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Final Report: New Quasi Low-Dimensional 4d and 5d Transition Metal Oxides with Correlated Electronic Properties - Synthesis and Characterizations

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6. AUTHORS
Martha Greenblatt

5d. PROJECT NUMBER

5e. TASK NUMBER

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7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
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14. ABSTRACT

Polar oxides are of much interest due to their symmetry-dependent properties including ferroelectricity/multiferroics, magnetoelectricity, piezoelectricity, pyroelectricity, and second-order harmonic generation (SHG) effect, which are all important for technological applications.[1] However, polar crystal design and synthesis is challenging, because multiple effects, such as steric or dipole-dipole interactions, typically combine to form non-polar structures, and the number of known polar, especially magnetoelectric materials, is still extremely few.[2] Therefore, as one of the focus of this program, we embarked on high pressure (HP) and high

15. SUBJECT TERMS

synthesis, solid state oxides, corundum and double perovskites, crystal and magnetic structure, magnetic, transport, second harmonic generation superconducting, dielectric and magnetoelectric properties

| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT | 15. NUMBER OF PAGES | 19a. NAME OF RESPONSIBLE PERSON |
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| a. REPORT | b. ABSTRACT | c. THIS PAGE | | | Martha Greenblatt |
| UU | UU | UU | UU | | 19b. TELEPHONE NUMBER 848-445-3277 |

## Report Title

Final Report: New Quasi Low-Dimensional 4d and 5d Transition Metal Oxides with Correlated Electronic Properties - Synthesis and Characterizations

## ABSTRACT

Polar oxides are of much interest due to their symmetry-dependent properties including ferroelectricity/multiferroics, magnetoelectricity, piezoelectricity, pyroelectricity, and second-order harmonic generation (SHG) effect, which are all important for technological applications. [1] However, polar crystal design and synthesis is challenging, because multiple effects, such as steric or dipole-dipole interactions, typically combine to form non-polar structures, and the number of known polar, especially magnetoelectric materials, is still extremely few.[2] Therefore, as one of the focus of this program, we embarked on high pressure (HP) and high temperature (HT) synthesis to find new interesting and potentially useful polar materials. As will be shown here, we have been exceedingly successful, and opened a new path to design new polar and potentially multifunctional useful materials with corundum-type structure of general formula A2BB'O6. In addition, HP and HT were also used to prepare new metastable double perovskites and quadruple perovskites with unusual structures and properties. In addition, ambient pressure and more conventional solid state methods to synthesize new phases with 3d, 4d and 5d transition metals and exotic correlated electronic properties was used in parallel with the HP/HT projects.

As the results enumerated below show, a large number of new materials were synthesized; their physical properties were characterized in detail with a multitude of state-of-the-art techniques, and coupled experiment and theory lead to deeper understanding of the observed properties, as well as guiding synthesis of new phases

**Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:**

**(a) Papers published in peer-reviewed journals (N/A for none)**

| Received | | Paper |
|---|---|---|
| 02/16/2016 | 4.00 | Maria Retuerto, Zhiping Yin, Thomas J. Emge, Peter W. Stephens, Man-Rong Li, Tapati Sarkar, Mark C. Croft, Alexander Ignatov, Z. Yuan, S. J. Zhang, Changqing Jin, Robert Paria Sena, Joke Hadermann, Gabriel Kotliar, Martha Greenblatt. Hole Doping and Structural Transformation in CsTl, Inorganic Chemistry, (02 2015): 1066. doi: 10.1021/ic502400d |
| 02/16/2016 | 12.00 | J. W. Freeland, S. Barraza-Lopez, M. Greenblatt, J. Chakhalian, D. Choudhury, P. Rivero, D. Meyers, X. Liu, Y. Cao, S. Middey, M. J. Whitaker. Anomalous charge and negative-charge-transfer insulating state in cuprate chain compound, Physical Review B, (11 2015): 201108. doi: 10.1103/PhysRevB.92.201108 |
| 02/16/2016 | 11.00 | V. Balédent, S. Chattopadhyay, P. Fertey, M._B. Lepetit, M. Greenblatt, B. Wanklyn, F._O. Saouma, J._I. Jang, P. Foury-Leylekian. Evidence for Room Temperature Electric Polarization in RMn2O5 Multiferroics, Physical Review Letters, (03 2015): 117601. doi: 10.1103/PhysRevLett.114.117601 |
| 02/16/2016 | 10.00 | M Retuerto, T Sarkar, M-R Li, A Ignatov, M Croft, J P Hodges, T Thao Tran, P Shiv Halasyamani, M Greenblatt. Crystallographic and magnetic properties ofPb2?xBixIr2O7?? (0?x?2) , Materials Research Express, (10 2014): 46304. doi: 10.1088/2053-1591/1/4/046304 |
| 02/16/2016 | 9.00 | Maria Retuerto, Zheng Deng, Man-Rong Li, Peter W. Stephens, Mark Croft, Qingzhen Huang, Hui Wu, Xiaoyu Deng, Gabriel Kotliar, Javier Sánchez-Benítez, Joke Hadermann, David Walker, Martha Greenblatt. Giant Magnetoresistance in the Half-Metallic Double-Perovskite Ferrimagnet Mn, Angewandte Chemie International Edition, (10 2015): 1. doi: 10.1002/anie.201506456 |
| 02/16/2016 | 8.00 | Man-Rong Li, Mark Croft, Peter W. Stephens, Meng Ye, David Vanderbilt, Maria Retuerto, Zheng Deng, Christoph P. Grams, Joachim Hemberger, Joke Hadermann, Wen-Min Li, Chang-Qing Jin, Felix O. Saouma, Joon I. Jang, Hirofumi Akamatsu, Venkatraman Gopalan, David Walker, Martha Greenblatt. Mn 2 FeWO 6 : A New Ni 3 TeO 6 -Type Polar and Magnetic Oxide, Advanced Materials, (04 2015): 2177. doi: 10.1002/adma.201405244 |
| 02/16/2016 | 7.00 | Zheng Deng, Man-Rong Li, Arnab Sen Gupta, Sun Woo Kim, Hirofumi Akamatsu, Venkatraman Gopalan, Martha Greenblatt. PbMn(IV)TeO6: A New Noncentrosymmetric Layered Honeycomb Magnetic Oxide, Inorganic Chemistry, (02 2016): 1333. doi: 10.1021/acs.inorgchem.5b02677 |
| 02/16/2016 | 6.00 | Maria Retuerto, Man-Rong Li, Peter W. Stephens, Javier Sánchez-Benítez, Xiaoyu Deng, Gabriel Kotliar, Mark C. Croft, Alexander Ignatov, David Walker, Martha Greenblatt. Half-Metallicity in Pb, Chemistry of Materials, (06 2015): 4450. doi: 10.1021/acs.chemmater.5b01442 |
| 02/16/2016 | 5.00 | Man-Rong Li, Maria Retuerto, Zheng Deng, Tapati Sarkar, Javier Sánchez-Benítez, Mark C. Croft, Tanusri Saha Dasgupta, Tilak Das, Trevor A. Tyson, David Walker, Martha Greenblatt. Strong Electron Hybridization and Fermi-to-Non-Fermi Liquid Transition in LaCu, Chemistry of Materials, (01 2015): 211. doi: 10.1021/cm503781s |
| 08/05/2013 | 1.00 | Man-Rong Li, David Walker, Maria Retuerto, Tapati Sarkar, Joke Hadermann, Peter W. Stephens, Mark Croft, Alexander Ignatov, Christoph P. Grams, Joachim Hemberger, Israel Nowik, P. Shiv Halasyamani, T. Thao Tran, Swarnakamal Mukherjee, Tanusri Saha Dasgupta, Martha Greenblatt. Polar and Magnetic Mn, Angewandte Chemie International Edition, (06 2013): 8406. doi: 10.1002/anie.201302775 |

