International Workshop on Synthesis of Functional Oxide Materials

August 19 – 23, 2007
Engineering Sciences Building
University of California, Santa Barbara

Organized by
Anthony K. Cheetham, UCSB
David Mandrus, Oak Ridge National Laboratory
Kenneth R. Poeppelmeier, Northwestern University
Ram Seshadri, UCSB

Sponsored by
International Center for Materials Research, UCSB
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Table of Contents

Support for this program is provided by the International Materials Institute Program of the National Science Foundation and the University of California, Santa Barbara.

Sunday, August 19, 2007 – Lagoon Plaza, UCEN	
12:00 pm onward	Check in at Santa Ynez Apartments
5:30 pm to 7:30 pm	Reception and Registration at Lagoon Plaza, University Center
Monday, August 20, 2007 – Engineering Sciences Building, Room 1001	
8:15 am to 8:45 am	Continental Breakfast at the Engineering Sciences Building, Room 1001
Chair: David Mandrus	
8:50 am to 9:00 am	Opening remarks by Ram Seshadri
9:00 am to 9:45 am	Ken Poeppelmeier, “Synthesis of oxides and oxide fluorides: Reactions in aqueous hydrofluoric acid”
9:45 am to 10:30 am	John Greedan, “Geometrically frustrated magnetism in transition metal oxides”
10:30 am to 11:00 am	Break
11:00 am to 11:45 am	Jin-Ho Choy, “Intercalative nanohybrid materials with superconducting property”
11:45 am to 12:30 pm	Linda Nazar, “Beyond layered metal oxides: Multifunctional polyanion materials: synthesis, and ion/electron transport properties”
12:30 pm to 2:00 pm	Lunch at De La Guerra Dining Commons[*] (lunch served between 12:30 – 1:30)
Chair: Nicola Spaldin	
2:00 pm to 2:45 pm	R. Ramesh, “Correlated oxide heterostructures”
2:45 pm to 3:30 pm	Darell Schlom, “Synthesis of ferroelectrics and multiferroics by MBE”
3:30 pm to 4:00 pm	Break
4:00 pm to 4:45 pm	Paul Salvador, “Thin film synthesis of complex titanates: layered-perovskites, pyrochlores, perovskites, and novel intergrowth structures”
4:45 pm to 5:30 pm	Judith Driscoll, “Spontaneous ordering, strain control, and multifunctionality in vertical nanocomposite heteroepitaxial thin films”
5:45 pm to 7:15 pm	Dinner at De La Guerra Dining Commons
Tuesday, August 21, 2007 – Engineering Sciences Building, Room 1001	
8:15 am to 9:00 am	Continental Breakfast at the Engineering Sciences Building, Room 1001
Chair: Ken Poeppelmeier	
9:00 am to 9:45 am	Thom Palstra, “Magnetoelectric coupling in multiferroic oxides”
9:45 am to 10:30 am	Ram Seshadri, “Spinel oxides: Magnetocapacitance and multifunctional composites”

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[*] Lunch and dinner arrangements at De La Guerra Dining Commons are for participants holding meal cards.

10:30 am to 11:00 am	Break
11:00 am to 11:45 am	Shiv Halasyamani, “Polar oxide materials: Synthetic strategies and characterization techniques”
11:45 am to 12:30 pm	Seong-Ju Hwang, “A lattice manipulation route to mesoporous transition metal oxides with multipurpose catalytic activity”
12:30 pm to 2:00 pm	Lunch at De La Guerra Dining Commons (lunch served between 12:30 – 1:30)
Chair: Claudia Felser	
2:00 pm to 2:45 pm	Amparo Fuertes, “Functional mixed anion systems: Synthesis, ordering, and properties”
2:45 pm to 3:30 pm	Masaki Azuma, “High pressure synthesis of functional transition metal oxides”
3:30 pm to 4:00 pm	Break
4:00 pm to 4:45 pm	Tona Señaris Rodriguez, “Searching for oxide materials with high permittivity and magnetodielectric properties”
4:45 pm to 5:30 pm	David Mandrus, “Studies of charge order in single crystals of Fe_2OBO_3
5:45 pm to 7:15 pm	Dinner at De La Guerra Dining Commons
Wednesday, August 22, 2007 – Engineering Sciences Building, Room 1001	
8:15 am to 9:00 am	Continental Breakfast at the Engineering Sciences Building, Room 1001
Chair: Miguel Alario-Franco	
9:00 am to 9:45 am	Bernard Raveau, “New routes to the discovery of electrode materials”
9:45 am to 10:30 am	Peter Battle, “Cation ordering in mixed-metal oxides”
10:30 am to 11:00 am	Break
11:00 am to 11:45 am	Christopher Wiebe, “Orbital ordering transitions in the vanadium oxides Sr_2VO_4 and $Lu_2V_2O_{7+x}$
11:45 am to 12:30 pm	Prasenjit Guptasarma, “Unconventional superconductivity and magnetism in complex oxides”
12:30 pm to 2:00 pm	Lunch at De La Guerra Dining Commons (lunch served between 12:30 – 1:30)
2:00 pm to 4:45 pm	Poster Session, ESB 1001
Chair: Tony Cheetham	
4:45 pm to 5:30 pm	Paul Attfield, “New electronic oxides – simple or complex?”
6:15 pm to 8:15 pm	Banquet Dinner at Faculty Club – Invited Speakers, Chairs, Poster Presenters and Registered Participants

Thursday, August 23, 2007 – Engineering Sciences Building, Room 1001	
8:15 am to 9:00 am	Continental Breakfast at the Engineering Sciences Building, Room 1001
Chair: Warren Pickett	
9:00 am to 9:45 am	Miguel Alario-Franco, “The combined use of pressure and temperature in the synthesis of materials”
9:45 am to 10:30 am	John Mitchell, “Tuning into frustration: Synthesis and structural studies of the kagome antiferromagnet $YBaCo_4O_{7+x}$”
10:30 am to 11:00 am	Break
11:00 am to 11:45 am	Robert Schloegl, “Dynamic response of oxides in heterogeneous catalysis”
11:45 am to 12:30 pm	Matt Rosseinsky, “New oxides – ferroelectric, almost ferroelectric and ionically conducting”
12:30 pm to 2:00 pm	Lunch at De La Guerra Dining Commons (lunch served between 12:30 – 1:30)
2:00 pm to 4:45 pm	Poster Session, ESB 1001
Chair: Ram Seshadri	
4:45 pm to 5:30 pm	Tony Cheetham, “Hybrid metal oxides and their properties”
5:45 pm to 7:15 pm	Dinner at De La Guerra Dining Commons
Friday, August 24, 2007	
8:00 am to 12:00 pm	Continental breakfast at Jameson Patio, Santa Ynez Apartments
8:00 am to 12:00 pm	Checkout from Santa Ynez Apartments must be completed by 12:00 pm

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APRIL 2006

Abstracts

Monday, August 20

Synthesis of Oxides and Oxide Fluorides: Reactions in Aqueous Hydrofluoric Acid

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The preparation of electrochemically active, high silver density oxides and oxide fluorides will be presented to illustrate the general use of HF(aq) in hydrothermal chemistry both as a mineralizer and a source of fluoride. $Ag_2V_4O_{11}$, or silver vanadium oxide (SVO), is used commercially as a cathode material in primary lithium batteries for high rate applications, such as those used in implantable cardioverter defibrillators (ICDs).[1-3] A long-term goal of the medical battery industry is to increase the capacity of the cathode above 3 V while maintaining electrode stability. Various low temperature hydrothermal techniques will be discussed that can be used to synthesize new high silver density materials, for example $Ag_4V_2O_6F_2$ (SVOF).[4] Owing to the high mole fraction of silver and the incorporation of fluoride into the structure, SVOF has a higher capacity above 3 V of 148 mAh/g in comparison to 100 mAh/g in SVO and the upper discharge plateau at 3.5 V is nearly 300 mV over the silver reduction potential of the commercial primary battery material $Ag_2V_4O_{11}$ (SVO).

References:

1. Liang, C. C.; Bolster, M. E.; Murphy, R. M. US Patent 4,310,609, January 12, 1982.
2. Liang, C. C.; Bolster, M. E.; Murphy, R. M. US Patent 4,391,729, July 5, 1983.
3. Takeuchi, K. J.; Marschilok, A. C.; Davis, S. M.; Leising, R. A.; Takeuchi, E. S. *Coord. Chem. Rev.* **2001**, *219*, 283-310.
4. Sorensen, E. M.; Izumi, H. K.; Vaughey, J. T.; Stern, C. L.; Poeppelmeier, K. R. *J. Am. Chem. Soc.* **2005**, *127*, 6347-6352.

