Final Report (1/24/2017)

Proposal Title:	**Exploring Electric Polarization Mechanisms in Multiferroic Oxides**
Award:	DOE DEFG02-07ER46402
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Award Period (full grant)	7/15/2008 to 7/14/2016
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Exploring Electric Polarization Mechanisms in Multiferroic Oxides

Abstract

Multiferroic oxides are a class of systems which exhibit coupling between the electrical polarization and the magnetization. These materials show promise to lead to devices in which ferromagnetic memory can be written with magnetic fields or magnetic bits can be written by an electric field. The work conducted in our research focuses on single phase materials. We studied the detailed coupling of the spin and lattice correlations in these systems. In the first phase of the proposal, we explored the complex spin spiral systems and low temperature behavior of hexagonal layered REMnO3 (RE= rare earth, Y and Sc) system following the detailed structural changes which occurred on crossing into the magnetic states. The techniques were applied to other layered materials such as superconductors and thermoelectric where the same layered motif exists.

The second phase of the proposal focused on understanding the mechanisms involved in the onset high temperature ferroelectricity ion hexagonal REMnO3 and at low temperature in E-Type magnetic ordered perovskite $REMnO_3$. We wsynthesized preovskite small A site multiferroics by high pressure and high temperature methods. Detailed measurement of the structural properties and dynamics were conducted over a range of length scales from atomic to mesoscopic scale using, x-ray absorption spectroscopy, x-ray diffuse scattering, x-ray and neutron pair distribution analysis and high resolution x-ray diffraction. Changes in vibration modes which occur with the onset of polarization were probed with temperature and pressure dependent infrared absorption spectroscopy. In addition the orthorhombic system (small radius RE ions) which is believed to exhibit electronically driven ferroelectricity and is also not understood was examined. The multiple length scale synchrotron based measurements may assist in developing more detailed models of these materials and possibly lead to device applications. The experimental work was complemented by density functional methods to determine the magnetic ground states and ab initio molecular dynamics methods (AIMD) to determine the high temperature structures. Simulation were carried out on supercomputers at the National Energy Research Scientific Computing Center (NERSC). An important contribution of this work was the training of graduate students and postdoctoral researchers in materials synthesis, high pressure methods and synchrotron based spectroscopy and x-ray scattering techniques.

A. Personnel Funded Under Grant DOE DEFG02-07ER46402

Graduate Students (Ph. D.)	Peng Gao (100%) Zhiqiang Chen (100%) Tian Yu (100%) Tao Wu (100%)
Postdoctoral Researchers	Peng Gao (100%) Haiyan Chen (10 %) Zhiqian Chen (100%) Ahmad Masadeh (10 %)
Senior Investigators:	Trevor A. Tyson (100%)

B. Theses, Presentations and Publications

Ph. D. Theses Completed

1. T. Yu, "SYNTHESIS AND CHARACTERIZATION OF NOVEL MULTIFERROIC MATERIALS: HEXAGONAL AND PEROVSKITE SMALL R-ION SYSTEMS", NJIT December 2013.

2. T. Wu. "TUNING COMPLEX OXIDES ATOMIC LEVEL AND PHYSICAL PROPERTIES FOR THERMOELECTRIC AND MULTIFUNCTIONAL SENSOR APPLICATIONS", NJIT May 2013.

Accepted/Published Papers

1. T. Wu, T. A. Tyson, H. Chen, P. Gao, T. Yu, Z. Chen, Z. Liu, K. H. Ahn, X. Wang and S.-W. Cheong, "Pressure Dependent Structural Changes and Predicted Electrical Polarization in Perovskite RMnO3", J. Phys. Cond. Matt **28**, 056005 (2016).

2. M. Feygenson, J. C. Neuefeind, T. A. Tyson, N. Schieber and W. Q. Han, "Average and Local Crystal Structures of (Ga1-xZnx)(N1-xOx) Solid Solution Nanoparticles", Inorg. Chem. **54** (23), 11226-11235 (2015).

3. H. Zhang, T. Yu, Z. Chen, C. S. Nelson, L. N. Bezmaternykh, A. M. M. Abeykoon and T. A. Tyson, "Probing magnetostructural correlations in multiferroic HoA l3(B O3)4", Phys. Rev. B Condens. Matter Mater. Phys. **92** (10) , 104108 (2015).

4. Y. Wang, G. L. Pascut, B. Gao, T. A. Tyson, K. Haule, V. Kiryukhin and S. W. Cheong, "Unveiling hidden ferrimagnetism and giant magnetoelectricity in polar magnet Fe2Mo3O8" Sci. Rep. **5** 12268 (2015).

5. M.-R. Li, M. Retuerto, Z. Deng, T. Sarkar, J. Sanchez-Benitez, M. C. Croft, T. S. Dasgupta, T. Das, T. A. Tyson, D. Walker, and M. Greenblatt, "Strong Electron Hybridization and Fermi-to-Non-Fermi Liquid Transition in $LaCu_3Ir_4O_{12}$", Chem. Mater. **27**, 211 (2015).

6. T. A. Tyson, T. Yu, M. Croft, M. E. Scofield. D. Bobb-Semple, J. Tao, C. Jaye, D. Fischer and S. S. Wong, "Polar State in Freestanding Strontium Titanate Nanoparticles", Appl. Phys. Lett. **105**, 091901 (2014).

7. T. Yu, T. A. Tyson, P. Gao, T. Wu, X. Hong, S. Ghose, and Y.-S. Chen, "Structural changes related to the magnetic transitions in hexagonal InMnO3", Phys. Rev. B. **90**, 174106 (2014).

8. T. Yu, T. A. Tyson, H. Y. Chen, A. M. M. Abeykoon, Y.-S. Chen and K. H. Ahn , "Absence of significant structural changes near the magnetic ordering temperature in small-ion rare earth perovskite *R*MnO3", J. Phys.: Condens. Matter **26,** 495402 (2014).

9. T. Yu, P. Gao, T. Wu, T. A. Tyson, and R. Lalancette, *"Ferroelectricity in Single Crystal InMnO3",* Appl. Phys. Lett. ***102**, 172901 (2013).*

10. H. Chen, T. Yu, P. Gao, J. Bai, J. Tao, T. A. Tyson, L. Wang, and R. Lalancette, *"Synthesis and Structure in Perovskite-Type ScMnO3",* Inorganic Chemistry 52, 5692 (2013).

11. T. A. Tyson, T. Wu, H. Y. Chen, J. Bai, K. H. Ahn, K. I. Pandya, S. B. Kim and S. W. Cheong, "*Measurements and ab initio molecular dynamics simulations of the high temperature ferroelectric transition in hexagonal RMnO3*",J. Appl. Phys. **110** , 084116 (2011).

12. P. Gao, Z. Chen, T. A. Tyson, T. Wu, K. H. Ahn, Z. Liu, R. Tappero, S. B. Kim and S. W. Cheong, "*High-pressure structural stability of multiferroic hexagonal RMnO3 (R = Y, Ho, Lu)*",Phys. Rev. B: Condens. Matter Mater. Phys. **83,** 224113 (2011).

