magnetization (σs): > 50 emu/g (d) coercivity (Hc): > 8 KOe (e) maximum energy product (BH_{max}): > 20 MGOe (f) shell coverage: > 70 % with 15 ± 5 nm (g) production rate: > 1.0 g/h (h) Produce $Fe_{65}Co_{35}$ nanoparticles < 20 nm size **Actual Performance: All milestones for Q6 are met.** (a) core size: ~30 - 200 nm (b) shell thickness: 10 - 20 nm (c) saturation magnetization (σ_s): ~58 emu/g (at H = 7 T) - 100 emu/g (semi-empirical) (d) coercivity (H_c): ~1.2 Tesla (e) maximum energy product (BH_{max}): 23.5 MGOe (semi-empirical) (f) shell coverage: > 70 % with 15 ± 5 nm (g) production rate: > 10 g/h (h) produce $Fe_{65}Co_{35}$ nanoparticles < 20 nm size
Task 2: Development of core-shell magnet with M-type hexaferrite core: Yang-Ki Hong (UA)	

Tasks	Milestones and Deliverables
2.1 Synthesis of precursor particles	**Q2 Milestones:** Produce precursor particles: (a) size: < 300 nm (b) shape: worm shape of > 3:1 aspect ratio (c) purity: > 90 v.% in hematite and Ba (or Sr) oxides phases (d) batch size: 2 g/batch **Actual Performance: All milestones for Q2 are met.** (a) size: 55-85 nm water-based S-Mag nanoparticles (b) shape: worm shape of > 5:1 aspect ratio for hematite and Ba oxides (c) purity: > 99 v.% in hematite and Ba oxides phases and magnetite phases (d) batch size: 2 g/batch
2.2 Synthesis of M-type hexaferrite core particles	**Q2 Milestones:** Produce M-type hexaferrite core particles: (a) size: < 200 nm (b) purity: > 80 v.% (c) saturation magnetization (σ_s): > 30 emu/g (d) coercivity (H_c): > 2 KOe (e) batch size: 1.8 g/batch **Actual Performance: All milestones for Q2 are met.** (a) size: 85-115 nm (b) purity: 97 v.% (c) saturation magnetization (σ_s): 49 emu/g at 10 kOe (d) coercivity (H_c): 2841 Oe (d) batch size: 2 g/batch
	Q4 Milestones: Produce M-type hexaferrite core particles: (a) size: < 200 nm (b) purity: > 80 v% (c) saturation magnetization (σ_s): > 50 emu/g (d) coercivity (H_c) : > 3 KOe (e) batch size: 2 g/batch **Actual Performance: All milestones for Q4 are met.** (a) size: 173 nm in avg. (b) purity: 93.3 v.% (c) saturation magnetization (σ_s): 51 emu/g at 10 kOe (d) coercivity (H_c): 3263 Oe (d) batch size: 2 g/batch

Tasks	Milestones and Deliverables
2.3 Synthesis of M-type hexaferrite core-shell particles	**Q6 Milestone:** Synthesis of M-type hexaferrite core-shell particles: (a) core size: < 200 nm (b) shell thickness: < 30 nm (c) fraction of core-shell particles: > 50% (d) saturation magnetization (σ_s): > 60 emu/g (e) coercivity (H_c): > 4 KOe (f) batch size: 3 g/batch. **Actual Performance: All milestones for Q6 are met.** (a) core size: > 200 nm (b) shell thickness: > 30 nm (c) fraction of core-shell particles: > 95 % (d) saturation magnetization (σ_s): 82 emu/g (e) coercivity (H_c): > 4 KOe (f) batch size: 3 g/batch
2.4 Synthesis of M-type hexaferrite core-shell-shell particles	**Q6 Milestone:** Synthesis of M-type hexaferrite core-shell-shell particles (a) core size: < 200 nm (b) magnetic shell thickness: < 30 nm (c) second shell thickness: < 10 nm (d) saturation magnetization (σ_s): > 60 emu/g (e) coercivity (H_c) : > 4 KOe (f) batch size: 2 g/batch **Actual Performance: All milestones for Q6 are met.** (a) core size: < 200 nm (b) magnetic shell thickness: < 30 nm (c) second shell thickness: < 10 nm (d) saturation magnetization (σ_s): > 60 emu/g (e) coercivity (H_c) : > 4 KOe (f) batch size: 2 g/batch
Task 3: Analyze the performance of core-shell magnets and improve hard-magnetic core: Oleg Mryasov (UA) and Seong-Gon Kim (MSU)	
1.1 Statistical and micromagnetic simulation on M-type hexaferrite and MnBi core-shell particles (UA)	**Q2 Milestones:** Set up test model for $(BH)_{max}$ as a function of shell thickness (thinner than 2 x domain wall thickness) and core diameter (< single magnetic domain size) **Actual Performance: All milestones for Q2 are met.** The milestone has been met. We set up and tested statistical and micro-magnetic models for coercive force, anisotropy and T_c : (a) Statistical model of magnetic anisotropy temperature dependence