Geometrically Frustrated Magnetism in Transition Metal Oxides

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and Lachlan Cranswick [c]

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In the rapidly growing field of geometrically frustrated magnetism, most attention has been focused on materials with pyrochlore or Kagomé magnetic topologies which present infinite lattices of corner-sharing tetrahedra or corner-sharing triangles, respectively. Somewhat overlooked are the B-site ordered double perovskites, $A_2BB'O_6$, wherein both the B and B' sublattices are f.c.c., comprised of edge-sharing tetrahedra and, therefore, geometrically frustrated. Due to the rich crystal chemistry of double perovskites, systematic studies can be designed in which for example the roles of spin and orbital degeneracy in the determination of the magnetic ground state can be separated. We present here studies of $La_2LiB'O_6$ and $Ba_2YB'O_6$ in which the B' sublattice is occupied by Mo^{5+}(S=1/2), Re^{5+}(S=1) and Ru^{5+}(S=3/2). The $La_2LiB'O_6$ materials are monoclinic, $P2_1/n$ and the t_{2g} orbital degeneracy is raised, while at least two members of the $Ba_2YB'O_6$ series remain cubic, Fm3m, to 2.8K, preserving t_{2g} orbital degeneracy in apparent violation of the Jahn-Teller theorem. All of the materials show evidence for geometric frustration in large values of the “frustration index” $f \sim |\theta|/T_{ord}$. The B' $=Ru^{5+}$ (S=3/2) compounds both show long range AF order but for the “quantum spin” systems, S = 1 and 1/2, the situation changes drastically and long range order is not generally observed, indicating a critical role for spin degeneracy. As well, there are significant differences between $P2_1/n$ and Fm3m phases of the same S, which demonstrates the importance of orbital degeneracy.
Other rather under investigated materials which are candidates for exhibiting geometric frustration are some ordered rock salt phases. We will discuss the contrasting behaviour of isostructural Li_4MgReO_6 and Li_5OsO_6, both S = 1/2, where the former is a spin glass while the latter shows conventional AF order. Finally, a new type of frustrated magnetic lattice is found in $Li_3Mg_2RuO_6$, Fddd, consisting of ribbons of edge-sharing triangles which are connected by corner sharing.

Intercalative Nanohybrid Materials with Superconducting Property

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We have successfully synthesized inorganic-inorganic and organic-inorganic nanohybrids by applying an intercalation technique systematically to Bi-based cuprate oxides, $Bi_2Sr_2Ca_{m-1}Cu_mO_y$ (m=1, 2, and 3; BSCCO), those which are of high importance in terms of basic understanding of intercalation reactions and of their applications. The metal salts, such as AgI, HgI_2 and AuI_3, were intercalated into layered transition metal oxide to form inorganic-inorganic (halide-oxide) hybrids, in which the molecular symmetry of intercalant halides was turned out to be unusual compared to the conventional solid state compounds. In order to realize the organic-inorganic hybrids, pre-intercalated metal halide (HgI_2) was further treated with the organic salt of bis-alkylpyridinium iodide, $Py\text{-}C_nH_{2n+1}I$ (Py=pyridine). DC magnetic susceptibility measurements and X-ray absorption spectroscopic studies revealed that their physical properties are closely related to the changes in electronic structure of inorganic host matrix as well as guest species.

We also achieved superconducting colloidal suspension from the organic-intercalates, from which the fabrication of high-quality superconducting thin film could be realized. The intercalative complexation in this work is expected to be a new route to the nanocomposite with unique structure and property unattainable by conventional methods.

References

1. Choy, J.-H.; Kwon, S. J.; Park, G.-S, *Science,* **1998**, *280*, 1589.
2. Choy, J.-H.; Kim, Y.-I.; Hwang, S.-J.; Huong, P. V, *J. Phys. Chem. B,* **2000**, *104*, 7273.
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4. Jang, E.-S.; Jang, J.-J.; Jeon, S. H.; Khim, Z.-G.; Choy, J.-H, *Adv. Mater.,* **2005**, *17*, 1745.
5. Chung, I.-W.; Kwon, S. J.; Kim, S.-J.; Jang, E.-S.; Hwang, S.-J.; Choy, J.-H, *J. Phys. Chem. B,* **2006**, *110*, 16197.

Beyond layered metal oxides: multifunctional polyanion materials: synthesis, and ion/electron transport properties

Linda F. Nazar, B. Ellis, W. R. Makahnouk and E. Nicolas

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Lithium-ion batteries classically rely on layered solid-state compounds that are able to reversibly uptake Li cations and electrons at both negative and positive electrodes. Cell potential and capacity are dictated by internal redox processes, and ion and electron transport in the lattice. For well over a decade, materials at the positive electrode have been completely dominated by the chemistry of layered lithium metal oxides with the α-$NaFeO_2$ structure, including recent newcomers such as $Li[Co_{1/3}Mn_{1/3}Ni_{1/3}]O_2$. Recently, however, another class of materials – the so-called lithium metal polyanions,$Li_xM_y(XO(F))_4]_z$ - have started to make an enormous impact. Although they lack the good semiconducting properties of the layered oxides, they have other highly desirable functional properties such as suitable (and tunable) redox potentials, facile ion transport, highly reversible lithium intercalation and low electrolyte reactivity that have made them amongst the most promising of today's new electrode materials. Their localized carrier transport properties result in particularly complex phase transitions on charge/discharge of the cell that range from charge-order driven two phase transitions to solid solution behavior over a range of composition. These factors, related to ion/electron coupling, and apparently crystallite size *via* control of synthesis method, strongly affect the electrochemical properties and will be the subject of this presentation.

Correlated Oxide Heterostructures

Ramamoorthy Ramesh
University of California—Berkeley

Complex perovskite oxides exhibit a rich spectrum of functional responses, including magnetism, ferroelectricity, highly correlated electron behavior, superconductivity, etc. The basic materials physics of such materials provide the ideal playground for interdisciplinary scientific exploration. At Berkeley, we are exploring the science of such materials (for example, colossal magnetoresistance, ferroelectricity, etc) in thin film form by creating epitaxial heterostructures and nanostructures. Among the large number of materials systems, there exists a small set of materials which exhibit multiple order parameters; these are known as multiferroics. Using our work in the field of ferroelectric and ferromagnetic oxides as the background, we are now exploring such materials, as epitaxial thin films as well as nanostructures. Specifically, we are studying the role of thin film growth, heteroepitaxy and processing on the basic properties as well as magnitude of the coupling between the order parameters. A new development has been the discovery of the formation of spontaneously assembled nanostructures consisting of a ferromagnetic phase embedded in a ferroelectric matrix that exhibit very strong coupling between the two order parameters. This involves 3-dimensional heteroepitaxy between the substrate, the matrix perovskite phase and spinel phase that is embedded as single crystalline pillars in this matrix. In this talk I will describe to you some aspects of such materials as well as the scientific and technological excitement in this field

Synthesis of Ferroelectrics and Multiferroics by MBE

D.G. Schlom, J.F. Ihlefeld, A. Soukiassian, M.D. Biegalski, J.H. Lee,
M. Warusawithana, C.M. Brooks, R.W. Ulbricht, J.H. Haeni, V. Vaithyanathan,
W. Tian, X. Ke, D.A. Tenne, A.V. Rao, A. Kumar, L. Tian, A. Sharan, S. Choudhury,
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D.D. Fong, M.A. Zurbuchen, J.A. Eastman, P.H. Fuoss, O.H. Auciello,
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Y.B. Chen, H.P. Sun, and X.Q. Pan
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T. Heeg and J. Schubert
Forschungszentrum Jülich GmbH, Germany
R.S. Katiyar
University of Puerto Rico, Puerto Rico
A. Cros and A. Cantarero
University of Valencia, Spain
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L. Fitting Kourkoutis and D.A. Muller
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J. Klug and M.J. Bedzyk
Northwestern University, U.S.A.
J.C. Woicik
NIST, U.S.A.
L.P. Wang
Intel, U.S.A.
H. Li
Motorola, U.S.A.
P. Ryan
Ames Laboratory, U.S.A.
W. Chang and S.W. Kirchoefer
Naval Research Laboratory, U.S.A.