13. T. Wu, T. A. Tyson, H. Chen, J. Bai, H. Wang, and C. Jaye, *"A structural change in $Ca_3Co_4O_9$ associated with enhanced thermoelectric properties", J. Phys. Cond. Mat. **24**, 455602 (2012).* I

14. T. Wu, T. A. Tyson, J. Bai, K. Pandya, C. Jaye and D. Fischer, *"On the Origin of Enhanced Thermoelectricity in Fe doped $Ca_3Co_4O_9$ ", J. Mat. Chem C. **1**, 4114 (2013).*

15. X. Luo, Y. S. Oh, A. Sirenko, P. Gao, T. A. Tyson, K. Char, and S. W. Cheong, *"High Carrier Mobility in Transparent Ba1-xLaxSnO Crystals with Wide Band Gap*", Appl. Phys. Lett. **100**, 172112 (2012).

16. T. A. Tyson, T. Yu, S. J. Han, M. Croft, G. D. Gu, I. K. Dimitrov and Q. Li, "*Local structure of the superconductor K0.8Fe1.6+xSe2: evidence of large structural disorder*", Phys. Rev. B **85**, 024504 (2012).

17. P. Gao, H. Y. Chen, T. A. Tyson, Z. X. Liu, J. M. Bai, L. P. Wang, Y. J. Choi and S. W. Cheong, "*Observation of anomalous phonons in orthorhombic rare-earth manganites*",Applied Physics Letters **97** (26), 262905 (2010).

18. T. A. Tyson, T. Wu, K. H. Ahn, S.-B. Kim and S.-W Cheong, "*Local spin-coupled distortions in multiferroic hexagonal HoMnO3*", Phys. Rev. B: Condens. Matter Mater. Phys. **81**, 054101 (2010).

19. T. A. Tyson, Z. Chen, M. A. DeLeon, S. Yoong, and S. W. Cheong, "*Local structure of multiferroic RMn2O5: Important role of the R site*", J. Magn. Magn. Mater. **321**, 1714 (2009).

20. V. V. Poltavets, K. A. Lokshin, A. H. Nevidomskyy, M. Croft, T. A. Tyson, J. Hadermann, G. Van Tendeloo, T. Egami, G. Kotliar, N. ApRoberts-Warren, A. P. Dioguardi, N. J. Curro and M. Greenblatt, "*Bulk Magnetic Order in a Two-Dimensional Ni1+/Ni2+ (d9/d8) Nickelate, Isoelectronic with Superconducting Cuprates*", Physical Review Letters **104** (20), 206403 (2010).

21. T. A. Tyson, T. Wu, J. C. Woicik, B. Ravel, A. Ignatov, C. L. Zhang, Z. Qin, T. Zhou and S. W. Cheong, "*Temperature-dependent local structure of LaFeAsO1-xFx: Probing the atomic correlations*", Journal of Applied Physics **108** (12), 123715 (2010).

22. T. A. Tyson, Z. Chen, Q. Jie, Q. Li, and J. J. Tu, "Local structure of thermoelectric Ca3Co4O9", Phys. Rev. B: Condens. Matter Mater. Phys. **79**, 024109/1 (2009).

Submitted Manuscripts

H. Zhang , S. Liu , M. E. Scofield , S. S. Wong, X. Hong, V. Prakapenka, E. Greenberg and Trevor A. Tyson, "Size-Dependent Structural Phase Transitions in $SrTiO_3$ Nanoparticles", submitted to Phys. Rev. Lett. ArXiv preprint 2016arXiv161108935Z

Conference Presentations

2016 (Work to be presented at March 2016American Physical Society Meeting)

Tyson, Trevor; Yu, Tian; Zhang, Han; Abeykoon, Milinda,
Temperature Dependent Structure of $BiFeO_3$: Probing For Spin Lattice Correlations
APS March Meeting 2016 (Baltimore), abstract #R30.011

Zhang, Han; Yu, Tian; Chen, Zhiqiang; Nelson, Christie; Bezmaternykh, Leonard; Chen, Yu-Sheng; Abeykoon, Milinda; Tyson, Trevor
Structure of Multiferroic $RAl_3 (BO_3)_4$ and $RFe_3 (BO_3)_4$ in the Region of High Electric Polarization
APS March Meeting 2016 (Baltimore), abstract #R30.008

Liu, Sizhan; Zhang, Han; Ghose, Sanjit; Emge, Thomas; Kaplan, Daniel; Jaye, Cherno; Fisher, Daniel; C heong, Sang-Wook; Tyson, Trevor
Temperature Dependent Atomic and Electronic Structure of LuFe2 O4
APS March Meeting 2016 (Baltimore), abstract #R30.007

Wu, Tao; Tyson, Trevor; Zhang, Han; Abeykoon, Milinda
Temperature Dependent Structure of Thermoelectric $Ca_3 Co_4 O_9$
APS March Meeting 2016 (Baltimore), abstract #P32.012

Yu, Tian; Zhang, Han; Croft, Mark; Scofield, Megan; Bobb-Semple, Dara; Tao, Jing; Jaye, Cherno; Fisher, Daniel; Wong, Stanislaus; Tyson, Trevor
Phase Transitions in Nanoscale $SrTiO_3$
APS March Meeting 2016 (Baltimore), abstract #C30.005

2015 (Work to be presented at March 2015 American Physical Society Meeting)

Tyson, Trevor; Yu, Tian; Bai, Jianming; Abeykoon, Milinda; Lalancette, Roger
On Structural States of Multiferroic $InMnO_3$
APS March Meeting 2015 (San Antonio), abstract #V1.130

Yu, Tian; Zhang, Han; Tyson, Trevor; Chen, Zhiqiang; Abeykoon, Milinda; Nelson, Christie; Bezmatern ykh, Leonard
A study of the origin of large magnetic field coupled electric polarization in $HoAl(BO3)_4$
APS March Meeting 2015 (San Antonio), abstract #Q6.004

Tyson, Trevor; Yu, Tian; Croft, Mark; Scofield, Megan; Bobb-Semple, Dara; Tao, Jing; Jaye, Cherno; Fischer, Daniel; Wong, Stanislaus
Polar State in Freestanding Strontium Titanate Nanoparticles
APS March Meeting 2015 (San Antonio), abstract #D6.012

Zhang, Han; Tyson, Trevor; Hong, Xinguo; Scofield, Megan; Wong, Stanislaus

Structural Stability of Nano-scale $SrTiO_3$ Under Pressure
APS March Meeting 2015, abstract #B6.002

2014 (Work to be presented at March 2014 American Physical Society Meeting)

1. H. Zhang, T. Yu, T. A. Tyson, C. Nelson and Leonard Bezmaternykh, Probing the Origin of Large Magnetic Field coupled Electric Polarization in the RAl3(BO3)4 system, Abstract A41.00012 (Denver, March 2014)