Tasks	Milestones and Deliverables
	for LTP MnBi (b) Statistical model of Curie point in LTP MnBi (c) Micro-magnetic model has tested and used to calculate coercive force for spherical core-shell structures as a function of core thickness for core materials i) LTP MnBi (at T=485 K) and ii) M-type hexaferrite (at T = 300 K).
	Q4 Milestones: Set up micromagnetic model and quantify $(BH)_{max}$ as a function of interfacial exchange coupling (J_i): $0 < J_i < J_b$ (bulk exchange coupling constant) **Actual Performance: All milestones for Q4 are met.** The 100% Q4 and 50 % Q6 milestones are met. The completion of Q6 milestones is due by 04/31/2013. The Q4 milestones have been completed with micromagnetic model taking into account J_i and T - dependence of magnetic properties including both K_1 and K_2 anisotropy constants for MnBi and BaM. We partially completed (about 50%) of Q6 statistical analysis and micromagnetic for MnBi and BaM core shell nano-structures. Coercive force Hc and $(BH)_{max}$ have been evaluated for different nano-structures including non-co-centric deviations from ideal core shell geometry and for planar soft/hard/soft nanostructures.
	Q6 Milestone: Complete statistical and micromagnetic simulations on MnBi and M-type hexaferrite core-shell particles: Simulations of field alignment for core and core-shell MnBi and M-type hexaferrite nanoparticles **Actual Performance: All milestones for Q6 are met.** The Q6 milestones have been completed with conclusion that AF interface coupling is a leading mechanism for reduction of $(BH)_{max}$ from it theoretical upper limit followed by misalignment. We completed development of initial model of the test model for MnAl/Co interface for comparison with available thin film work. Corresponding micromagnetic modeling has been completed and initial model for MnBi/X, X=Fe, Co, Ni has been developed along with initial 8 grain microstructure model of sintered core-shell magnet (cylinder model Fig. 2).
1.2 Ab-initio simulation (MSU)	**Q2 Milestones:** Complete ab-initio simulation of magnetic properties of pure $SrFe_{12}O_{19}$ **Actual Performance: All milestones for Q2 are met.** The milestones are met. We completed the ab-initio simulation of magnetic properties of pure $SrFe_{12}O_{19}$ using Density Functional

Tasks	Milestones and Deliverables
	Theory. We computed the total saturation magnetization as well as the magnetic moments of individual atomic sites. We also obtained the magnetic anisotropy energy and anisotropy constant. In addition, we obtained the structural parameters and total density of states.
	Q4 Milestones: Complete ab-initio simulation of magnetic properties of (Ba/Sr-X)(Fe-Y)$_{12}$(O-Z)$_{19}$ with Zn and Sn doping $SrFe_{12-x}(Sn_{0.5}Zn_{0.5})_xO_{19}$ for x = 1.0 doping level **Actual Performance: All milestones for Q4 are met.** The milestones are met. We completed the ab-initio simulation of magnetic properties of Zn-Sn substituted $SrFe_{12-x}(Sn_{0.5}Zn_{0.5})_xO_{19}$ for x = 1.0 using Density Functional Theory. We determined the lowest-energy structure of Zn-Sn substituted $SrFe_{12-x}(Sn_{0.5}Zn_{0.5})_xO_{19}$ and the site occupancy of Zn and Sn atoms. We also computed its total saturation magnetization and magnetocrystalline anisotropy.
	Q6 Milestone: Complete ab-initio simulation of magnetic properties of (Mn-X)(Bi-Y) with Co and Fe doping $MnBiCo_x$ for x = 1.0 doping level $MnBiFe_x$ for x = 1.0 doping level **Actual Performance: All milestones for Q6 are met.** We completed the ab-initio simulation of magnetic properties of $MnBiCo_x$ for x = 0 to 1.0 doping level and $MnBiFe_x$ for x = 0 to 1.0 doping level using Density Functional Theory. We determined the the magnetic anisotropy energy and magnetic anisotropy constant of MnBiCox and MnBiFex for the concentration x = 1.
Task 4: Motor performance analysis: Timothy Haskew (UA)	
4.1 Motor modeling	**Q2 Milestones:** Implement a motor performance model based on M-type hexaferrite and Mn-Bi magnetic properties to predict torque and back-emf constants (0.73 Nm/A or Vs/rad). Initial estimates should result in performance at 25% of base COTS motor. **Actual Performance: All milestones for Q2 are met.** A motor performance model has been implemented in MATLAB Simulink. The model is capable accommodating configurations with arbitrary magnetic material properties including those of M type hexaferrite and Mn-Bi. The attached report provides more detail, and the also presents a simple simulation example.
	Q4 Milestones: Improve motor design to achieve performance to 35% of base COTS motor.