08/21/2014 2.00 Man-Rong Li, Maria Retuerto, David Walker, Tapati Sarkar, Peter W. Stephens, Swarnakamal Mukherjee, Tanusri Saha Dasgupta, Jason P. Hodges, Mark Croft, Christoph P. Grams, Joachim Hemberger, Javier Sánchez-Benítez, Ashfia Huq, Felix O. Saouma, Joon I. Jang, Martha Greenblatt. Magnetic-Structure-Stabilized Polarization in an Above-Room-Temperature Ferrimagnet,
Angewandte Chemie International Edition, (08 2014): 0. doi: 10.1002/anie.201406180

08/22/2014 3.00 Man-Rong Li, Peter W. Stephens, Maria Retuerto, Tapati Sarkar, Christoph P. Grams, Joachim Hemberger, Mark C. Croft, David Walker, Martha Greenblatt. Designing Polar and Magnetic Oxides: Zn2FeTaO6 - in Search of Multiferroics,
Journal of the American Chemical Society, (05 2014): 8508. doi: 10.1021/ja502774v

**TOTAL:** **12**

**Number of Papers published in peer-reviewed journals:**

## (b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

**TOTAL:**

**Number of Papers published in non peer-reviewed journals:**

## (c) Presentations

282. Designing Polar and Magnetic Oxides in the A2BB'O6-Type Corundum Derivatives, April 30, 2015, Center for Nanomaterials and Physics, University of Maryland, College Park, MD 20742 invited

283. Designing Polar and Magnetic Oxides in the A2BB'O6-Type Corundum Derivatives, ACS National Meeting, August 17, 2015, Boston MA, invited

**Number of Presentations:** 2.00

## Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

**TOTAL:**

**Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):**

## Peer-Reviewed Conference Proceeding publications (other than abstracts):

| Received | Paper |
|---|---|

**TOTAL:**

**Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):**

## (d) Manuscripts

| Received | Paper |
|---|---|
| 02/16/2016 13.00 | Maria Retuerto, Tapati Sarkar, Brian M. Abbett, Jan Pokorný, Maxim Savinov, Dmitry Nuzhnyy, Jan Prokleška, Stella Skiadopoulou, Man-Rong Li, Artem M. Abakumov, Mark. Croft, Alexander Ignatov, Peter W Stephens, Jason P. Hodges, P?emysl Van?k, Craig J. Fennie,, Karin M. Rabe, Stanislav Kamba, Martha Greenblatt1, Milinda Abeykoon. Pb2MnTeO6 double perovskite: an antipolar antiferromagnet, Inorganic Chemistry (01 2016) |
| 02/16/2016 14.00 | Zheng Deng, Mark Croft, Bijuan Chen, Man-Rong Li, Maria Retuerto, Changqing Jin, Martha Greenblatt1. 463. Induced Re-moment ferromagnetism and carrier localization in Sr2-xLaxMnReO6 ( double perovskites , PHYSICAL REVIEW B (01 2016) |
| 02/17/2016 15.00 | S. Chattopadhyay, V. Balédent, F. Damay, A. Gukasov, E. Moshopoulou, P. Auban-Senzier, C. Pasquier, G. André, F. Porcher, E. Elkaim, C. Doubrovsky, M. Greenblatt, P. Foury-Leylekian. Evidence of incommensurate multiferroicity in NdMn2O5, PHYSICAL REVIEW B (06 2015) |
| 02/17/2016 16.00 | Man-Rong Li, Maria Retuerto, Peter W. Stephens, Mark Croft, Denis Sheptyakov, Vladimir Pomjakushin, Zheng Deng, Hirofumi Akamatsu, Venkatraman Gopalan, Javier Sánchez-Beníte, Felix O. Saouma, Joon I. Jang, David Walker, Martha Greenblatt. Unprecedented Low-Temperature Cationic Rearrangement in a Bulk Metal Oxide, Angewandte Chemie International Edition (12 2015) |
| 02/17/2016 17.00 | Man-Rong Li, Jason P. Hodges, Maria Retuerto, Zheng Deng, Peter W. Stephens, Mark C. Croft, Xiaoyu Deng, Gabriel Kotliar, Javier Sánchez-Benítez, David Walker, Martha Greenblatt*a. Mn2MnReO6: synthesis and magnetic structure determination of a new transition-metal-only double perovskite canted antiferromagnet, Chemical Science (03 2016) |