2. H. Chen, T. Yu, T. A. Tyson, A. Abeykoon, K. Ahn and Y. Chen, Temperature Dependent Properties of E-Phase Perovskite ScMnO3, Abstract S41.00001 (Denver, March 2014)

3. T. Yu, P. Gao, T. Wu, T. Tyson, X. Hong, Y. Chen and R. Lalancette, Local Structural Changes at Low Temperature in Hexagonal InMnO3, Abstract S41.00002 (Denver, March 2014)

4. Y. Zhang, T. Yu and T. A. Tyson, Crystal Structure and Physical Properties of Multiferroic TmMnO3single crystals, Abstract S41.00005 (Denver, March 2014)

5. T. Tyson, T. Wu, T. Yu and M. Abeykoon, "Local and Intermediate Range Structure of Thermoelectric Ca3Co4O9" , Abstract H1.00090 (Denver, March 2014)

2013

1. 2013APS..MARB21011W **(Oral)**
Wu, Tao; Tyson, Trevor A.; Chen, Haiyan; Chen, Zhiqiang; Tappero, Ryan; Ahn, Keun H.; Kim, Sungbaek; Cheong, Sang-Wook
Insights on Electric Polarization in E-type $RMnO_3$
American Physical Society, APS March Meeting 2013, March 18-22, 2013, abstract #B21.011

2. 2013APS..MARB21010T **(Oral)**
Tyson, Trevor; Yu, Tian; Wu, Tao; Dubourdieu, Catherine; Cheong, Sang-Wook
Critical Structural Parameters Influencing Magnetic Transition Temperatures in Multiferroic Hexagonal $RMnO_3$
American Physical Society, APS March Meeting 2013, March 18-22, 2013, abstract #B21.010

3. 2013APS..MARB21009C **(Poster)**
Chen, Haiyan; Yu, Tian; Gao, Peng; Tyson, Trevor; Ahn, Keun Hyuk
Temperature Dependent Properties of Perovskite Small R-Ion $RMnO_3$ Systems
American Physical Society, APS March Meeting 2013, March 18-22, 2013, abstract #B21.009

4. 2013APS..MAR.H1061T **(Oral)**
Tyson, Trevor; Yu, Tian; Dubourdieu, Catherine
Chen, Haiyan; Yu, Tian; Gao, Peng; Tyson, Trevor; Ahn, Keun Hyuk
Structure and Properties of Hexagonal R_xMnO_{3+d}
American Physical Society, APS March Meeting 2013, March 18-22, 2013, abstract #H1.061

5. 2013APS..MARN12010B **(Oral)*)***

Bai, Jianming; Wu, Tao; Tyson, Trevor A.; Chen, Haiyan; Pandya, Kaumudi; Jaye, Cherno; Fischer, Daniel

Role of Chemical Doping in Enhancement of Thermoelectric Properties of $Ca_3Co_4O_9$

American Physical Society, APS March Meeting 2013, March 18-22, 2013, abstract #N12.010

2012

1. 2012APS..MART32011G

Low Temperature Structural of ScMnO3

Gao, Peng; Yu, Tian; Tyson, Trevor A.; Hong, Xinguo; Chen, Zhiqiang; Ghose, Sanjit; Ehm, Lars; Liu, Zhenxian

American Physical Society, APS March Meeting 2012, February 27-March 2, 2012, abstract #T32.011 Feb 2012 ***(Oral)***

2. 2012APS..MART32010Y

Synthesis of Perovskite ScMnO3 under High Temperature and Pressure

Yu, Tian; Gao, Peng; Tyson, Trevor A.

*American Physical Society, APS March Meeting 2012, February 27-March 2, 2012, abstract #T32.010 Feb 2012****(Oral)***

3. 2012APS..MART32006C

Electronic and Structural Properties Near the Ferroelectric Transition in Multiferroic Hexagonal RMnO3

Chen, Haiyan; Tyson, Trevor; Wu, Tao; Bai, Jianming; Ahn, Ken; Pandya, Kumi; Kim, S. B.; Cheong, Sang-Wook

American Physical Society, APS March Meeting 2012, February 27-March 2, 2012, abstract #T32.006 Feb 2012 ***(Oral)***

4. 2012APS..MAR.K1113Y

Electronic, Magnetic and Thermal Properties of Electron Doped YMnO3

Yu, Tian; Gao, Peng; Tyson, Trevor A.

American Physical Society, APS March Meeting 2012, February 27-March 2, 2012, abstract #K1.113 Feb 2012 ***(Oral)***

5. 2012APS..MARD22007T

Local Atomic and Electronic Structure of K0.8Fe1.6+xSe2: Structural Order and Disorder

Tyson, Trevor; Yu, Tian; Han, Su Jung; Croft, Mark; Gu, Genda D.; Dimitrov, Ivo; Li, Qiang

American Physical Society, APS March Meeting 2012, February 27-March 2, 2012, abstract #D22.007 Feb 2012 ***(Oral)***

6. 2012APS..MARA17010W

The Origin of Enhanced High Temperature Electron Transport in Thermoelectric Ca3Co4O9

Wu, Tao; Tyson, Trevor A.; Chen, Haiyan; Bai, Jianming; Jaye, Cherno

American Physical Society, APS March Meeting 2012, February 27-March 2, 2012, abstract #A17.010 Feb 2012 ***(Oral)***

7. 2012APS..MARA17007B
Thermoelectric and Structural Properties of the Chemically Doped Ca3Co4O9 System
Bai, Jianming; Wu, Tao; Tyson, Trevor A.; Chen, Haiyan
American Physical Society, APS March Meeting 2012, February 27-March 2, 2012, abstract #A17.007 Feb 2012 ***(Oral)***

2011

T. Wu, H. Chen, T. A. Tyson, R. Tappero, L. Huang, S. Kim and S.-W. Cheong, "Local and Long-Range High Pressure Structure of Orthorhombic REMnO3", to be presented at oral at March 21–25, 2011; Dallas, Texas, Abstract D33.00005 *(Oral)*

T. Yu, P. Gao and T. A. Tyson, "Structure and Magnetic Properties of Electron Doped $YMnO_3$", to be presented at oral at March 21–25, 2011; Dallas, Texas, Abstract B33.00013 *(Oral)*

P. Gao, H. Chen, T. A. Tyson, Z. Liu, J. Bai, L. Wang, Y. Choi, and S.-W. Cheong "Anomalous Phonon Behavior in Orthorhombic LuMnO3 at Low Temperature", to be presented at oral at March 21–25, 2011; Dallas, Texas, Abstract D33.00007 *(Oral)*

2010

1. T. Wu, L. Wang, T. A. Tyson, H. Chen, S. Kim and S. W. Cheong, "High pressure structure of Orthorhombic Multiferroic Systems", ", Presented at the APS 2010 March Meeting (Portland), March 15-19, abstract #D24.002. (Oral)