Tasks	Milestones and Deliverables
	Actual Performance: All milestones for Q4 are met. A motor performance model based on system interactions has been implemented in MATLAB Simulink. Theoretical efforts have been focused on determining the impact of new permanent magnet materials on simulation parameters in the motor model. Specifically, the model is impacted in the flux per pole and direct and quadrature inductance parameters. Based upon theoretical expectations of the proposed magnetic materials, many existing motor topologies will enable the target performance. Experimental validation of the model and parameter estimation is expected in the near term.
	Q6 Milestone: Improve motor design to achieve performance to 50% of base COTS motor. **Actual Performance: All milestones for Q6 are met.** Theoretical analyses using expected properties have indicated that the proposed MnBiCo magnets will reach the 50% COTS performance targets compared to Sm_2Co_{17} magnets at temperatures ranging from 25 to 200 ^{o}C. An axial gap motor that can have a new rotor with new magnetic materials easily fabricated has been modeled and simulated with the results validated against physical test data. Modeling efforts to include nonlinear controller effects in the system simulation were fully successful.

╬Project Activities

The main goal of this project is to develop new iron- and manganese-based composite materials for use in the electric motors of EVs and renewable power generators that will demonstrate magnetic properties superior to today's best rare-earth-based magnets. In order to realize this goal, we developed RE-free permanent magnets based on the concept of combining (i) novel two-phase (hard/soft) RE-free core-shell nano-structures to achieve high maximum energy product $(BH)_{max}$ and (ii) advanced hexagonal closed-packed (hcp) based high anisotropy material systems including Mn-Bi-X and M-type hexaferrite.

For exchange coupled M-type hexaferrite based magnet, core(SrM)-shell(Fe-Co) and core(SrM)-shell(Fe-Co)-shell(SiO_2) particles were synthesized. The exchange coupling was clearly observed, and the saturation magnetization increased to 70 emu/g from 61 emu/g, and coercivity decreased to 4 kOe from 4.4 kOe for SrM/Fe-Co particles. The temperature coefficient of saturation magnetization (α) for SrM core particles was -0.16 (%/^{o}C), while -0.08 (%/^{o}C) was measured for core (SrM)-shell (Fe-Co) particles.

For exchange coupled MnBi based magnet, spark erosion process was used to synthesize non-magnetic MnBi nanoparticles (e.g., 20 - 30 nm particles). Such smaller

nanoparticles would naturally tend to have an amorphous structure by higher power spark erosion. The coercivity can be enhanced by adding a non-magnetic interlayer between particles (e.g., using the jumping-particle-sputtering technique), or working at a temperature and composition that partially segregates some Bi or other phases to act as a domain-wall pinning barrier. The achieved saturation magnetization and coercivity are 58 emu/g at 7 T and 1.2 T, respectively.

Micromagnetic simulation and advanced *ab initio* calculations of structural and magnetic properties interfacial exchange coupling have been used to guide better design of core-shell magnets. We have performed the simulations and calculations (i) to enhance K_1, K_2, M_s, and T_c, (ii) to explore new hcp phases using materials search based on material templates $(Ba\text{-}X)(Fe\text{-}Y)_{12}(O\text{-}Z)_{19}$, (Mn-X)(Bi-Y), Co_3GeMn_2, and Co_3W, and (iii) to investigate interfacial exchange coupling. We completed the ab-initio simulation of magnetic properties of $MnBiCo_x$ for x = 0 to 1.0 doping level and $MnBiFe_x$ for x = 0 to 1.0 doping level using Density Functional Theory. We determined the lowest-energy spin structures of Co-alloyed and Fe-alloyed MnBi. We also computed the saturation magnetization and magnetic anisotropy energy of $MnBiCo_x$ and $MnBiFe_x$ as a function of the doping concentration *x*.