The synthesis of oxide ferroelectrics, ferroelectric superlattices, and multiferroics with perovskite structures by MBE will be described. The importance of the underlying substrate on the perfection and properties of the grown film will be emphasized. The use of adsorption-controlled growth to synthesize the multiferroics $BiFeO_3$ and $BiMnO_3$ by MBE will be described. Aided by theoretical predictions, we have used epitaxy and the misfit strain imposed by an underlying substrate to enhance the ferroelectric properties of $SrTiO_3$, $BaTiO_3$, $EuTiO_3$, and $BaTiO_3/SrTiO_3$ superlattices. These enhancements include shifting the paraelectric-to-ferroelectric transition temperature by *hundreds* of degrees, maintaining ferroelectricity in $BaTiO_3$ layers as thin as one unit cell in $BaTiO_3/SrTiO_3$ superlattices, and achieving ferroelectricity at room temperature in commensurate $SrTiO_3$ films grown on (100) Si.

Thin Film Synthesis of Complex Titanates: Layered-Perovskites, Pyrochlores, Perovskites, and Novel Intergrowth Structures

Paul Salvador
Carnegie Mellon University

Thin film deposition methods allow for one to synthesize rationally specific compositions in targeted crystal structures. Although it is clear that thermodynamic and kinetic variables ultimately control the range of new and metastable materials that can be synthesized by design, most of these parameters are unknown for specific compounds/processes. As such, epitaxial stabilization of materials and design of artificially layered crystals generally are driven through empirical investigations. Using examples taken primarily from the family of complex titanates, the thermodynamic and kinetic factors that control materials design using thin film deposition are discussed. Complex titanates exhibit a range of interesting physicochemical behaviors; they are useful dielectrics, ferroelectrics, photocatalysts, electrodes, and ion-conductors, to name a few. These properties are closely coupled to both the composition and crystal structure of a particular compound. The phase competition between the pyrochlore and the (110) layered perovskite structure in the $RE_2Ti_2O_7$ family (RE = rare-earth) will be explored, using pulsed laser deposition as a synthesis method. For RE = Gd, Sm, Nd, and La, the phase stability over a wide range of conditions is dictated entirely by substrate choice, indicating that the free energies of the phases are similar enough such that by controlling nucleation one controls the phase formation. Several examples will then be discussed with respect to the $(SrO)_m(TiO_2)_n$ system, which includes the perovskite $SrTiO_3$ and the Ruddlesden-Popper phase Sr_2TiO_4, grown using layer-by-layer molecular beam epitaxy. The solid phase epitaxial formation of the perovskite $SrTiO_3$ from superlattices of rock-salt SrO and anatase TiO_2 is discussed from both a kinetic and thermodynamic perspective by exploring the growth of a range of m and n values. Using similar arguments for stability, new layered intergrowths in the Sr_mTiO_{2+m} family are presented and their structures are discussed.

Spontaneous Ordering, Strain Control and Mutlifunctionality in Vertical Nanocomposite Heteroepitaxial Films

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Two-phase nanocomposite heteroepitaxial films with vertical microstructures hold great promise for various (mutli)functional electronic device applications. The ultimate goals are creation of ordered structures (including their formation on a large scale), prediction of which combinations of materials are compatible, and control of strain coupling between the phases. Here we demonstrate advances on all these fronts: remarkable spontaneously ordered phase assemblies were produced, novel heteroepitaxial compositions were demonstrated, two-dimensional vertical strain control was achieved in up to 440 nm thick films, and, finally, vertical strain manipulation was demonstrated. In one of two new systems studied, the strain state was switched from *compressive* (for the pure film) to *tensile* (for the composite), and in the other it was switched from *tensile* (for the pure film) to *compressive (*for the composite). Careful design of nanocomposite systems through materials selection is key to realising strain control, ordering, and enhanced (multi)functionality.

Abstracts

Tuesday, August 21

Magnetoelectric coupling in Multiferroic Oxides

Thomas T.M. Palstra

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University of Groningen, The Netherlands

Multiferroic and magnetoelectric compounds allow coupling between the magnetic and electric moments. In recent years a number of compounds have been discovered that display such coupling, often introducing novel coupling mechanisms. In my talk I will discuss the magnetoelectric coupling in several transition metal oxides. We have probed the coupling by measuring the dielectric response in applied magnetic fields. The temperature and magnetic field dependence of the response identify the nature of the coupling mechanism, and can yield critical behavior near the phase transitions. Our measurements yield quantitative information about the nature of the coupling.

Spinel oxides: Magnetocapacitance and multifunctional composites

Brent Melot,[a] Daniel Shoemaker,[a] Claude Ederer,[a,b] Gavin Lawes[c] and
Ram Seshadri[a]

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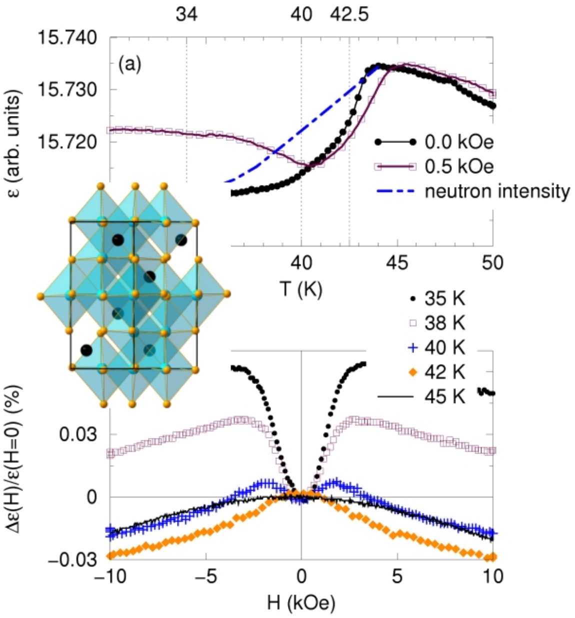
Spinel oxides with the formula AB_2O_4 possess a number of interesting characteristics: two independent, possibly magnetic sublattices, each allowing the electron counts to be tuned at will; narrow energy bands and hence easily accessed semiconducting and yet (ferri)magnetic phases; lattice topologies that lend themselves to magnetic frustration ... In addition, both the A and the B sites can accommodate Jahn-Teller ions leading to the possibility of interesting orbital physics in these materials, and the prospect for microscopic phase separation. Finally, as a host for multiple (magnetic) transition metal ions, the spinel lattice is a reactive precursor to a variety of spontaneously patterned composite magnetic materials.



Temperature dependence of the dielectric constant, and isothermal magnetocapacitance of hausmanite Mn_3O_4 which has a structure derived from a Jahn-Teller distortion of the spinel structure. The structure is depicted in the inset.

This talk will describe recent work from Santa Barbara on (i) insulating magnetic spinels and the magnetocapacitive behavior they display, (ii) A-site magnetism in spinels and the tuning of different (frustrated) ground states, (iii) the preparation of exchange biased composites of single-domain Ni on MnO starting from the spinels, and finally, (iv) some initial attempts to engineer exciting orbital physics at phase boundaries between cubic and tetragonal spinels.

References:

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Polar Oxide Materials: Synthetic Strategies and Characterization Techniques

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Polarity, the presence of a dipole moment, is seemingly common in molecular systems, e.g. H_2O, NH_3, HCl, etc. In extended structures, solid-state materials, the concept of polarity is a bit more complicated. For a solid-state material to be considered polar, the compound must crystallize in one of ten crystal classes, 1, 2, 3, 4, 6, m, mm2, 3m, 4mm, or 6mm. Interest in polar materials stems from two technologically important properties, pyroelectricity and ferroelectricity. One question that remains is how to synthesize new polar materials. We will describe our strategy toward the synthesis of new polar materials, as well as characterization techniques. A new polar material, $(NH_4)_2Te_2WO_8$ will be discussed.

A Lattice Manipulation Route to Mesoporous Transition Metal Oxides with Multipurpose Catalytic Activity

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We are successful in synthesizing a series of mesoporous transition metal oxide nanohybrids through an exfoliation–reassembling technique. In the present study, we have hybridized the colloidal nanosheets of layered titanate with narrow bandgap transition metal oxide nanoclusters (transition metal = Cr, Ni, Fe, Zn, etc). According to X-ray diffraction, electron microscopy, and N_2 adsorption–desorption isotherm measurements, the titanate nanosheets and the nanosized transition metal oxide particles are well ordered in layer-by-layer way, leading to the formation highly porous heterostructures. Diffuse UV–vis spectroscopic analyses clearly demonstrate that the optical property of layered titanate can be effectively modified through the hybridization with transition metal oxide nanoparticles. Of special importance is that the obtained nanohybrids can induce the photodegradation of organic pollutant under irradiation of low energy visible light ($\lambda < \sim 550$ nm) and the efficient epoxidation of cyclohexene with high selectivity. The present results underscore that the exfoliation–reassembling route can provide a very powerful way of developing novel porous transition metal oxide-based nanohybrids with multifunctional catalytic activities.