2. P. Gao, Z. Liu, T. A. Tyson, and S. W. Cheong, "Low Temperature Phonon Properties of Orthorhombic $REMnO_3$", ", Presented at the APS 2010 March Meeting (Portland), March 15-19, abstract #D24.001. (Oral)

3. P. Gao, A. Masadeh, T. A. Tyson, Th. Profen, S. Goche and S.-W. Cheong, "Low Temperature Local Structure of Multierroic of $ReMn_2O_5$", ", Presented at the APS 2010 March Meeting (Portland), March 15-19, abstract #B36.008. (Oral)

4. T. A. Tyson, T. Wu, H. Chen, and S. W. Cheong, "Local Structure of Hexagonal $HoMnO_3$ at High Temperature", Presented at the APS 2010 March Meeting (Portland), March 15-19, abstract #D24.005. (Oral)

5. Tao Wu, Trevor A. Tyson, Hsin Wang and Haiyan Chen
"Thermoelectric and Structural Properties of the Cu Doped Ca3Co4O9 System"
Fall 2010 MRS Meeting Boston, Oral Presentation LL6.11

6. T. Wu, T. A. Tyson, H. Wang and Q. Li, "Thermoelectric Properties of the Chemically Doped $Ca_3Co_4O_9$ System: A Structural Perspective", Presented at the APS 2010 March Meeting (Portland), March 15-19, abstract #Y29.005. (Oral)

7. H. Chen, J. Bai, T. A. Tyson, "In-situ XRD Investigations of the Solid--state Synthesis of Doped Thermoelectric Cobalt Oxides", ", Presented at the APS 2010 March Meeting (Portland), March 15-19, abstract #C1.129. (Poster)

2009

1. Chen, Zhiqiang; Gao, Peng; Tyson, Trevor. A.; Liu, Zhenxian; Hu, Jinzhu; Zhang, Chenglin; Kim, Sung-Baek; Cheong, Sang-Wook, "Pressure Dependence of Structure Stability of Multiferroic Hexagonal-$RMnO_3$"American Physical Society, 2009 APS March Meeting, March 16-20, 2009, abstract #J30.006, Oral Presentation

2. Deleon, M.; Tyson, T. A.; Chen, Z.; Cheong, S.-W., "Magnetic Field Dependent Changes in the Local Structure of $ReMn_2O_5$", American Physical Society, 2009 APS March Meeting, March 16-20, 2009, abstract #J30.003, Oral Presentation

3. Masadeh, A.; Tyson, T.; Cheong, S.-W., "Local Structure Investigation of $ReMn_2O_5$", American Physical Society, 2009 APS March Meeting, March 16-20, 2009, abstract #J30.002, Oral Presentation

4. Wu, T.; Tyson, T. A.; Chen, Z.; Jie, Q.; Li, Q.; Tu, J. J., "High Pressure Structural and Electrical Transport Properties of the $Ca_3Co_4O_9$ System", American Physical Society, 2009 APS March Meeting, March 16-20, 2009, abstract #K1.179, Oral Presentation

5. Wu, T.; Chen, Z.; Tyson, T. A.; Qin, Z.; Zhou, T.; Zhang, C.; Cheong, S.-W., "High Pressure Structure and Transport Properties of the $FeSe_{0.88}$ Superconductor", American Physical Society, 2009 APS March Meeting, March 16-20, 2009, abstract #Z35.005, Oral Presentation

6. Tyson, T. A.; Wu, T.; Woicik, J.; Ravel, B.; Ignatov, A.; Zhang, C.; Qin, Z.; Zhou, T.; Cheong, S.-W. , "Temperature Dependent Local Structure of $LaO_{1-x}F_xFeAs$", American Physical Society, 2009 APS March Meeting, March 16-20, 2009, abstract #Q35.011, Oral Presentation

2008

1. T. A. Tyson, M. Deleon, Q. Qian, A. Ignatov, S. Yoong, and S. W. Cheong, "Local Structure of the Multiferroic System RMn_2O_5", American Physical Society, APS March Meeting, March 13-17, 2006, abstract #D20.001. Oral Presentation.

2. Y. Qin, T. A. Tyson, S.-W. Cheon, and X Xu, "Phase diagram for Bi1-xCaxMnO3 ($x < 0.4$)", American Physical Society, 2008 APS March Meeting, March 10-14, 2008, abstract #W37.003. Oral Presentation.

Invited Talks

1. T. A. Tyson, P. Gao, H. Chen, T. Wu, K.H. Ahn,S-W. Cheong,
" Low Temperature Spin-Coupled Distortions and an Unusual Ferroelectric State in Multiferroic Hexagonal $REMnO_3$"
The first North American Core Shell Spectroscopy Conference held jointly with the 59th Denver X-Ray Conference, 2-6 August 2010, at the Denver Marriott Tech Center Hotel, Denver, CO, U.S.A. Invited talk

2. T. A. Tyson, Probing Local Structural Changes in Magnetic Oxides, presented at the "Analysis Techniques and Development, SSRL User Workshop", at the Stanford Synchrotron Radiation Laboratory on October 15th, 2008.

3. T. A. Tyson, " Spin-Lattice Coupling in RMn_2O_5 Multiferroic Oxides". European Materials Society Meeting in Strassbourg, France on May 28th , 2008.

4. T. A. Tyson, "Atomic Level Properties of Multiferroic and Thermoelectric Oxides", University of Vermont, Physics Department Seminar, Oct. 2008

5. T. A. Tyson, "Origin of Thermoelectricity in Layered Hexagonal Cobaltates", NSLS Brookhaven National Laboratory, 2008.

C. Summary of Work Completed Under DOE DEFG02-07ER46402

A detailed list of the publications resulting from the work under this grant precedes this summary. It includes a list of published papers, manuscripts in preparation, completed Ph. D. Theses and contributed talks. The following is an itemized summary of results from these publications.

Pressure Dependent Structural Changes and Predicted Electrical Polarization in Perovskite $RMnO_3$

High pressure x-ray diffraction (XRD) measurements on perovskite RMnO$_3$ (R=Dy, Ho and Lu) reveal that varying structural changes occurs for different R ions. Large lattice changes (orthorhombic strain) occur in $DyMnO_3$ and $HoMnO_3$ while the Jahn-Teller (JT) distortion remains stable. On the other hand, in the small R-ion system $LuMnO_3$, Mn-O bond distortions are observed between 4 and 8 GPa with a broad minimum in the JT distortion. High pressure infrared measurements indicate that a phonon near 390 cm^{-1} corresponding to the complex motion of the Mn and O ions changes anomalously for $LuMnO_3$. It softens in the 4 to 8 GPa region, which is consistent with the structural change in Mn-O bonds and then hardens at higher pressures. By contrast, the phonons continuously harden with increasing pressure for $DyMnO_3$ and $HoMnO_3$. Density functional theory methods show that E-phase $LuMnO_3$ is the most stable phase up to the 10 GPa pressure examined. Simulations indicate that the distinct structural change under pressure in $LuMnO_3$ can possibly be used to optimize the electric polarization by pressure/strain.