**TOTAL:** **5**

**Number of Manuscripts:**

## Books

Received Book

**TOTAL:**

Received Book Chapter

**TOTAL:**

## Patents Submitted

## Patents Awarded

## Awards

none

## Graduate Students

| NAME | PERCENT_SUPPORTED | Discipline |
|---|---|---|
| Bin Liu | 0.00 | |
| **FTE Equivalent:** | **0.00** | |
| **Total Number:** | **1** | |

## Names of Post Doctorates

| NAME | PERCENT_SUPPORTED |
|---|---|
| Tapati Sarkar | 0.75 |
| Maria Retuerto | 0.25 |
| Manrong Li | 0.75 |
| Zheng Deng | 1.00 |
| Sun Woo Kim | 0.50 |
| **FTE Equivalent:** | **3.25** |
| **Total Number:** | **5** |

## Names of Faculty Supported

| NAME | PERCENT_SUPPORTED |
|---|---|
| **FTE Equivalent:** | |
| **Total Number:** | |

## Names of Under Graduate students supported

| NAME | PERCENT_SUPPORTED |
|---|---|
| **FTE Equivalent:** | |
| **Total Number:** | |

## Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: ..... 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense ..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 0.00

## Names of Personnel receiving masters degrees

| NAME |
|---|
| **Total Number:** |

## Names of personnel receiving PHDs

| NAME |
|---|
| **Total Number:** |

## Names of other research staff

| NAME | PERCENT_SUPPORTED |
|---|---|

**FTE Equivalent:**
**Total Number:**

## Sub Contractors (DD882)

## Inventions (DD882)

## Scientific Progress

See attached Final Report

## Technology Transfer

none

**Final Report**
**Attachments**
**62130-PH, Agreement Number:**
**W911NF-12-1-0172**

**Martha Greenblatt**
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**List of Attached Documents:**

1. Final Report with Figures (Figs. 1-4).

## 1. Foreword

Polar oxides are of much interest due to their symmetry-dependent properties including ferroelectricity/multiferroics, magnetoelectricity, piezoelectricity, pyroelectricity, and second-order harmonic generation (SHG) effect, which are all important for technological applications.[1] However, polar crystal design and synthesis is challenging, because multiple effects, such as steric or dipole-dipole interactions, typically combine to form non-polar structures, and the number of known polar, especially magnetoelectric materials, is still extremely few.[2] Therefore, as one of the focus of this program, we embarked on high pressure (HP) and high temperature (HT) synthesis to find new interesting and potentially useful polar materials. As will be shown here, we have been exceedingly successful, and opened a new path to design polar and potentially multifunctional useful materials. In addition, HP and HT were also used to prepare new metastable double perovskites and quadruple perovskites with unusual structures and properties. Moreover, ambient pressure and more conventional solid state methods to synthesize new phases with 3d, 4d and 5d transition metals and exotic correlated electronic properties was pursued in parallel with the HP/HT projects.
As the results enumerated below show, a large number of new materials were synthesized; their physical properties were characterized in detail with a multitude of state-of-the-art techniques, and experiment and theory were coupled lead to deeper understanding of the observed properties, as well as guiding new synthesis.

## 2. Statement of the Problem Studied

In collaboration with Dave Walker of the Lamont-Doherty Earth Observatory, Columbia University, so far, we have synthesized 7 new noncentrosymmetric compounds at high pressure (3-10 GPa) and high temperature (>1000 °C) (HP/HT) in Walker-type multi-anvil press. Although the formula, $A_2BB'O_6$ is the same as that of the double perovskites, these structures are an extension of the corundum ($Al_2O_3$)-based noncentrosymmetric structure of $LiNbO_3$-type, and centrosymmetric ilmenite-type $ABO_3$ phases, where all the cations (A and B) are octahedrally coordinated, and the octahedra edge, face, and corner share to create a three-dimensional network structure. In these structures the A cation is too small to stabilize the perovskite structure (tolerance factor < 1). Before our group's efforts to synthesize $A_2BB'O_6$ corundum-type phases at high pressure, there were only two reports on similar $A_2BB'O_6$ analogs of the double perovskites, $Mn_2BSbO_6$ (B = Fe, V, Cr, Ga, Al) with a small A ($Mn^{2+}$)

and mixed B-site cations have been stabilized under HP.[3,4] Occupation of the A-site by magnetic, or non-magnetic ions, and the octahedral B sublattice by two or more different cations can generate a multitude of new phases with potentially interesting structures and physical properties.
The complex structural relationship between the various corundum-based phases is illustrated in Figure 1 below.
High temperature and ambient pressure was also used to prepare the new $Ni_3TeO_6$-type analogs Several of the corundum materials that were synthesized and studied are noncentrosymmetric, and multiferroic, some potentially magnetoelectric. The $Ni_{3-x}M_xTeO_6$ (M = Mn, Co) compounds are new magnetoelectric phases at the highest temperature (~80 K for Mn; x = 1). The $Mn_2FeMoO_6$ phase evidenced ionic exchange of Fe and Mn at unprecedented low temperature (starting at ~ 200 °C, and complete at <500 °C in a bulk solid); the large structural change that resulted was also accompanied by significant changes of the magnetic and transport properties.