Functional Mixed Anion Systems: Synthesis, Ordering, and Properties

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In recent years different mixed anion nitrides have been investigated with the aim of finding novel materials showing interesting physical properties or completely new crystal structures. Nitrogen doping is an important method for modifying the properties of oxides, for example, tuning the bandgap of the photocatalyst TiO_2 from the UV to the Visible region. Ruddlesden-Popper strontium niobium oxides have not been reported, but the introduction of one nitrogen atom in each perovskite block allows the stabilization of these structure types in the family of oxynitrides $(SrO)(SrNbO_2N)_n$.[1] Oxynitrides have been also reported as new anode materials for rechargeable lithium batteries, showing high reversibility and capacity as well as enhanced chemical stability with respect to the nitrides.[2] Intercalated zirconium and hafnium nitride halides have shown to exhibit superconductivity with high critical temperatures (up to 25 K) within non oxidic materials. The structure of β-MNX (M=Zr, Hf) can be described as a stacking along the c axis of double layers with composition [X-M-N-N-M-X], separated by a van der Waals gap where different species can be intercalated. Superconductivity in β-ZrNX or β-HfNX is induced by intercalation of alkaline metals or Lewis bases as cobaltocene or pyridine between the double layers [X-M-N-N-M-X]. This lecture will present different aspects of the synthesis and crystal chemistry of functional mixed anion systems as selected oxynitrides and intercalated nitride halides, focussing on the relationships between the chemical compositions, the defect structure, the ordering of anions[3], the ordering of intercalated cations (staging)[4] and the physical properties.

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High Pressure Synthesis of Functional Transition Metal Oxides

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High-pressure (HP) synthesis is a powerful tool in searching for new functional materials. Our recent results on single crystal growth and material search will be reviewed

1. Single crystal growth of transition metal oxides at several GPa.

High-energy, high-flux synchrotron X-ray enabled the *in-situ* observation of the chemical reaction in a HP cell. We have performed single crystal growth of various transition metal oxides based on such obtained information. The results on $(VO)_2P_2O_7$, $PrNiO_3$ and $Ca_{2-x}Na_xCuO_2Cl_2$ will be presented.

2. "Super tetragonal" $BiCoO_3$ and $PbVO_3$

These compounds have enhanced tetragonal $PbTiO_3$ type structures with $c / a > 1.2$ and $P_S > 100$ μC/cm^2 expected from point charge model. From the magnetic measurements on single crystalline $PbVO_3$, we found that these large distortions can be attributed to d^1 ($PbVO_3$) and d^6 ($BiCoO_3$) electronic configurations.

3. Pressure induced intetmetallic charge transfer in a parovskite $BiNiO_3$

$BiNiO_3$ has the unusual charge distribution $Bi^{3+}{}_{0.5}Bi^{5+}{}_{0.5}Ni^{2+}O_3$ with ordering of Bi^{3+} and Bi^{5+} charges on the A sites of a highly distorted perovskite structure. High pressure neutron diffraction measurements show that the pressure-induced melting of the charge disproportionated state leads to a simultaneous charge transfer from Ni to Bi, so that the high pressure phase is metallic $Bi^{3+}Ni^{3+}O^3$ (in collaboration with Prof. Attfield's group).

Searching for oxide materials with high permittivity and magnetodielectric properties

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Dielectric materials with high dielectric permittivities and low loss factors over a wide frequency range are always of great interest due, on one hand, to the important applications of such properties in many electronic devices; and on the other, to the fundamentally interesting relationships among their crystal/electronic structure and physical properties Among them, mixed oxides with perovskite structure constitute an outstanding family in which high dielectric constants have been most commonly associated to ferroelectric or relaxor properties.

In this talk, after a general overview, we will focus in recent advances in the field such as the discovery of frequency independent "colossal" dielectric constant in the complex mixed oxide $CaCu_3Ti_4O_{12}$ [1]. We will also refer to the attractive topic of possible alternative electronic mechanisms that could give rise to high ε_r values [2, 3].

We will then move to another hot topic: the search for materials whose dielectric properties can be controlled by a magnetic field [4], and that are of high technological interest for example for the development of novel multifunctional storage components .

The two main strategies used will be presented: a) investigations in compounds in which ferroelectricity and cooperative magnetism coexist and are strongly coupled (the so-called "magnetoelectric multiferroics") [5,6] ; b) composite materials combining different phases with magnetostrictive and piezoelectric properties [4,6].

Other new possibilities, that make use of the complex electronic characteristics of transition metal oxides, will also be introduced [7,8].

Reference to the outstanding influence of the synthetic methods on the dielectric and/or magnetodielectric properties of these materials will be a constant throughout the talk.

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Studies of Charge Order in Single Crystals of Fe_2OBO_3

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Fe_2OBO_3 crystallizes in the orthorhombic Warwickite structure with structurally distinct $Fe(1)O_6$ and $Fe(2)O_6$ octahedra building ribbons consisting of four edge-sharing chains along *a*. Charge order in Fe_2OBO_3 was first reported by Attfield, *et al.* [1] on polycrystalline material, but no superstructure due to charge order was observed. Here we report the synthesis of single crystals of Fe_2OBO_3, and in-depth characterization of the charge order with electrical transport, differential scanning calorimetry, Mössbauer spectroscopy, high-resolution X-ray diffraction, and first-principles electronic structure calculations. We find at low temperature the development of a charge-ordered superstructure with a doubled unit cell and discrete valence states for Fe ions with full valence separation. These observations suggest that Fe_2OBO_3 is the best example of "ionic charge order" of any oxide yet investigated. Despite the ionic charge order, the superstructure modulations in an intermediate-T phase are, surprisingly, *incommensurate* and vary strongly with temperature. The incommensurate CO can be understood as arising from anti-phase boundary defects, which in one crystallographic direction can be created very easily due to geometrical charge frustration.

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Abstracts

Wednesday, August 22

New routes to the discovery of electrode materials

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Numerous investigations have been carried out these last three decades for the research of lithium batteries and cathode materials, on layered cobaltates, nickelates and manganites, leading to very promising properties for applications. Nevertheless, less effort has been put on the research of new structures as well as new methods of synthesis for the research of such properties, in spite of the discovery ten years ago of the phosphate $LiFePO_4$ on a potential low cost material for cathode. We report herein on the investigations that we carried out in three directions these last two years. The first direction deals with the exploration of hydrogenophosphates which represent a great potential for lithium intercalation/desintercalation: we describe here the synthesis of the structure, lithium intercalation and performances of the hydroxy phosphates $VO(H_2PO_4)_2$, $(H_3O)[Fe(H_2O)]_3H_{8(}PO_4)_6.3H_2O$, $Fe(H_2PO_4)_3$, $Ti(HPO_4)_2.H_2O$. In a second direction we have investigated known oxides, mainly the layered structure $HTiNbO_5$ and the 3D structure $VMoO_4$. We generate topotactically a new layered structure for $LiTiNbO_5$ and we show the ability of this phase to intercalate 0.8Li, leading to a reversible capacity of 120mAh/g, with a redox potential of 1.67V which makes this material attractive as an electrode for Li-ion batteries. The third route deals with the use of nanochemistry for enhancing Li-intercalation and in this way generating new cathode materials. We have applied this method to TiO_2 and we synthesized nanocrystalline rutile and brookite TiO_2, using either sol gel method or other soft chemistry techniques and we show that lithium intercalated nanocrystalline phases rutile $LiTiO_2$ and brookite $Li_{0.9}TiO_2$ can be synthesized. The electrochemical characteristics of these lithiated materials are very attractive for electrodes as shown for instance for brookite $Li_{0.9}TiO_2$ which reaches a high reversible capacity of 170mAh/g.