Magneto-Structural Correlations in Multiferroic $HoAl_3(BO_3)_4$

The system $HoAl_3(BO_3)_4$ has recently been found to exhibit a large magntoelectric effect. To understand the mechanism, macroscopic and atomic level properties of $HoAl_3(BO_3)_4$ were explored by temperature and magnetic field dependent heat capacity measurements, pressure and temperature dependent x-ray diffraction measurements, as well as temperature and magnetic field dependent x-ray absorption fine structure measurements. The experimental work was complemented by density functional theory calculations. An anomalous change in the structure is found in the temperature range where large magnetoelectric effects occur. No significant structural change or distortion of the HoO_6 polyhedra is seen to occur with magnetic field. However, the magnetic field dependent structural measurements reveal enhanced correlation between neighboring HoO_6 polyhedra. This observed response is seen to saturate near 3 T. A qualitative atomic level description of the mechanism behind the large electric

polarization induced by magnetic fields in the general class of $RAl_3(BO_3)_4$ systems (R= rare earth) is developed.

Strong Electron Hybridization and Fermi-to-Non-Fermi Liquid Transition in $LaCu_3Ir_4O_{12}$

Heavy transition metal (4*d* and 5*d)* oxides with spin-orbit coupling exhibit many interesting physical properties. The $AA'_3B_4O_{12}$- type quadruple perovskite $LaCu_3Ir_4O_{12}$ prepared at high pressure (9 GPa) and temperature (1523 K) crystallizes in cubic symmetry (*Im*-3, *a* = 7.52418(3) Å) with square planar CuO_4 and octahedral IrO_6 coordination as established from synchrotron powder x-ray diffraction studies. Both crystal structure and x-ray absorption near edge spectroscopy analyses indicate formal oxidation states of $LaCu^{2+}{}_3Ir^{3.75+}{}_4O_{12}$. The temperature dependence of resistivity of $LaCu_3Ir_4O_{12}$ is metallic down to 5 K, with Femi-liquid behavior above *T** ~ 155 K, and non-Fermi-liquid behavior blow *T**. The two-fluid behavior of magnetic susceptibility and the dramatic downturn of the resistivity at T* indicate strong Cu^{2+} 3*d* and $Ir^{3.75+}$ 5*d* orbital hybridization below T*, also supported by an enhanced electronic specific heat coefficient at low temperature. Theoretical calculations are in good agreement with the experimental results and show that the electronic structure of $LaCu_3Ir_4O_{12}$ is different from that of $CaCu^{2+}{}_3Ir^{4+}{}_4O_{12}$, which is also metallic down to 0.5 K, but presents non-Fermi liquid behavior above T* ~ 80 K, and strong Cu-3*d* – Ir-5*d* orbital coupling at significantly lower temperature (T < T* ~ 80 K).

Polar State in Freestanding Strontium Titanate Nanoparticles

Monodispersed strontium titanate nanoparticles were prepared and studied in detail. It is found that ~10 nm as-prepared stoichiometric nanoparticles are in a polar structural state (with possibly ferroelectric properties) over a broad temperature range. A tetragonal structure, with possible reduction of the electronic hybridization is found as the particle size is reduced. In the 10 nm particles, no change in the local Ti-off centering is seen between 20 and 300 K. The results indicate that nanoscale motifs of $SrTiO_3$ may be utilized in data storage as assembled nano-particle arrays in applications where chemical stability, temperature stability and low toxicity are critical issues.

Observation of Magnetic Transitions Coupled with Structural Changes in Hexagonal $InMnO_3$

Two magnetic ordering temperatures are found in $InMnO_3$, the paramagnetic to antiferromagnetic temperature near ~118 K and a lower possible spin rotation transition near ~42 K. Multiple length scale structural measurements reveal enhanced local distortion found to be connected with tilting of the MnO_5 polyhedra as temperature is reduced. Strong coupling is observed between the lattice and the spin manifested as changes in the structure near both of the magnetic ordering temperatures (at ~42 K and ~ 118 K). External parameters such as pressure are expected to modify the coupling.

Absence of Significant Structural Changes Near the Magnetic Ordering Temperature in Small-Ion Rare Earth Perovskite *R*MnO_3

Detailed structural measurements on multiple length scales were conducted on a new perovskite, $ScMnO_3$, and on orthorhombic $LuMnO_3$ as a benchmark. Complementary density functional theory (DFT) calculations were carried out, and predict that $ScMnO_3$ possesses E-phase magnetic order at low temperature with displacements of the Mn sites (relative to the high

temperature state) of ~0.07 Å, compared to ~ 0.04 Å predicted for $LuMnO_3$. However, detailed local, intermediate and long-range structural measurements by x-ray pair distribution function analysis, single crystal x-ray diffraction and x-ray absorption spectroscopy, find no local or long-range distortions on crossing into the low temperature E-phase of the magnetically ordered state. The measurements place upper limits on any structural changes to be at most one order of magnitude lower than density functional theory predictions and suggest that this theoretical approach does not properly account for the spin-lattice coupling in these oxides and may possibly predict the incorrect magnetic order at low temperatures. The results suggest that the electronic contribution to the electrical polarization dominates and should be more accurately treated in theoretical models.

Observation of Ferroelectricityin $InMnO_3$

Single crystals of InMnO3 were synthesized in our laboratory and detailed electric polarization and structural studies were conducted. Single crystal synthesis, structure, electric polarization and heat capacity measurements on hexagonal $InMnO_3$ show that this small R ion in the $RMnO_3$ series is ferroelectric (space group $P6_3cm$). Structural analysis of this system reveals a high degree of order within the MnO_5 polyhedra but significant distortions in the R-O bond distributions compared to the previously studied materials. Point-charge estimates of the electric polarization yield an electrical polarization of ~7.8 $\mu C/cm^2$, 26% larger than the well-studied $YMnO_3$ system. This system with enhanced room temperature polarization values may serve as a possible replacement for $YMnO_3$ in device application. This work resolved conflicting measurements on polycrystalline samples previously published and shows that the system is a stable ferroelectric.

New E-Phase Perovskite System, $ScMnO_3$

The rare-earth manganites $RMnO_3$ (R = rare earth) are a class of important multiferroics with stable hexagonal structures for small R ion radius (Sc, Lu, Yb, ...). Metastable perovskite phases of these systems possess intriguing electronically driven electrical polarization, but the synthesis of the perovskite phase for the end member $ScMnO_3$ system has proven to be elusive. To understand the origin of electric polarization in E-phase magnetically order systems, we sensitized a new small ion perovskite with very simple atomic and electronic structure and the smallest ion size available to date, $ScMnO_3$. We report the structure of a new monoclinic P21/n perovskite phase of $ScMnO_3$ synthesized from the hexagonal phase under high-pressure and high temperature conditions. This extends the small ion region for so-called E-phase electronically driven ferroelectric manganese perovskites. The systems serves as a simple test of theories of E-phase perovskite (no magnetic ions on the R site and low number of electrons at each atomic site).