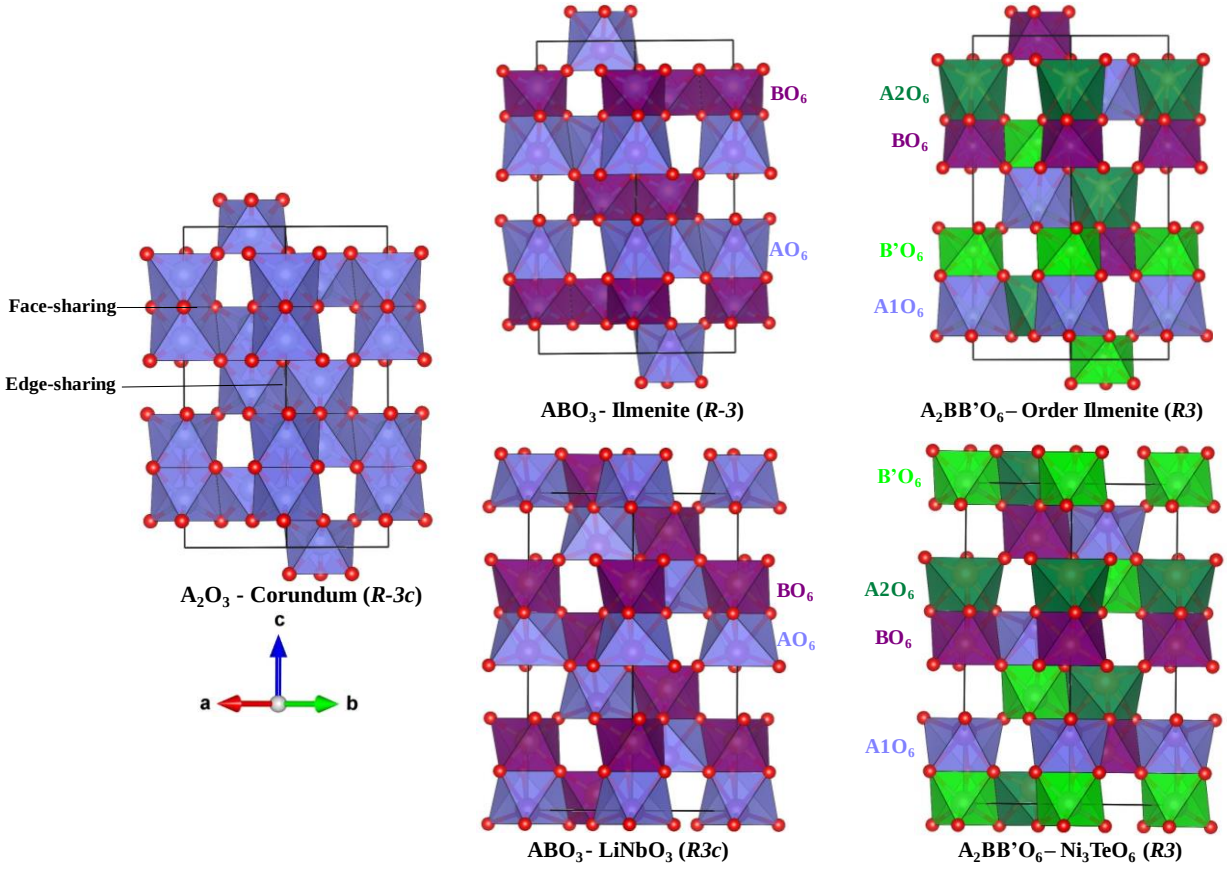


**Fig. 1** Cation ordering tree of corundum related phases to show the crystal structures of: $A_2O_3$-type corundum; $ABO_3$-type ilmenite; $ABO_3$-type $LiNbO_3$; $A_2BB'O_6$-type ordered ilmenite, and $A_2BB'O_6$-type $Ni_2NiTeO6$, viewing along [110] direction. Octahedral color: blue, $AO_6$, or $A1O_6$ purple, $BO_6$; green, $B'O_6$.

## 3. Summary of major accomplishments emphasized in the period 08/01/2014-to-08/31/2016, and briefly summarized for the time of the grant 5-2012-to-8-2015

### A. $A_2BB'O_6$ Corundum-Type Phases

**1**. A reprint describing the properties of $\mathbf{Mn^{2+}_2Fe^{3+}M^{5+}O_6}$ with M = Nb, Ta appeared in Angewandt. Chem. Int. Ed., was uploaded to a previous report.

**2**. $\mathbf{Mn_2FeMoO_6}$ has been published in Angewandt. Chem. Int. Ed. and was uploaded as a reprint in the previous Interim Report.

**3.** $\mathbf{Mn_2FeWO_6}$ a reprint of this work is uploaded in this report:

**Multiferroic $Mn_2FeWO_6$ – a new corundum-based polar compound.** Man-Rong Li, Mark C. Croft, Meng Ye, David Vandrbilt, Maria Retuerto, Zheng Deng, Christoph P. Grams, Joke Hadermann, Joachim Hemberger, Joon I. Jang Chang-Qing Jin Maria Retuerto, Felix O. Saouma, Peter W. Stephens, David Walker, Martha Greenblatt, Adv. Mater. **27**, 2177-2181 (2015).