Cation Ordering in Mixed-Metal Oxides

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The perovskite structure possesses a very high degree of compositional flexibility, being able to tolerate a wide variety of cations on both the A and B sites. Variations in the relative size and charge of the A and B cations can be accommodated in a number of ways. Some involve distortions of the ideal cubic structure (usually involving a tilting of the B-site octahedra), and others involve the introduction of face-sharing octahedra into the network of vertex-sharing octahedra which is found in the cubic compounds. Both the A and B sites may be occupied by more than one cation species in a particular compound. In the case of the B sites this can involve cations of more than one element, or it may involve two oxidation states of the same element. In either case, the presence of more than one species raises the issue of cation ordering, either chemical ordering or charge ordering. The physical properties of the compound will be depend on whether or not this ordering occurs; charge ordering might only occur below room temperature and the properties will therefore change dramatically on cooling. The properties of a perovskite can also be varied by modifying the dimensionality of the structure, that is by limiting the thickness of the blocks of vertex-sharing octahedra along the z axis of the cubic (or pseudo-cubic) crystal structure. This approach recognises that perovskite is the end member of the Ruddlesden-Popper structural family. The introduction of vacancies onto the anion sublattice, as in the brownmillerite structure, is another method by which the properties can be varied. Examples showing the influence of cation ordering, anion vacancies, and changes in structural dimensionality on the electronic properties of perovskites will be presented. Recent work on compounds having the general formula $Ln_{18}Li_8B_4B'O_{39}$ will also be described.

Orbital ordering transitions in the vanadium oxides Sr_2VO_4 and $Lu_2V_2O_7$

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Correlated electron systems have remained in the spotlight of materials physics due to the rich and varied phenomena which occur due to the interplay of charge, spin and orbital degrees of freedom. Orbital ordering transitions are prime examples of the exotic behavior which can arise from these effects.[1] The first experimental evidence for these transitions occurred within the perovskites such as $YTiO_3$,[2] but over the last decade, orbital transitions have been observed in other systems such as the two-dimensional material $La_4Ru_2O_{10}$[3] and the spinel $MgTi_2O_4$.[4] The work presented in this talk highlights the discoveries of orbital ordering transitions in the layered perovskite Sr_2VO_4 and the pyrochlore $Lu_2V_2O_7$. An orbital ordering transition was predicted based on first-principle calculations in tetragonal Sr_2VO_4 at ~ 100 K,[5] but until now this transition has not been observed due to the difficulty in producing high quality samples. At the NHMFL, we have synthesized the pure tetragonal phase of Sr_2VO_4, and we provide evidence for orbital ordering at ~ 94 K, accompanied by a structural phase transition. In $Lu_2V_2O_7$, which has a frustrated magnetic sublattice, preliminary evidence for orbital ordering at ~73 K was first suggested by neutron scattering measurements.[6] We have synthesized single crystals at the NHMFL to search for this transition. Anomalous features observed in the specific heat, thermal conductivity, and resistivity are noted which are consistent with orbital ordering. As well, this material is found to have significant magnetoresistance in high magnetic fields.

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Unconventional Superconductivity & Magnetism in Complex Oxides

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Complex multinary oxides display a fascinating variety of phenomena such as unconventional superconductivity, magnetism, and magneto-ferro-electricity. Using examples from our crystal growth and studies of cuprate, ruthenate, manganite, and titanate oxides, I will discuss how certain synthesis practices become critically important to a correct elucidation of the fundamental physics underlying such phenomena. I will end by describing our recent studies of new magnetoelectric phases.

New Electronic Oxides – Simple or Complex?

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Exploration of the electronic properties of transition metal oxides has led to spectacular discoveries; notably of high-temperature superconductivity in layered cuprates and CMR (colossal magnetoresistances) in manganite perovskites; and continues to inspire experimental studies. Paradoxically, both simple materials showing ‘clean’ physics and complex, ‘dirty’ materials tuned through chemical variations can lead to new discoveries, as illustrated by recent results from our research group.

$SrCrO_3$ is a simple cubic perovskite, prepared at high pressures, in which a low temperature spin and orbitally ordered state has been discovered [1]. Long range electronic phase separation is observed. Solid solutions with $SrRuO_3$ are disordered semiconductors in the x = 0.4-0.6 range of $SrRu_{1-x}Cr_xO_3$ but have surprisingly high magnetic ordering temperatures (T_N = 400-500 K) in comparison to other Cr and Ru oxides [2]. $Cr^{4+} + Ru^{4+} \leftrightarrow Cr^{3+} + Ru^{5+}$ spin-polarised charge transfer is proposed as the mechanism for the strong antiferromagnetism.

$RuSr_2(R,Ce)_2Cu_2O_{10-\delta}$ ruthenocuprates are a complex family of layered perovskites in which small changes of doping (controlled by the R/Ce ratio and oxygen deficiency δ) and the R^{3+} cation size lead to large changes in electronic property. Both superconducting and CMR properties (up to MR = –47% at 4 K and 9 T) are found [3,4]. Low doped materials can be tuned from negative to positive magnetoresistances as the R size decreases from Nd to Gd.

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Abstracts

Thursday, August 23

The Combined Use of Pressure and Temperature in the Synthesis of Materials

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Although temperature is the usual tool in promoting chemical reactions, the joint use of pressure multiplies the possibilities of making them, in particular in the solid state. The main result of applying pressure and temperature to a single solid is either a phase transformation or a chemical decomposition reaction. However, when more than a single chemical component is employed, the possibilities of making new compounds are very much increased. In other words, the very fact of working in a three dimensional space: Composition, temperature & pressure, makes the search of new materials much more yielding, although this is not necessarily an easier job. In particular, impurities are a common plague of this procedure, especially if one can not control the homogeneity of P and T.

We will briefly describe the main aspects of HP & HT synthesis and then illustrate them with a few examples of our recent work. In particular, we will deal with the following systems:

- M-1212 cuprates ($MSr_2RECu_2O_8$: RE <> Rare earth, M <> Ru, Cr, Ir).

- The Sr- Cr(IV)-O-system.

- The $Pb(Ti_{1-x}M_x)O_3$ Perovskites.

- The Pr-Cu-O system.

Structural and microstructure characterisation has been performed and we have also measured magnetic and transport properties.

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Tuning into Frustration: Synthesis and Structural Studies of the Kagome Antiferromagnet $YBaCo_4O_{7+x}$

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The transition metal framework of the mixed-valent compound $YBaCo_4O_7$ (Y-114) is topologically related to that of the pyrochlore lattice, containing Kagome sheets of vertex-sharing CoO_4 tetraheda linked in the third dimension by a triangular layer of CoO_4 tetrahedra. Given this topology, the potential for geometric frustration of the formally S=3/2 Co^{2+} and S=2 Co^{3+} sites is apparent. Indeed, this material bears striking relationship to the known geometrically frustrated SCGO system, albeit Y-114 is more three-dimensional magnetically. In this talk I will discuss the structural chemistry of the Y-114 system, particularly with respect to its uptake of large O (~1 per formula unit). I will discuss how the structure responds both to temperature and composition, and its relevance to geometric frustration of this new family. I will relate the magnetic behavior, as probed by neutron powder diffraction, to the structural responses, arguing for a 'tuning' of geometric frustration via structural modification on the nonmagnetic sublattice. Finally, I will comment on the generality of these behaviors upon substituting other trivalent ions for Y^{3+}.

Dynamic Response of Oxides in Heterogeneous Catalysis

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Catalytic oxidation of hydrocarbons to olefins and oxygenates accounts for more than 50% of the total activity of chemical industry providing all important monomers for polymer materials. The overall efficiency of these processes is about 50% leaving much room for improvements. Despite of 60 years intensive research there is still controversy about all fundamental aspects of these reactions as hardly any surface science experiments re possible in this arena.

Most practical catalysts are mixed oxides containing Mo and/or V as essential component. There is strong belief that lattice oxygen is involved in the reaction requiring bulk catalysts although there are supported V/M_xO_y systems of technical relevance in dehydrogenation catalysis.

Selective oxidation requires activation of oxygen resulting in either electrophilic or nucleophilic surface oxygen species. It is the oxidation state of the partially reduced metal centre underneath that determines its reactivity.

Nanostructured and supported vanadium oxides have been studied in butane oxidation. Some insights into the dynamics of oxidation states and the metal-to-oxygen ratio will be discussed.

A mixed oxide MoVNbTe of a specific orthorhombic structure is a highly active catalyst for selective oxidation of propane to acrylic acid in a one-step reaction. A brief description about synthesis of this delicate compound will be followed by initial results on the search of its active phase. This study describes the analytical challenges in “real-world” oxidation catalysis.

A generalized summary of the mode of operation will be given highlighting the roles of structural dynamics and nanostructuring of functional oxides in oxidation catalysis.

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New oxides – ferroelectric, almost ferroelectric and ionically conducting

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The synthesis of polar perovskites without the use of lead on the A site is a challenge for solid state chemistry – the difficulties will be illustrated with new materials prepared at ambient and high pressures.