Stability and Structural Changes of Hexagonal $RMnO_3$ Under Pressure at High Temperature

High pressure infrared and high pressure x-ray diffraction measurements have been conducted on a broad range of hexagonal $RMnO_3$ systems at ambient temperature. Pressures up to 20 GPa were explored. Interestingly, no structural transition to the higher density orthorhombic phase was observed in either $YMnO_3$, $HoMnO_3$ or $LuMnO_3$. This shows that thermal energy is needed to effect the reconstructive phase transition (involving breaking of

bonds) between the hexagonal and orthorhombic phases. It is found that the a-axis is more readily compressed that the c-axis. $LuMnO_3$ exhibits the largest asymmetry in the c-axis to a-axis compressibility and is expected to show the strongest changes in coupling between the in-plane Mn-Mn and Ho-Ho interactions. Infrared measurements were conducted over the frequency range 100 to 8000 cm^{-1}. Analysis of the phonon modes based on density functional calculation frozen phonon calculations reveal that the dominant change with pressure corresponds to the frequency of the apical O2 mode on the MnO_5 pyramids indicating that the tilting of the pyramids is modified under pressure. Investigation of the electrical polarization under pressure may enable the determination of strain stabilized highly polarized phases. In further experiments we combined the high pressure measurements in diamond anvil cells with moderate sample temperatures. For temperatures of 373, 473 , 573, 673 K and pressures up to ~10 GPa no transformation of the hexagonal phase to the orthorhombic phase occurs.

Measurements molecular dynamics simulations in hexagonal $RMnO_3$

Measurements of the structure of hexagonal RMnO3 [R=rare earths (Ho) and Y] for temperatures significantly above the ferroelectric transition temperature (T_{FE}) were conducted to determine the nature of the transition. The local and long range structural measurements were complemented by ab initio molecular dynamics simulations. With respect to the Mn sites in $YMnO_3$ and $HoMnO_3$, we find no large atomic (bond distances or thermal factors), electronic structure changes, or rehybridization on crossing TFE from local structural methods. The local symmetry about the Mn sites is preserved. With respect to the local structure about the Ho sites, a reduction of the average Ho–O bond with increased temperature is found. Ab initio molecular dynamics calculations on HoMnO3 reveal the detailed motions of all ions. Above ~900 K there are large displacements of the Ho, O3, and O4 ions along the z axis which reduce the buckling of the MnO3/O4 planes. The changes result in O3/O4 ions moving to toward central points between pairs of Ho ions on the z-axis. These structural changes make the coordination of Ho sites more symmetric thus extinguishing the electric polarization. At significantly higher temperatures, rotation of the MnO5 polyhedra occurs without a significant change in electric polarization. The Born effective charge tensor is found to be highly anisotropic at the O sites but does not change appreciably at high temperatures.

Ferroelectricity in Nanomaterials

Monodisperse $SrTiO_3$ nanoparticles were prepared and studied. It is found that as-prepared nanoparticles nearly 10 nm in size are ferroelectric over a broad temperature range. No change in the local Ti-off centering is seen between 20 and 300 K. Indicating the stability of the ferroelectric state. The results indicate that nanoscale motifs of $SrTiO_3$ may be utilized in data storage as an alternative to $PbTiO_3$ and $BaTiO_3$ as assembled arrays (See attached manuscript). A broad range of particles sizes will be studied starting from the preliminary work. High pressure structural measurements on the nanoparticles will complement the large range of films measurements already available in the literature. The high temperature region will be explored in structural measurements between 10 K and 800 K.

Application of Developed methods to Complex Oxide Thermoelectrics and Layered Superconductors

We have utilized the techniques developed for this project to study the origin of thermoelectricity in cobalt oxide thermoelectrics .

Temperature dependent electrical resistivity, crystal structure and heat capacity measurements reveal a resistivity drop and electrical transport behavior change corresponding to a structural change near 400 K in $Ca_3Co_4O_9$. The lattice parameter c varies smoothly with increasing temperature while anomalies in a, b1 and b2 lattice parameters occur near 400 K. The Ca site in the Ca_2CoO_3 block becomes distorted and a change in electrical transport behavior is found above 400 K. Resistivity and heat capacity measurements as a function of temperature under magnetic field combined with Co L-edge x-ray absorption spectra reveal only a weak spin contribution to this change. Reduced resistivity associated with the structural change enhances the thermoelectric properties at moderately high temperatures and points to the electrical transport behavior change as a mechanism for improved ZT in this thermoelectric oxide.

Resistivity and Seebeck coefficient measurements on $Ca_3Co_{4-x}Fe_xO_9$ (x = 0, 0.05, 0.1, 0.2 and 0.25) reveal enhanced thermoelectric performance with an optimal x value of 0.2. X-ray diffraction measurements show continuous Fe doping into the host lattice, while X-ray absorption experiments reveal that Fe substitutes for Co in the Ca2CoO3 (rock salt) block. The Fe substitution for Co produces electron doping. The local structure around Fe in the Ca2CoO3 block becomes disordered, while the structure in the conducting CoO_2 layer becomes more ordered. The structural change in the CoO2 layer plays the key role to enhance the electron transport. The highest ordered structure is achieved at x = 0.2 with the lowest resistivity. Soft X ray absorption measurements find no Co site spin-state change with Fe doping. Thermoelectric property enhancement associated with doping induced structural change points to a new approach for creating materials with improved ZT in complex oxide systems.

Application of Methods to Fe-based Superconductors.

In collaboration Dr. Q. Li's group (Brookhaven National Laboratory), the local structure of superconducting single crystals of $K_{0.8}Fe_{1.6+x}Se_2$ with T_c = 32.6 K was studied by x-ray absorption spectroscopy. Near-edge spectra reveal that the average valence of Fe is 2+. The room temperature structure about the Fe, K, and Se sites was examined by iron, selenium, and potassium *K*-edge measurements. The structure about the Se and Fe sites shows a high degree of order in the nearest-neighbor Fe-Se bonds. On the other hand, the combined Se and K local structure measurements reveal a very high level of structural disorder in the K layers. Temperature-dependent measurements at the Fe sites show that the Fe-Se atomic correlation follows that of the Fe-As correlation in the superconductor LaFeAsO0.89F0.11, having the same effective Einstein temperature (stiffness). In $K_{0.8}Fe_{1.6+x}Se_2$, the nearest-neighbor Fe-Fe bonds have a lower Einstein temperature and higher structural disorder than in $LaFeAsO_{0.89}F_{0.11}$. The moderate Fe site and high K site structural disorder is consistent with the high normal state resistivity seen in this class of materials. For higher shells, an enhancement of the second-nearest neighbor Fe-Fe correlation is found just below T_c, possibly due to changes in magnetic or local structural ordering.