4. $\mathbf{Mn_2FeMoO_6}$**-II**-a preprint of this article, which was reviewed, revised and resubmitted to Angewandt. Chem., is uploaded in this report

**Unprecedented Low-Temperature Cationic Rearrangement in a Bulk Metal Oxide**. Man-Rong Li, Maria Retuerto, Peter W. Stephens, Mark Croft, Denis Sheptyakov, Vladimir Pomjakushin, Zheng Deng, Hirofumi Akamatsu, Venkatraman Gopalan, Javier Sánchez-Benítez, Felix O. Saouma, Joon I. Jang, David Walker, Martha Greenblatt, Angewandt. Chem., revised resubmitted, 2-8-2016.

**5.** $\mathbf{Ni_{3-x}M_xTeO_6}$ **(M= Mn, Co)-** Magnetoelectric effect (T ~ 80 K) was confirmed in $Ni_2MnTeO_6$. A draft of a manuscript of this work is near in its final is uploaded in this report:

**Magnetoelectric properties of the multiferroic $Ni_2MnTeO_6$**. M. Retuerto, S. Skiadopoulou, J. Prokleška, F. Borodavka, C. Kadlec, F. Kadlec, Z. Deng, M. Savinov, S. Kamba and M.Greenblatt, to be submitted to PRB; draft of manuscript is uploaded in this report.

Work continues on the Co phases ($Ni_2CoTeO_6$ and $(NiCo)CoTeO_6$); powder neutron diffraction PND was recently collected, the magnetic structures are analyzed and the dielectric and magnetoelectric, as well as measurement of the phonon modes of vibration in these phases is in progress.

B. **<u>New Double Perovskite Phases of 3d, 4d and 5d Transition Metal Ions</u>**

High pressure and temperature was also used to prepare new double perovskites, $A_2BB'O_6$ with unusually small cation, $Mn^{2+}$. These new materials have important properties including high ferromagnetic transition temperature (e.g., $T_N$ ~ 520 K, for Mn2FeMoO6), half-metallic and giant magnetoresistant properties.

**6.** $\mathbf{Mn_2FeReO_6}$ – A reprint is uploaded in this report of this work titled:

**Giant Magnetoresistance in Half-Metallic Double Perovskite Ferrimagnet $Mn_2FeReO_6$.** Man-Rong Li, Maria Retuerto, Zheng Deng, Peter W. Stephens, Mark C. Croft, Qingzhen Huang, Hui Wu,

Xiaoyu Deng, Gabriel Kotliar, Javier Sánchez-Benítez, Joke Hadermann, David Walker, Martha Greenblatt, Angewandt. Chem. Int. Ed., 54, 1-6 (2015).

**7. $Mn_2MnReO_6$** A draft of this paper is attached, which will be submitted in a few days, titled:

**$Mn_2MnReO_6$: synthesis and magnetic structure determination of a new transition-metal-only double perovskite canted antiferromagnet**. Man-Rong Li, Jason P. Hodges, Maria Retuerto, Zheng Deng, Peter W. Stephens, Mark C. Croft, Xiaoyu Deng, Gabriel Kotliar, Javier Sánchez-Benítez, David Walker, Martha Greenblatt, to be submitted to Chem. Science, 2-2016

**8. $Mn_2Fe_{0.8}Mo_{1.2}O_6$** is a line phase in $Mn_2Fe_{1-x}Mo_{1+x}O_6$ which can be prepared between 5-8 GPa at 1623 K. Rietveld refinements of XRD data demonstrate the distorted GdFeO3-type structure of $Mn_2Fe_{0.8}Mo_{1.2}O_6$ (Fig. 12), isostructural with $Mn_2BReO_6$, B = Fe, and Mn). Magnetic properties and other characterizations are still undergoing. Recently we collected powder neutron data and are proceeding with the magnetic structure determination.