The developed magnets have been characterized in terms of their performance in electric machines. A commercially available machine was modeled to account for magnet properties. This model was validated through multiple simulation comparisons with physical data acquired through dynamometer testing. A detailed analysis of the model with the new magnet properties provided predicted performance data for the modified machine. No machine design modifications were necessary to reach the target performance goals. Theoretical analyses using expected properties have indicated that the proposed MnBiCo magnets will reach the 50% COTS performance targets compared to Sm_2Co_{17} magnets at temperatures ranging from 25 to 200 ^oC.

Project Outputs

A. Journal Articles

- Jihoon Park, Yang-Ki Hong, Seong-Gon Kim, Sungho Kim, Laalitha S.I. Liyanage, Jaejin Lee, Woncheol Lee, Gavin S. Abo, Kang-Heon Hur, Sung-Yong An, "Maximum energy product at elevated temperature for hexagonal strontium ferrite ($SrFe_{12}O_{19}$) magnet, " *Journal of Magnetism and Magnetic Materials*, **355**, 1 (2014).
- Yang-Ki Hong, Jihoon Park, Oleg N. Mryasov, Seong-Gon Kim, Sungho Kim, Jaejin Lee, Gavin S. Abo, Chul-Jin Choi, "Magnetic properties of MnBi based alloys: First-principles calculations for MnBi-Co and MnBi-Co-Fe cases," *AIP Advances*, **3**, 052137 (2013).
- Laalitha S.I. Liyanage, Sungho Kim, Yang-Ki Hong, Jihoon Park, Steven C. Erwin, Seong-Gon Kim, "Theory of magnetic enhancement in strontium hexaferrite through Zn-Sn pair substitution," *Journal of Magnetism and Magnetic Materials*, **348**, 75 (2013).
- Phi-Khanh Nguyen, Sungho Jin, and Ami E. Berkowitz, "Unexpected magnetic domain behavior in LTP-MnBi", *IEEE Transactions on Magnetics* **49**, 3387 (2013).

B. Papers

C. Status Reports

Q1 report: submitted to ARPA-e on April 14, 2012
Q2 report: submitted to ARPA-e on July 11, 2012
Q3 report: submitted to ARPA-e on October 15, 2012
Q4 report: submitted to ARPA-e on January 15, 2013
Q5 report: submitted to ARPA-e on April 15, 2013
Q6 report: submitted to ARPA-e on July 15, 2013
Q7 report: submitted to ARPA-e on October 13, 2013

D. Media Reports

Research, Spring 2013 Volume XVI, The University of Alabama

E. Invention Disclosures

- University of Alabama ID 14-0002; Inventors Yang-Ki Hong, Xia Xu, Jihoon Park, and Alan Lane, "Remanent Magnetization assisted Self-Assembled Core-Shell Magnets for Magnetic Exchange Coupling," approved for protection on December 09, 2013 .
- University of Alabama ID 14-0041; Inventors Yang-Ki Hong, Xia Xu, Jihoon Park, and Alan Lane, "Manufacturing Method for Hard Magnetic Metal/Soft Magnetic Metal Alloy Composite (Exchange Coupled) Magnets ," approved for protection on March 03, 2014

F. Patent Applications

- University of California, San Diego #2012-123-2, Ami Berkowitz and Sungho Jin, "Manufacturable Spark Erosion Apparatus for Nanoparticles, Method of Fabrication, and Articles Fabricated From Nanoparticles", filed for PCT patent application filed on 10/12/2012, #PCT/US12/060141.

- University of California, San Diego #2013-287, Chulmin Choi, Youngjin Kim, Sungho Jin, "Magnetic Nanoparticle Systems and Synthesis Processes", Provisional application #61828163, filed 5/28/14.

G. Licensed Technologies

H. Networks/Collaborations Fostered

I. Websites Featuring Project Work Results

J. Other Products (e.g. Databases, Physical Collections, Audio/Video, Software, Models, Educational Aids or Curricula, Equipment or Instruments)

K. Awards, Prizes, and Recognition

Follow-On Funding

Table 2. Follow-On Funding Received.

Source	Funds Committed or Received
University of Maryland/DOE-Subaward to University of Alabama: Z713208 (10/1/13 – 3/31/15)	$285,520
University of Maryland/DOE-Subaward to University of California, San Diego: Z713207 (10/1/13 – 3/31/15)	$286,000