High carrier mobility in transparent $Ba_{1-x}La_xSnO_3$ crystals with a wide bandgap

We discovered that perovskite (Ba,La)SnO_3 can have excellent carrier mobility even though its band gap is large. The Hall mobility of Ba0.98La0.02SnO3 crystals with the n-type carrier concentration of ~8-10_10^{19} cm^{-3} is found to be ~10^3 cm^2 V^{-1} s^{-1} at room temperature, and the precise measurement of the band gap Δ of a $BaSnO_3$ crystal shows Δ = .05 eV, which is

significantly larger than those of other transparent conductive oxides. The high mobility with a wide band gap indicates that (Ba,La)SnO_3 is a promising candidate for transparent conductor applications and also epitaxial all-perovskite multilayer devices.

2007-2008

Exploring the Orthorhombic RM_2O_5 Systems

Our initial measurements of the temperature dependent (3 K to 500 K) local structure of $TbMn_2O_5$ showed that (1) the Tb-O bond distribution contributed significantly to the observed low temperature polarization and (2) that significant structural changes in the Tb-O distribution occur when the Tb ions order magnetically at low temperature. We conducted a series of measurement of the local structure of $DyMn_2O_5$ covering the temperature range 3K to 300 and covering magnetic fields from 0 to 9 T at 3 K. These magnetic field dependent local structural measurements were conducted at 3 K in magnetic fields verifying from 0 to 9 T (0.33 T steps). **A very weak but reproducible variation of the Dy-O distribution with magnetic field was observed. The Dy-O thermal factor is enhanced with magnetic field (high polarization state.). These results indicate that in this system, the R site is central to the observed spin-lattice coupling. The weak variation of the Dy-O distribution with magnetic field is consistent with the low polarization observed. The results provide direct evidence that theoretical models of these materials must properly treat the spin ordering on the R sites (and not just the Mn sites).**

Experiments on the Spin-Lattice Coupling in hexagonal $RMnO_3$Systems

Detailed temperature dependent XAFS local structure measurements were conducted on the hexagonal $HoMnO_3$ system (and on the $LuMnO_3$ and $YMnO_3$ systems). Previous heat capacity measurements revealed second order transitions at ~70 K, ~33 K and ~5 K. Neutron diffraction measurements associated these features with the Neel temperature and the spin reorientation temperatures of the triangular Mn lattice. The lowest temperature feature corresponds to the Ho site magnetic ordering temperature. The nature of the crystal structure enabled us to extract information on the out-of plane Mn-O bonds and the in-plane Mn-O and Mn-Mn bonds. **No changes are observable in the out-of-plane (along c) Mn-O distribution. However, the in-plane Mn-O distribution shows second order λ-type features at all three magnetic ordering temperatures. The in-plane Mn-Mn bond distances reveal the same effect. This system thus possesses very strong spin-lattice coupling which may be tuned by in-plane strain.**

High pressure infrared and high pressure x-ray diffraction measurements have been conducted on a broad range of hexagonal REMnO3 systems. We have found large anisotropies in the compressibility of the a and c lattice parameters. The a-axis is significantly more compressible than the c axis. **Also, we have observed the creation of a new crystalline phase in the LuMnO3 system at ~10 GPa.** No change in structure was found in the IR and XRD measurements on YMnO3 and HoMnO3 for pressures up to 22 GPa.

Complex Oxide Thermoelectrics

We have utilized the techniques developed for this project to study the origin of thermoelectricity in cobalt oxide thermoelectrics as a collaboration with Dr. Q. Li (Brookhaven Nat. Lab.). Determining the origin of thermoelectricity in complex oxides is important from the perspectives of device application and fundamental physics. We have combined temperature dependent local structural measurements with first principles density functional calculations to develop a three dimensional local structure model of the misfit system $[Ca_2CoO][CoO_2]_{1.61}$ (referred to as $Ca_3Co_4O_9$) which has a rocksalt structure stacked incommensurately on a hexagonal CoO_2 lattice. The local structural measurements reveal a low coordination of Co(2) in the rock salt layer. The temperature dependence of the Co(1) in the CoO_2 layer

is found to be normal above ~75K. Density functional computations show that the reduction of the coordination of Co(2) is due to the formation of chains of $Co(2)O_x$ in the a-b plane linked to the Ca-O layers by c-axis Co(2)-O bonds. **The reduced dimensionality introduced by the chain-like structure in the rock-salt layer and high atomic order in the CoO_2 layer may be the origin of the low thermal conductivity and high electrical conductivity in the respective layers yielding a high thermoelectric figure of merit.**

2008-2009

Exploring the Spin-Lattice Coupling and Multiferroic Behavior in Hexagonal RMnO3 Systems

Local structural measurements were performed on hexagonal HoMnO3 in order to ascertain the changes in bond distances which accompany magnetic ordering transitions. Changes in bond distances on crossing the magnetic ordering temperatures reveal spin-driven lattice distortions (spin Jahn-Teller distortions) The transition from paramagnetic to the antiferromagetic (noncollinear) phase near ~70 K is dominated by changes in the a-b plane nearest neighbor Mn-Mn bond distances. The spin rotation transition near 40 K involves both Mn-Mn and nearest neighbor Ho-Mn interactions while the low temperature transition below 10 K involves all interactions, Mn-Mn, Ho-Mn (nearest and next nearest) and nearest neighbor a-b plane Ho-Ho correlations. The similarity in magnitude of the change in J(Mn-Mn) and J(Ho-Mn) enhances the system frustration. The structural changes were interpreted in terms of a model of competing spin
order and local structural distortions. Density functional (DFT) calculations are used to estimate the energies associated with ionic displacements and yield bond energy changes consistent with observed optical mode shifts. They also reveal asymmetric polarization of the charge density at the Ho, O3 and O4 sites along the z-axis in the ferroelectric phase. The polarization facilitates coupling between Ho atoms on neighboring z-axis planes. The results indicate that hydrostatic pressure or chemical pressure may be used to enhance the electrical polarization in these materials and couple it more strongly with the spin degrees of freedom.

Stability and Structural Changes of Hexagonal $RMnO_3$ Under Pressure at High Temperature

High pressure infrared and high pressure x-ray diffraction measurements have been conducted on a broad range of hexagonal $RMnO_3$ systems at ambient temperature. Pressures up to 20 GPa were explored. Interestingly, no structural transition to the higher density orthorhombic phase was observed in either$YMnO_3$, $HoMnO_3$ or $LuMnO_3$. This shows that thermal energy is needed to effect the reconstructive phase transition (involving breaking of bonds) between the hexagonal and orthorhombic phases. It is found that the a-axis is more readily compressed that the c-axis. $LuMnO_3$ exhibits the largest asymmetry in the c-axis to a-axis compressibility and is expected to show the strongest changes in coupling between the in-plane Mn-Mn and Ho-Ho interactions. Infrared measurements were conducted over the frequency range 100 to 8000 cm^{-1}.