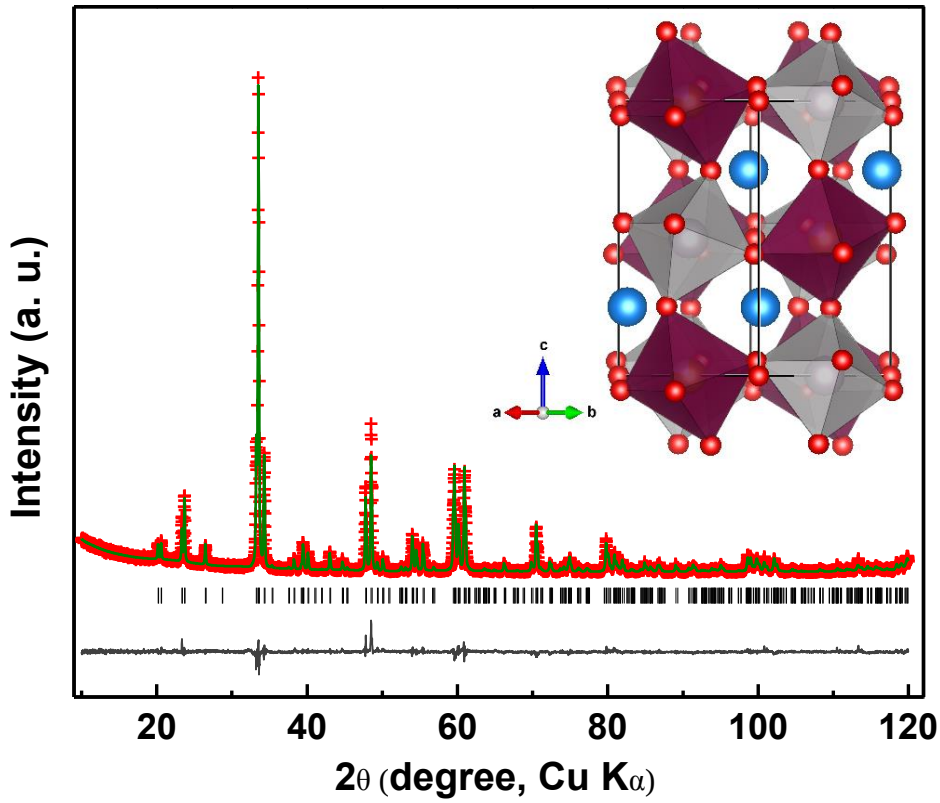


**Fig. 2** XRD pattern of $Mn_2Fe_{0.8}Mo_{1.2}O_6$ refined in the *P2₁/n* space group. Inset is the crystal structure showing the corner sharing $(Fe_{0.8}Mo_{0.2})O_6$ (brown) and $MoO_6$ (grey) octahedra. The 8-folded Mn are shown as blue spheres

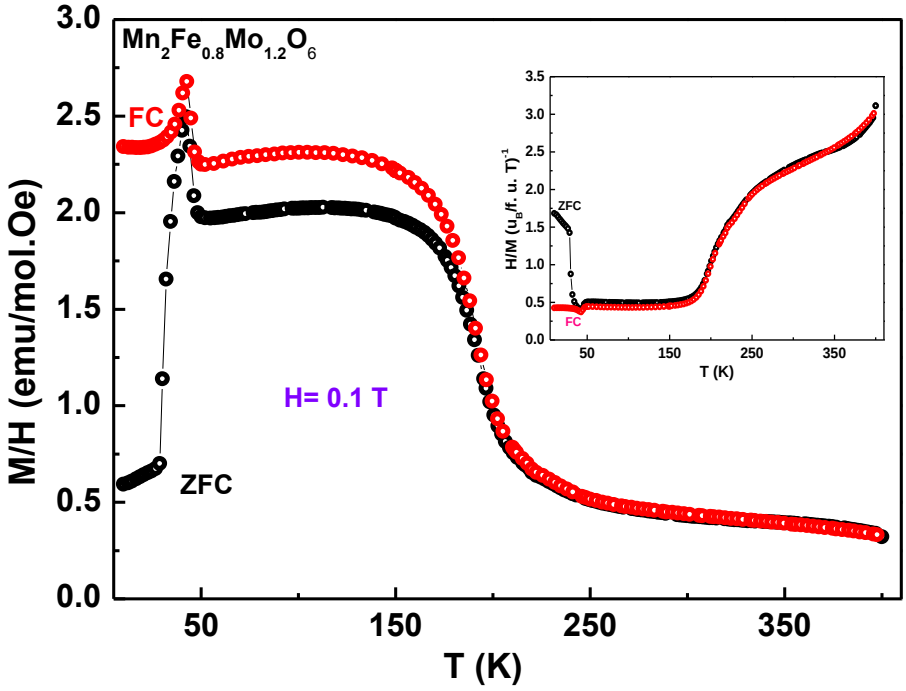


Fig. 3 Magnetic susceptibility of $Mn_2Fe_{0.8}O_{1.2}O_6$ that shows an antiferromagnetic (AFM) transition at $T_N$ ~ 50 K and dispersion of the ZFC and FC magnetic lines at ~200 K; the inset shows $1/\chi$ that suggests a $T_c$ ~160 K and near constant magnetization in the range 50-160 K and AFM. Below 50 K another large dispersion of ZFC and FC behavior.

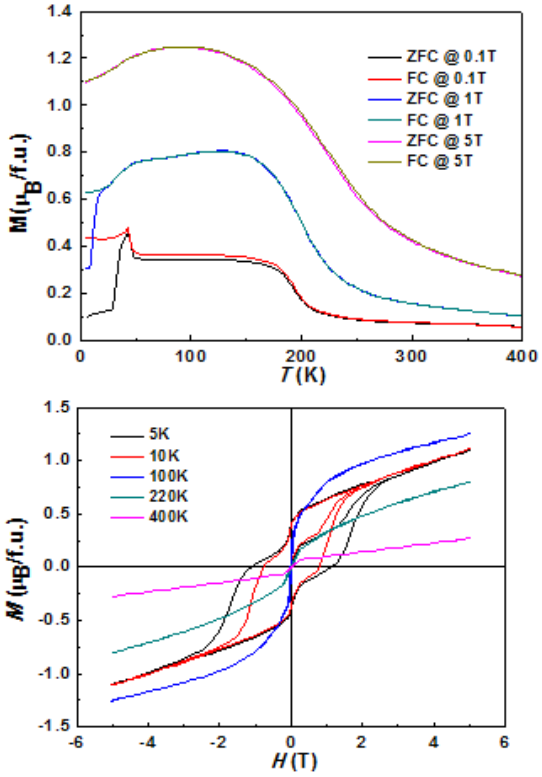


**Fig. 4 Magnetization as a function of temperature (top) and H(Tesla) showing that the AFM transition at ~50 K is suppressed at high field (1T)**

**9. $Pb_2CoReO_6$ and $Pb_2CrReO_6$ -** a reprint of the paper is is uploaded in this report, titled:

**Crystal and magnetic study of $Pb_2CoReO_6$ and $Pb_2CrReO_6$ perovskites**. Maria Retuerto, Manrong Li, P. W. Stephens, Javier Sánchez-Benítez, Xiaoyu Deng, Gabriel KotliarM. C. Croft, A. Ignatov, D. Walker, M. Greenblatt, Chem. Mater., 27, 4450-4458 (2015).