New routes to materials with efficient ionic conduction pathways are topical in view of the demands of lower temperature fuel cells and both catalytic and gas separation membrane devices. Structural mechanisms for accommodating charge carriers under highly reducing conditions will be discussed, together with the introduction of ionic mobility into new structure types.

Hybrid Metal Oxides and their Properties

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Inorganic framework materials, such as the aluminosilicate zeolites and the open-framework aluminum phosphates, find widespread applications in separation processes, ion-exchange, and catalysis. During the last 20 years, this field has grown through the discovery of framework materials based upon many other types of chemistries, e.g. oxides, sulfides, halides and nitrides [1]. It has also evolved in another direction with the growing interest in inorganic-organic framework structures, which contain both inorganic and organic components as part of a single framework architecture. Such materials include *coordination polymers,* in which isolated metal ions or clusters are linked into arrays by organic ligands, and *extended inorganic hybrids*, such as hybrid metal oxides in which there is M-O-M connectivity in 1-, 2-, or 3-dimensions [2,3]. They may be nanoporous or dense. The presentation will focus on some aspects of our recent work on hybrid systems with metal-oxygen bonding. The synthesis of carboxylates with structures of different dimensionalities will be described, and we shall examine the factors that control structural trends in hybrid materials, such as ligand geometry, ligand flexibility, chirality, synthesis temperature, pH and so on [4-11]. We shall also consider the use of high throughput methods for exploring phase space in hybrid materials [12]. Finally, we shall examine some of the potential applications of hybrid materials in areas such as enantiomerically-selective catalysis, hydrogen storage, and photoluminescence [13-14].

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Poster Abstracts

Wednesday and Thursday, August 22-23

#	Presenting Author	Title
1	Albrecht, T. A.	Unique cathodic high-density silver materials for high specific energy, long life power sources
2	Ambrosini, A.	Double-substituted perovskites $La_xSr_{1-x}Co_{1-y}Mn_yO_{3-\delta}$ for use in high-temperature oxygen separations
3	Appelhans, L. N.	Development of hybrid framework phosphors
4	Arévalo-López, A.	Cr(IV) substitution in $PbTiO_3$
5	Balasubramanian, K. R.	Synthesis of layered multiferroic materials--thin film growth of metastable $\mathit{RE}\mathrm{MnO}_3$
6	Behera, R. K.	Effect of surface and domains on ferroelectricity in $PbTiO_3$ thin films by molecular dynamics simulation
7	Birkel, A.	Up-converting properties in the system $\mathit{Ln}_2\mathrm{BaZnO}_5$
8	Callender, C. J.	Properties of $BaFeO_3$-based thin films and superlattices
9	Castillo-Martinez, E.	High pressure synthesis of new misfit-type phases in the Cr-Sr-O system
10	Chaudhary, Y. S.	Microemulsion based facile synthesis of functional metal oxide nanoparticles
11	Chernova, N.	Structural characterization and reactivity of vanadium oxide nanotubes, nanourchins and their isostructural bulk counterparts
12	Das, J.	Non-aqueous synthesis of titanium oxide with novel morphology
13	Devine, B. D.	Computational study of the interfacial structure of aluminum/α-alumina
14	Falcao, E. H. L.	A novel ligand for hybrid frameworks
15	Feller, R. K.	Polytypism, homochirality, interpenetration, and hydrogen-bonding in a new family of coordination polymers
16	Furman, J.	High aspect ratio nanostructures of conductive vanadium oxides
17	Gundiah, G.	Novel red phosphors based on vanadate garnets for solid state lighting applications
18	Havelia, S.	Epitaxial growth of metastable (110) layered perovskites using pulsed laser deposition
19	Johnston, K. E.	Synthesis and characterization of perovskite structures using solid-state NMR
20	Kam, K. C.	Hybrid frameworks of chiral magnesium tartrate and their racemic and *meso* analogues
21	Kim, Y-I.	Structural and optical characterizations of polycrystalline wurtzites $Zn_{1-x}Mg_xO$
22	Li, J.	Redox-driven Pd nanoparticles in and out of hexagonal $YFeO_3$ host
23	McGuire, M. A.	Effects of potassium content on the structural, magnetic, and electronic properties of K_xCoO_2
24	Melot, B. C.	Coupling of magnetism and dielectric properties in transition metal spinels

25	Merrill, C. A.	Chromium ethylenediphosphonate: a 3D hybrid inorganic-organic framework with 1D pores
26	Moreira dos Santos, A.	SNAP - the high pressure beamline at SNS
27	Rodriguez, E. E.	Synthesis and characterization of technetium oxides
28	Rondinelli, J. M.	Magnetoelectric coupling and interfacial multiferroism in transition metal oxide heterostructures
29	Saenger, M.	IR to UV spectral ellipsometry investigation of the phonon-phonon interaction in electrochromic tungsten oxide thin films
30	Schade, C. S.	Synthesis and investigation of magnetic oxide nanoparticle systems
31	Shoemaker, D. P.	Spontaneous phase separation of exchange biased nanoparticle-monolith composites
32	Singelyn, J. M.	Porous silicon dioxide as a template for nanoconfinement of responsive hydrogels
33	Voora, V. M.	Electric and electrooptic investigation of spontaneous polarization coupling in PLD-grown ZnO-$BaTiO_3$ heterostructures
34	Welk, M. E.	Synthesis of doped TiO_2 by the hydrothermal pouch method
35	Wohlwend, J. L.	$SrTiO_3$ thin film deposition: a computational study
36	Han, A. R.	A low temperature dehydration method for the carbon coating of transition metal oxides
37	Kang, J-H.	Exfoliation and reassembling route to TiO_2-pillared MnO_2 with microporosity
38	Lee, S. H.	One-pot hydrothermal synthesis of 1D/3D nanostructured cobalt-substituted manganese oxides with electrochemical and catalytic activity

Unique Cathodic High-Density Silver Materials for High Specific Energy, Long Life Power Sources

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The silver vanadium oxide $Ag_2V_4O_{11}$ (SVO) is currently utilized as a cathode in batteries for medical devices, which require a high voltage and large capacity, owing to the high reduction potential of silver. An improved cathode material, $Ag_4V_2O_6F_2$ (SVOF) has been synthesized and shown to sustain a high voltage, actually increased from the presence of fluoride, due to the greater density of silver in the material. Our research focuses on the exploration of other typically all-oxide materials where we not only want to include a high density of silver but also to replace oxide with fluoride. Hydrothermal reactions at low temperatures (< 200 °C) and low pressures (< 20 atm) have been studied in the Ag_2O–V_2O_5–$HF_{(aq)}$ system. Results have shown that $Ag_2V_4O_{11}$, β-$AgVO_3$, $Ag_4V_2O_6F_2$, $Ag_4V_2O_7$, and α-Ag_3VO_4 can be formed. The composition space has been constructed to show the relationships between these different phases, as well as between SVOF and $Ag_4V_2O_7$, both of which have the same Ag:V ratio and are formed at different temperatures. In addition, hydrothermal conditions have afforded crystals of α–Ag_3VO_4 for single crystal X-ray diffraction; the structure of which exhibits a new structure-type with an "anti" sphalerite-type structure.

Double-substituted perovskites $La_xSr_{1-x}Co_{1-y}Mn_yO_{3-\delta}$ for use in high-temperature oxygen separations: Synthesis, characterization, and permeation properties

Andrea Ambrosini, Fred Gelbard, Terry Garino, and Tina M. Nenoff

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Efficient and environmentally sound methods of producing hydrogen are of great importance as the world explores the use of hydrogen as a clean fuel. Currently studies are in progress to investigate the use of high temperature thermochemical cycles, driven by nuclear and/or solar energy, for H_2 production. The use of such cycles would reduce the demand on hydrocarbons which are currently used to produce hydrogen. One promising candidate for thermochemical hydrogen production is the Sulfur-Iodine (S-I) cycle, in which the decomposition of H_2SO_4 into O_2, SO_2, and H_2O at 850°C is a necessary step. *In-situ* removal of O_2 from this reaction pushes the equilibrium towards dissociation, thereby increasing the overall efficiency. Any potential membrane for the separation of oxygen in this step must withstand the high temperatures and corrosive conditions inherent in this process.

Perovskites (formula unit ABO_3) and perovskite-related structures are promising materials for such membranes due to their stability at high temperatures, mixed ionic/electronic conductivities, and ability to stabilize relatively large oxygen nonstoichiometries. To this end, ceramics based on the double-substituted perovskites were investigated, in particular the family $La_xSr_{1-x}Co_{1-y}Mn_yO_{3-\delta}$ (LSCM). LSCM powders were synthesized by solid state methods and characterized using powder X-ray diffraction and thermogravimetric analysis. Thermogravimetric analysis data imply that the materials can reversibly adsorb and desorb oxygen versus temperature and partial oxygen pressure, an indication of oxygen separation potential, while maintaining the perovskite structure.