Analysis of the phonon modes based on density functional calculation frozen phonon calculations reveal that the dominant change with pressure corresponds to the frequency of the apical O2 mode on the MnO5 pyramids indicating that the tilting of the pyramids is modified under pressure. Investigation of the electrical polarization under pressure may enable the determination of strain stabilized highly polarized phases. In further experiments we combined the high pressure measurements in diamond anvil cells with moderate sample temperatures. For temperatures of 373, 473 , 573, 673 K and pressures up to ~10 GPa no transformation of the hexagonal phase to the orthorhombic phase occurs. In our recent high pressure synthesis experiments, polycrystalline $LuMnO_3$, $HoMnO_3$ in the orthorhombic phase were obtained by heating to 1573 K at a pressure of 6 GPa. A monoclinic perovskite-like phase of $ScMnO_3$was also prepared.

Nature of the Local Distortions in RMn_2O_5

XAFS measurements reveal large distortions of the Tb-O distributions away from the form predicted by the accepted Pbam space group. Understanding the structure in terms of the space group and local distortions is central to understanding multiferroic systems. Rather complex magnetic ordering schemes have been propose to break the inversion asymmetry present in Pbam (which does not allow for the observed electrical polarization). Determination of the structure on a long length scale (up to ~40 Å) for these highly ordered materials is being conducted. Hard x-rays (80 KeV) were used to measure total scattering including the diffuse pattern and the Bragg reflections (pair distribution function (PDF) measurements). The full spectrum was then inverted and fits were attempted in order to determine (1) the unit cell and space group and (2) the nature of the local or longer range distortions. Measurements at room temperature assuming the Pbam structure reveal that large deviation in the r-space fits beyond the first unit cell which get progressively worse with distance. Measurements at low temperatures reveal even more significant deviations away from the established Pbam structure. Examination of the thermal parameters shows that the oxygen clusters are distorted. Fits to models with larger super cells are in progress in order to accommodate the distortions.

Application of Developed methods to Complex Oxide Thermoelectrics and Layered Superconductors

We have utilized the techniques developed for this project to study the origin of thermoelectricity in cobalt oxide thermoelectrics as a collaboration with Dr. Q. Li (Brookhaven Nat. Lab.). Determining the origin of thermoelectricity in complex oxides is important from the perspectives of device application and fundamental physics. We have combined temperature dependent local structural measurements with first principles density functional calculations to develop a three dimensional local structure model of the misfit system $[Ca_2CoO_3][CoO_2]_{1.61}$ (referred to as $Ca_3Co_4O_9$) which has a rocksalt structure stacked incommensurately on a hexagonal CoO_2 lattice. The local structural measurements reveal a low coordination of Co(2) in the rock salt layer. The temperature dependence of the Co(1) in the CoO_2 layer is found to be normal above ~75K. Density functional computations show that the reduction of the coordination of Co(2) is due to the formation of chains of $Co(2)O_x$ in the a-b plane linked to the Ca-O layers by c-axis Co(2)-O bonds. The reduced dimensionality introduced by the chain-like structure in the rock-salt layer and high atomic order in the CoO layer may be the origin of the low thermal conductivity and high electrical conductivity in the respective layers yielding a high thermoelectric figure of merit.

The methods develop and utilized in this proposal were further applied to the new Fe based system of superconductors where we determine the nature of the electronic structure for the doped and parent in $LaO_{1-x}F_xFeAs$. Only the Fe layer is found to exhibit a chemical/valence response to doping. Local structural measurements reveal that doping reduces the stating disorder in the Fe-As correlation. More importantly, the Fe-Fe correlations are found to be enhanced by doping suggesting that the doped superconducting state is driven by Fe-Fe spin correlations.

More recently, we examined a possible new 2D superconducting system where order mixed valence Ni^{1+} and Ni^{2+} exists. Like the parent compound in $LaO_{1-x}F_xFeAs$, $La_4Ni_3O_8$ exhibits a spin density wave (SDW) transition which is supported by our XAFS measurements. Suppression of the SDW is expected to create a new superconducting material. The methods developed to explore the spin lattice correlations in the multiferroics have been crucial to shedding light on the superconducting state in both of these materials.

2009-2010

Nature of the ferroelectric and structural transitions in hexagonal $REMnO_3$.

The first temperature dependent (300 K to 1038 K) studies of the local structure about the RE and Mn site in hexagonal $REMnO_3$ across the ferroelectric transition for RE=Ho were conducted (Fig. 1 and Fig. 2). No abrupt changes are seen. However, shortening of the Ho-O bond and changes in the Mn(3d) and

neighboring Mn(4p) hybridization was observed indicating that a change in electronic structure may play the major role in the switching on/off the electrical polarization.

Parallel temperature dependent x-ray diffraction measurements were conducted on $HoMnO_3$ over the range 300K to 1400K. An abrupt change in the x-ray pattern at 1350K signals the onset of the high temperature paraelectric high symmetry structure. No abrupt changes in structure are observed on crossing the ferroelectric transition temperature near 875 K.

Properties of the orthorhombic phase E-magnetic phase perovskites

Samples of orthorhombic $LuMnO_3$ and $HoMnO_3$ were synthesized by high pressure (3 GPa) and high temperature (1273 K) treatment of the corresponding hexagonal materials. The origin of the theoretically predicted high electrical polarization was probed. Infrared absorption (10 K to 300K) revealed the onset of new phonons below 40K and as well as anomalous phonon hardening in the Lu system (Fig. 5). Temperature dependent XAFS measurements of the Dy, Ho and Lu systems revealed large changes in the Mn-Mn and Mn-O-Mn correlation in the Lu system only thus identifying the type of dynamic change responsible for the large polarization at low temperature.

High pressure x-ray diffraction measurements were conducted on $DyMnO_3$ and $LuMnO_3$ over the pressure range 1 atm to 11 GPa (110,000 atm) . The Lu system is found to have more isotropic ab plane compressibility. Application of pressure is found to enhance the electrical polarization and points to the use of strain as a parameter to tune the electrical polarization of these materials. These materials are predicted to be electronically driven ferroelectrics.

Structure and Dynamics of $REMn_2O_5$

The local a structure of $REMn_2O_5$ system was measured by x-ray and neutron total scattering (diffuse + Bragg scattering) pair distribution function (PDF) methods between 10 K and 300 K covering the magnetically ordered range (below ~ 45 K) with coupling between E and P. X-ray and neutron PDF measurements reveal the formation of nanoscale grains ~ 50 A at low temperature which lead to symmetry breaking (Fig. 9 and Fig. 10.). The nanoscale structures may play an important role in the observed low temperature polarization.

The low energy lattice excitations (phonons) and magnetic excitation were studied by inelastic neutron scattering. Measurements were made deep in the magnetically ordered state (9 K) and above it (at 50 K and 150 K). Data are being analyzed to determine the energies of the phonons and magnons. The full phonon structure is being compared with our DFT simulations to separate the measured magnetic and phonon peaks in the inelastic neutron scattering data.