**11. $Sr_{2-x}La_xMnReO_6$ ($0 \leq x \leq 1$)** – a draft of this paper is uploaded in this report :

**Induced Re-moment ferromagnetism and carrier localization in $Sr_{2-x}La_xMnReO_6$ ($0 \leq x \leq 1$) double perovskites.** Zheng Deng, Mark Croft, Bijuan Chen, Man-Rong Li, Maria Retuerto, Changqing Jin and Martha Greenblatt, Phys. Rev. B revised paper resubmitted, 2-2016.

### C. Quadrupole Perovskite with 5d Transition Metal Ion

**12. $LaCu_3Ir_4O_{12}$ -** a reprint of the paper is uploaded in this report, titled:

**Strong Electron Hybridization and Non-Fermi Liquid Behaviour in $LaCu_3Ir_4O_{12}$.** Man-Rong Li, Javier Sánchez-Benítez, Mark C. Croft, Zheng Deng, Swarnakamal Mukherjee, Maria Retuerto, Tanusri Saha Dasgupta, Tapati Sarkar, Trevor A. Tyson, David Walker, Martha Greenblatt, Chemistry of Materials 7(1), 211-217 (2015).

### D. Layered Honeycomb Magnetic Oxides

**13. $PbMn(IV)TeO_6$** - a reprint of this paper is uploaded in this report, titled

**$PbMn(IV)TeO_6$: A New Noncentrosymmetric Layered Honeycomb Magnetic Oxide.** Sun Woo Kim, Zheng Deng, Man-Rong Li, Arnab Sen Gupta, Hirofumi Akamatsu, Venkatraman Gopalan, Martha Greenblatt, Inorg. Chem., in press

**List of publication resulting from this grant (05-01-2012 - to – 7-31-2015)**


1. Polar and Magnetic $Mn_2FeMO_6$ (M = Nb, Ta) with $LiNbO_3$-Type Structure - High Pressure Synthesis. Man-Rong Li, David Walker, Maria Retuerto, Tapati Sarkar, Joke Hadermann, Peter W. Stephens, Mark C. Croft, Alex Ignatov, Joachim Hemberger, Israel Nowik, Kandalam V. Ramanujachary, P. Shiv Halasyamani, Thanh T. Tran, Swarnakamal Mukherjee, Tanusri Saha Dasgupta, Martha Greenblatt, Angew. Chem. Int. Ed.,52, 8406-8410 (2013).
2. $CsTlX_3$ (X = F, Cl): synthesis and properties of mixed-valent thallium halide perovskites: precursors for superconductivity? M. Retuerto, P. W Stephens, J. Hadermann, T. Emge, M. Croft, A. Ignatov, C. Jin, M. R. Li, Z. P. Yin, J. Simons, M. Aronson, H. Sun, A. Pan, D. N. Basov, G. Kotliar, M. Greenblatt, Chem. Mater., 25, 4071-4-79 (2013).
3. Above Room Temperature Insulating Polar Ferrimagnet $Mn_2FeMoO_6$. Man-Rong Li, David Walker, Maria Retuerto, Tapati Sarkar, Joke Hadermann, Peter W. Stephens, Mark Croft, Alex Ignatov, Joachim Hemberger, Jason Hodges, Swarnakamal Mukherjee, Tanusri Saha Dasgupta, Martha Greenblatt, , Angew. Chem. Inter. Ed., 53, 1-7 (2014) DOI: 10.1002/anie.201406180