Circular, 12 mm-diameter self-supported membranes of LSCM were synthesized by isostatic pressing and sintering of the powders. The resulting pellets were characterized by X-ray diffraction, four-probe conductivity, and scanning electron microscopy. Four probe measurements indicate that the materials are mixed ionic-electronic conductors. Oxygen permeation measurements were performed at temperatures between 800 – 950 ºC. These results, plus preliminary stability tests under H_2SO_4 decomposition conditions will be discussed.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the US DOE's NNSA, contract DE-AC04-94-Al85000.

Development of Hybrid Framework Phosphors

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University of California—Santa Barbara

Inorganic phosphors are widely used in solid state lighting and display applications, including LEDs and LCDs. Many types of inorganic phosphors have been developed to improve color-rendering and device efficiency. This work describes the development of hybrid framework materials (frameworks combining an organic ligand and a metal) as an alternative class of phosphor materials. The synthesis of a family of metal tartrate frameworks by hydrothermal methods is described. Nine new phases of strontium, calcium, and barium tartrates were obtained and characterized by single crystal X-ray diffraction. Doping the framework materials with luminescent rare earth ions yields fluorescent materials whose optical properties are briefly described.

Cr(IV) substitution in $PbTiO_3$

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$PbTiO_3$, a well known ferroelectric (FE) perovskite, shows, at room temperature, a large tetragonal distortion, space group *P4mm*. The presence of a "lone $6s^2$ pair" in Pb(II) and covalency effects in the Pb-O bond, as compared with isostructural $BaTiO_3$, which is also tetragonal and, indeed, the archetype of perovskite ferroelectrics, are quoted among the causes of the large tetragonality (c/a = 1.06)[1,2].

On the other hand, the $PbCrO_3$ perovskite synthesized under high-pressure and high-temperature conditions was claimed to be cubic (Pm-3m) by Roth and DeVries, who first prepared it at 1150ºC and 50 kbar in 1967 on a "belt" type apparatus[3]. This material presents antiferromagnetic G type behaviour ($a_{mag}=2a_{nucl}$) with T_N=240 K, and an electrical transport anomaly at 100 K[4].

Lead titanate is frequently used to dilute other complex lead-based perovskites, such as $Pb(Mg_{1/3}Nb_{2/3})O_3$, $Pb(Zn_{1/3}Nb_{2/3})O_3$, or $(Pb,La)ZrO_3$ to modify their piezoelectric properties by changing their phase transition temperature or by bringing them closer to the so-called morphotropic phase boundary[5,6].

However, no attempt seems to have being made to prepare a solid solution between $PbTiO_3$ and $PbCrO_3$. We have prepared $PbTi_{1-x}Cr_xO_3$ with $0 \leq x \leq 1$, by high pressure and high temperature conditions, to establish how does the replacement of Titanium by Chromium affect the structure and properties on this system.

We have observed that this replacement progressively destabilises the tetragonal structure of $PbTiO_3$ and the corresponding solid solution $PbTi_{1-x}Cr_xO_3$ becomes cubic for $x \geq 0.4$. By means of high temperature X-ray diffraction measurements, we have determined that T_c decrease following the equation $T_c = -3000x^2 + 40x + 742$ for $x \leq 0.3$; by TEM and HRTEM we have observed a complex microstructure with a two dimensional compositional modulation for the samples with $x \geq 0.7$. This seems to be related to lead deficiency.

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Synthesis of layered multiferroic materials – Thin film growth of metastable REMnO$_3$

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Hexagonal ferroelectrics are a set of layered compounds having the non-centrosymmetric point group symmetry *6mm*, where atomic displacements along the hexagonal axis lead to ferroelectricity. Three families have been experimentally identified as hexagonal ferroelectrics; they are *RE*GaO$_3$, *RE*InO$_3$, and *RE*MnO$_3$ with *RE* = Ho, Er, Tm, Yb, Lu, Y and Dy. Interestingly, the manganates are multiferroics, supporting both ferroelectric and ferromagnetic order. The subject of this poster will be on developing a synthetic method that will allow for a wider range of chemistries to be developed in thin film form. Specific emphasis of this poster is on the growth of metastable hexagonal multiferroics in the *RE*MnO$_3$ family.

*RE*MnO$_3$ (*RE* = Dy, Gd, Sm, La) films were deposited using PLD on (110) surfaces of single crystalline hexagonal (*h*-)YMnO$_3$. These films adopted the metastable multiferroic *h-RE*MnO$_3$ structure instead of the stable perovskite structure, except for *RE* = Dy, Gd, and Sm. Sharp (*hh*0) diffraction peaks with narrow rocking curves were found for these films. The peak widths increased with increasing size of the rare-earth cation. The c-axis/a-axis lattice parameter decreased/increased monotonically with increasing rare-earth size for these epitaxial films. All films exhibited the following epitaxial relationship $\{110\}_{REMnO_3} \| \{110\}_{YMnO_3}; \langle 1\bar{1}0\rangle_{REMnO_3} \| \langle 1\bar{1}0\rangle_{YMnO_3}$. The single-phase hexagonal films were kinetically robust against back transformation to the stable perovskite structure even to thicknesses of 50 nm. The importance and relevance of our results and synthetic approach to the facile realization of other layered ferroic materials that are difficult/impossible to synthesize by other synthesis methods will also be discussed.

Effect of surface and domains on ferroelectricity in $PbTiO_3$ thin films by molecular dynamics simulation

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Ultrathin ferroelectric (FE) films have potential application in non-volatile random access memories and microelectromechanical systems. Miniaturization of such devices demands the establishment of the thickness-property relationship, a detailed understanding of the surface termination and domain effects on the FE thin films. We use molecular dynamics simulations with a shell model approximation, where each atom is described by a core and shell. The model is tested for bulk $PbTiO_3$ (PT), where the simulated lattice parameter and polarization behavior with temperature shows an excellent qualitative agreement with experiment. We have performed a detailed investigation on the (001) terminated surface layers with both PbO and TiO_2 surface terminations in PT. The resulting surface energies indicate that the surface terminations with polarization out-of-the-surface are more stable than the cases where polarization occur into-the-surface. Analysis of atomic relaxation, surface rumpling and interlayer distance provide insight into the surface effects for each termination including polarization. Preliminary results on domain wall energy calculated for 180° domains show lower energy for a Ti-centered domain wall compared to a Pb-centered case. Structural analysis around the domain wall gives comparable match with first principle results. We acknowledge the support of the National Science Foundation through grant number DMR-0426870.

UP-CONVERTING PROPERTIES IN THE SYSTEM Ln_2BaZnO_5

Alexander Birkel[*], Alexander A. Mikhailovsky and Anthony K. Cheetham

August 15, 2007

Up-converting materials, i.e. substances that emit light with higher energies than the excitation radiation, have a large range of possible applications, such as LASER sources, coatings for solar cells or as infrared quantum counters.

We have investigated the up-converting properties of the oxide system Ln_2BaZnO_5, particularly the f^0 lanthanum La_2BaZnO_5 (tetragonal structure, space group *I4/mcm*) and the f^7 gadolinium Gd_2BaZnO_5 host (orthorhombic, space group *Pbnm*), doped solely with Er^{3+} or co-doped with Yb^{3+} and Tm^{3+} or Er^{3+}. Under 975nm excitation, the erbium-doped samples showed an emission band in the green, whereas the Yb,Er co-doped samples emitted green or red light, depending on the ytterbium to erbium ratio. The Yb,Tm co-doped compounds emitted in the blue.

We also synthesized both compounds via the Pecchini sol-gel method. The different performances of the sol-gel and solid-state prepared samples were compared, in addition to the dopant concentration dependence of the upconverting properties.

