

**Spring Seminar Series**  
**3:45pm - 4:45pm, Wednesday April 10, 2013**  
**The Marriott Hotel, Baton Rouge, Louisiana**

**Tuning the Properties of Low-Dimensional  
Transition Metal Oxides**

by  
**Prof. Martha Greenblatt**  
**Rutgers University**



Combined experimental and DFT theoretical results on low-dimensional new  $\text{Ni}^+/\text{Ni}^{2+}$  ( $d^9/d^8$ ) homologous series,  $\text{Ln}_{n+1}\text{Ni}_n\text{O}_{2n+2}$  with  $n = 2$  and 3 layered oxides with Ruddlesden–Popper (RP)–related structures and isostructural and isoelectronic with the high temperature superconducting cuprates are presented. Temperature variation of magnetization, transport, specific heat and  $^{139}\text{La}$  NMR data in  $\text{La}_4\text{Ni}_3\text{O}_8$  evidence the presence of a transition near  $\sim 105$  K. DFT calculations suggest similarity of the band structure with that of the cuprate superconductors and relate the transition at 105 K to a spin density wave nesting instability of the Fermi surface.

$\text{CsTiX}_3$  ( $X = \text{F}, \text{Cl}$ ) were predicted, by first principle calculations, to be superconducting when doped or under pressure. We prepared these compounds for the first time, and show that perovskite structures form as predicted by theory, and the charge ordering of  $\text{Ti}^+/\text{Ti}^{3+}$  observed by XAS has not been broken by high pressure.

Cheaper efficient catalysts made from abundant (not noble metals) and environmentally green materials are indispensable for extracting hydrogen from water, the essential precursor to all globally sustainable fuels. Achieving this goal and the reduction of  $\text{CO}_2$  to liquid fuels are necessary to replace fossil fuels. We have synthesized different polymorphs of  $\text{LiCoO}_2$  and compared their catalytic activity in water oxidation. Our results show that  $\text{LiCoO}_2$  is active exclusively in the low-temperature cubic “spinel-like” structure, while inactive as the high-temperature layered phase, which is thermodynamically more stable. The related spinel  $\text{LiMn}_2\text{O}_4$  is transformed from an inactive to a highly efficient water oxidation catalyst ( $\lambda\text{-MnO}_2$ ) upon the topotactic removal  $\text{Li}^+$ . These spinel phases contain cubical metal-oxo ( $\text{M}_4\text{O}_4$ ) subunits (absent in the layered  $\text{LiCoO}_2$  analog) that appear to be the key to catalytic activity. The biological basis of the mechanism for the high activity of the  $\text{M}_4\text{O}_4$ -cubical topology of various activated spinels in water oxidation will be discussed

**Martha Greenblatt** is Professor of Chemical Biology at Rutgers State University of New Jersey Department of Chemistry. She received her B.S. (1962) and Ph.D. (1967) degrees in Chemistry and Inorganic Chemistry from Brooklyn College, New York and Polytechnic Institute, Brooklyn, New York respectively. She joined the faculty at Rutgers University in 2003. Her current research focuses on solid state inorganic chemistry; synthesis and crystal growth of novel transition metal compounds with quasi-low-dimensional correlated electronic properties including transition metal (V, Mo, W, Nb) oxide bronzes, perovskite, double perovskite and Ruddlesden–Popper–based oxide phases (with 3d, 4d and 5d metals) with particular focus on magnetically ordered, multiferroic, CMR materials, and high temperature superconductors. Properties of compounds are characterized by X-ray neutron, and electron diffraction, transmission electron microscopy, magnetic susceptibility, electronic conductivity, Seebeck effect, thermal analysis and X-ray absorption spectroscopy. Structural–physicochemical property relationships are emphasized. Single crystal and polycrystalline materials are investigated. More recently inorganic transition metal oxide and chalcogenide nanomaterials are synthesized and characterized in search of earth abundant catalysts for the oxidation and reduction of water. Another area of research pursued is fast ionic ( $\text{H}^+$ ,  $\text{Li}^+$  and  $\text{O}^{2-}$ ) motion in solids and applications (solid state batteries, fuel cells and sensors).