4. Crystallographic and magnetic properties of $Pb_{2-x}Bi_xIr_2O_{7-\delta}$ ($0 \leq x \leq 2$). M. Retuerto, T. Sarkar, M.-R. Li, A. Ignatov, M. Croft, J. P. Hodges, T. Thao Tran, P. Shiv Halasyamani, and M. Greenblatt, Mater. Res. Express, 1(4), 046304/1-046304/12 (2014).
5. Designing Polar and Magnetic Oxides: $Zn_2FeTaO_6$ - in Search of Multiferroics. Man-Rong Li, Peter W. Stephens, Maria Retuerto, Tapati Sarkar, Christoph P. Grams, Joachim Hemberger, Mark C. Croft, David Walker, Martha Greenblatt, J. Am. Chem. Soc., 136, 8508-8511 (2014).
6. Structural transformations in hole-doped $CsTl_{1-x}Hg_xCl_3$. M. Retuerto, T. Emge, M. R. Li, J. Hadermann, P. W. Stephens, Z. P. Yin, M. Croft, A. Ignatov, S. J. Zhang, Z. Yuan, C. Jin, G. Kotliar, M. Greenblatt, Inorg. Chem., 54(3), 1066-1075 (2015).
7. Strong Electron Hybridization and Non-Fermi Liquid Behaviour in $LaCu_3Ir_4O_{12}$. Man-Rong Li, Javier Sánchez-Benítez, Mark C. Croft, Zheng Deng, Swarnakamal Mukherjee, Maria Retuerto, Tanusri Saha Dasgupta, Tapati Sarkar, Trevor A. Tyson, David Walker, Martha Greenblatt, Chemistry of Materials 7(1), 211-217 (2015).
8. Multiferroic $Mn_2FeWO_6$ – a new corundum-based polar compound. Man-Rong Li, Mark C. Croft, Zheng Deng, Christoph P. Grams, Joke Hadermann, Joachim Hemberger, Joon I. Jang Chang-Qing Jin Maria Retuerto, Felix O. Saouma, Peter W. Stephens, David Walker, Martha Greenblatt, Adv. Mater. 27, 2177-2181 (2015).
9. Thermodynamic and neutron diffraction studies on multiferroic $NdMn_2O_5$. S. Chattopadhyay, V. Baledent, A. Goukassov, P. Auban-Senzier, C. Pasquier, C. Doubrovsky, M. Greenblatt, P. Foury-Leylekian. Physica B, 160, 214-217 (2015).
10. Evidence for Room Temperature Electric Polarization in $RMn_2O_5$ Multiferroics. V. Balédent, S. Chattopadhyay, P. Fertey, M.B. Lepetit, M. Greenblatt, B. Wanklyn, F. O. Saouma, J. I. Jang, and P. Foury-Leylekian Phys. Rev. Lett., 114, 117601-1-5 (2015)
11. Crystal and magnetic study of $Pb_2CoReO_6$ and $Pb_2CrReO_6$ perovskites. Maria Retuerto, Manrong Li, P. W. Stephens, Javier Sánchez-Benítez, Xiaoyu Deng, Gabriel KotliarM. C. Croft, A. Ignatov, D. Walker, M. Greenblatt, Chem. Mater., 27, 4450-4458 (2015).
12. Anomalous charge and negative-charge-transfer insulating state in cuprate chain-compound $KCuO_2$. D. Choudhury, P. Rivero, D. Meyers, X. Liu, Y. Cao, S. Middey, M. J. Whitaker, S. Barraza-Lopez, J. W. Freeland, M. Greenblatt, and J. Chakhalian. PRB, rapid communication, in press, 11-04-2015.
13. $Pb_2MnTeO_6$ double perovskite: a new antiferroelectric antiferomagnet. M. Retuerto, A. Abakumov, T. Sarkar, M.-R. Li, A. Ignatov, M. Croft, J. P. Hodges. P. Stephens, Stella Skiadopoulou, Jan Pokorný, Maxim Savinov, Přemysl Vaněk, Jan Prokleška, Brian Craig Fennie, Karin Rabe, Stanislav Kamba and M. Greenblatt, submitted to Inorg. Chem. 1-2016
14. First evidence of the multiferroicity in $NdMn_2O_5$. S. Chattopadhyay, V. Balédent, F. Damay, A. Gukasov, E. Moshopoulou, P. Auban-Senzier, C. Pasquier, G. Andr´*e*, F. Porcher, E. Elkaim, C. Doubrovsky, M. Greenblatt, and P. Foury-Leylekian. PRB, in press, 2-2016
15. Giant Magnetoresistance in Half-Metallic Double Perovskite Ferrimagnet $Mn_2FeReO_6$. Man-Rong Li, Maria Retuerto, Zheng Deng, Peter W. Stephens, Mark C. Croft, Qingzhen Huang, Hui Wu, Xiaoyu Deng, Gabriel Kotliar, Javier Sánchez-Benítez, Joke Hadermann, David Walker, Martha Greenblatt, Angewandt. Chem. Int. Ed., 54, 1-6 (2015).
16. PbMn(IV)$TeO_6$: A New Noncentrosymmetric Layered Honeycomb Magnetic Oxide *Sun* Woo Kim, Zheng Deng, Man-Rong Li, Arnab Sen Gupta, Hirofumi Akamatsu, Venkatraman Gopalan, Martha Greenblatt, Inorg. Chem.,
17. Induced Re-moment ferromagnetism and carrier localization in $Sr_{2-x}La_xMnReO_6$ ($0 \leq x \leq 1$) double perovskites Zheng Deng, Mark Croft, Bijuan Chen, Man-Rong Li, Maria Retuerto, Changqing Jin and Martha Greenblatt, Phys. Rev. B revised paper resubmitted, 2-2016.
18. Unprecedented Low-Temperature Cationic Rearrangement in a Bulk Metal Oxide Man-Rong Li, Maria Retuerto, Peter W. Stephens, Mark Croft, Denis Sheptyakov, Vladimir Pomjakushin, Zheng Deng, Hirofumi Akamatsu, Venkatraman Gopalan, Javier Sánchez-Benítez, Felix O.

Saouma, Joon I. Jang, David Walker, Martha Greenblatt, Angewandt. Chem., revised resubmitted, 2-8-2016.

19. $Mn_2MnReO_6$: synthesis and magnetic structure determination of a new transition-metal-only double perovskite canted antiferromagnet. Man-Rong Li, Jason P. Hodges, Maria Retuerto, Zheng Deng, Peter W. Stephens, Mark C. Croft, Xiaoyu Deng, Gabriel Kotliar, Javier Sánchez-Benítez, David Walker, Martha Greenblatt, to be submitted to Chem. Science, 3-2016
20. $Ba_3(Cr_{0.97(1)}Te_{0.03(1)})_2TeO_9$: in Search of Jahn-Teller Distorted Cr(II) Oxide. Man-Rong Li, Zheng Deng, Saul H. Lapidus, Peter W. Stephens, Carlo U. Segre, Mark Croft, Robert Paria Sena, Sun Woo Kim, Joke Hadermann, David Walker, Martha Greenblatt, Inorg. Chem., 55, 1333−1338 (2016).
21. Magnetoelectric properties of the multiferroic $Ni_2MnTeO_6$. M. Retuerto, S. Skiadopoulou**,** J. Prokleška, F. Borodavka, C. Kadlec, F. Kadlec, Z. Deng, M. Savinov, S. Kamba and M.Greenblatt to be submitted

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