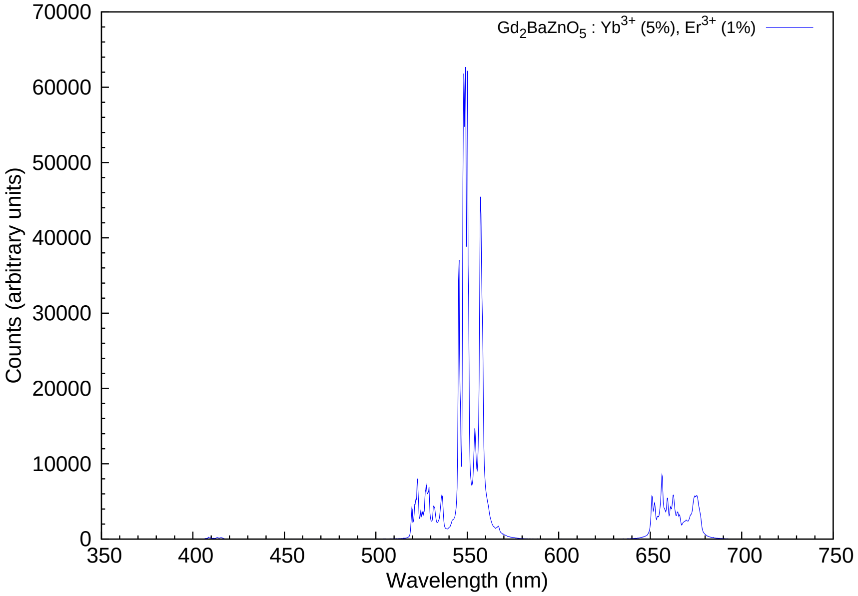

Figure 1: Up-converting spectrum of Gd_2BaZnO_5 under 975nm excitation

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Properties of $BaFeO_3$-based thin films and Superlattices

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The coupling of material properties (e.g. magnetic and ferroelectric) via the formation of artificial superlattices is of significant interest. These artificially-layered multiferroics add a new degree of freedom for tuning material properties. We will report on the synthesis and properties $BaFeO_3$ thin films and related superlattices involving $(Ba,Sr)TiO_3$ and $K(Ta,Nb)O_3$ ferroelectrics. In bulk, $BaFeO_3$ is a hexagonal structured material with ferromagnetic transition at 160 K. However, $BaFeO_3$ can be stabilized in a pseudo-cubic perovskite structure via epitaxial thin film. We will describe the synthesis, and structure of $BaFeO_3/K(Ta,Nb)O_3$ and $BaFeO_3/(Ba,Sr)TiO_3$ superlattices grown by pulsed laser deposition. Effects of oxygen stoichiometry on magnetic and structure properties will be discussed.

High Pressure synthesis of new Misfit-type phases in the Cr-Sr-O System.

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In the study of the Strontium-Chromium(IV) oxides synthesised at high pressure and high temperature[1] we have obtained other phases with a *misfit layer structure* type. Control over the reaction time in high pressure-high temperature conditions becomes crucial in stabilizing the perovskite or the misfit layer type structures. A new compound with chemical formula $Sr_2O_2(CrO_2)_{1.8}$ has been isolated. It seems to be the first example of high pressure, high temperature synthesised misfit layer oxide. Its structure, similar to that of thermoelectric cobalt oxides, [2] consists of two types of layers, H and Q which alternatively stack along the c axis. Electron Diffraction patterns and High Resolution Transmision Electron Microscopy Images along [001] shows the misfit character of the different layers composing the structure. Powder XRD are fitted with a (3+1) dimensional superspace group X-1(abg)0.

Electron microscopy and diffraction have provided substantial evidence for the presence of some other misfit layer compounds of the same family which have not yet been isolated since they are all stabilized in the same narrow window of synthesis conditions. More work is being done in this direction.

The existence of magnetic layers of sharing edges $[CrO2]_\infty$ octahedral, separated by non-magnetic rock salt type layers $[Sr_2O_2]_\infty$ are responsible of 2D magnetic interactions.[3] They are evidenced by a broad maximum in the magnetic susceptibility curve which can be fitted with the high temperature susceptibility of the Heisenberg model for a two dimensional antiferromagnet.

In this communication, we will describe and discuss the synthesis and characterization of these newcompounds in the Sr-Cr-O system.

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Microemulsion Based Facile Synthesis of Functional Metal Oxide Nanoparticles

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Metal-oxides are of great interest due to their applications in areas such as electronics, photonics, chemical sensing, catalysis *etc* and hence have been widely studied over the last few decades. For this reason, a lot of attention is being paid to develop a variety of new synthetic approaches such that metal oxides with different morphology (such as nanoparticles, nanospheres, wires, rods *etc.*) can be fabricated to exploit their size and shape dependent properties for various applications.

However, a generic synthetic approach to fabricate a variety of metal oxides with a narrow size distribution has not been explored to a great extent. We will present here the use of a single new amphiphile: alkyl glycoside, which exhibits interesting features such as non-toxicity, biocompatiblility, and temperature insensitive phase behavior. This sole amphiphile has been used to develop a generic microemulsion based synthetic approach to fabricate a variety of metal oxide nanoparticles, specifically TiO_2, V_2O_5 and ZrO_2. This approach has lead to the formation of metal oxide nanoparticles that are consistently on the order of ~50 nm as revealed by microscopy analysis and are stable for a prolonged period of time under ambient conditions. For this presentation, their detailed synthesis, characterization along with a growth mechanism will be presented.

Structural characterization and reactivity of vanadium oxide nanotubes, nanourchins and their isostructural bulk counterparts.

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We have determined optimum synthesis conditions for vanadium oxide nanotubes (VONTs, $VO_{2.4}[C_nH_{2n+1}NH_3]_{0.31}\cdot 0.56H_2O$) formation, their arrangement into nanourchin morphology and for the synthesis of $(en)V_7O_{16}$, which is believed to have the same vanadium oxide layer as VONTs, but is not scrolled. The compounds were characterized by x-ray diffraction, TGA, TEM, SEM, FTIR, and ESR; magnetic properties were studied using SQUID magnetometer. The emphasis in characterization was made on determination of V^{4+} and V^{5+} distribution in these mixed-valence oxides. From the temperature dependence of the magnetic susceptibility, paramagnetic V^{4+} ions were found in VONTs in the amount corresponding to the number of tetrahedral vanadium sites in the structure. It should be noted that tetrahedral coordination is extremely atypical for V^{4+}. VONTs also show a spin gap, which is well described by the simple model of magnetic dimers with AF exchange. About 40% of vanadium ions are involved in the magnetic dimer formation; the crystallographic sites of these V^{4+} ions are currently unknown. Ion-exchange and red-ox reactions of the compounds were studied. Upon ion exchange with BuLi the amount of isolated V^{4+} is preserved, but the spin-gap behavior is significantly disturbed. Magnetic characterization of nanourchins revealed about 45% of paramagnetic V^{4+} and no clear spin-gap behavior, which indicates different V^{4+}/V^{5+} distribution. Further structural, magnetic and ESR characterization of VONTs, nanourchins, $(en)V_7O_{16}$ and products of their red-ox and ion-exchange reactions are underway. The work is supported by the National Science Foundation through grant DMR 0313963.

NON-AQUEOUS SYNTHESIS OF TITANIUM OXIDE WITH NOVEL MORPHOLOGY

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One dimensional (1D) inorganic materials with ordered structures such as rods, wires, belts and tubes on the micron to nanometer length scale has become one of the most important research subjects in nanotechnology. Depending upon the shape and size, these 1D-structures are known to possess unique physical, optical, catalytic, magnetic and semi-conducting properties.

Among various transition metal oxides, titanium oxide (TiO_2) is particularly interesting, because it has been extensively used in a wide variety of potential technological applications such as catalysis, gas sensor, dye-sensitized solar cells, photochemical degradation of organic pollutants, white pigments for paints and cosmetics. The exploration of novel approaches for synthesis of TiO_2 with control particle size and morphology is quite challenging because the efficiency of TiO_2 in its different applications strongly depends on its shape, size and phases such as morphology, dimensions and crystallanity.

Here, we'll first report the synthesis of a unique titanium glycolate intermediate precursor with rod-like morphology by solvothermal method. Subsequently, the glycolate precursor was converted into different phases of TiO_2 after calcinating in air at various temperatures. Essentially, the rod-like morphology was preserved in the calcination process. Further, a possible growth mechanism will be discussed for the formation of Ti-based rods. Mainly, electron microscopy and X-ray diffraction were used to characterize the morphology, microstructure and crystallinity of Ti-based rods. Furthermore, different strategies have been developed for the fabrication of hybrid materials of metal nanoparticles (NPs) grafted onto these oxides. The detailed results of the formation of these composite materials along with their characterization by different techniques will be discussed.

Computational Study of the Interfacial Structure of Aluminum/α-Alumina

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Several experimentally observed orientations for the interface between FCC aluminum grown on the (0001) face of α-alumina were studied through molecular dynamics using a modified variable charge potential. This many-body, empirical potential allows for the realistic modeling of both the metallic and ceramic phases in large-scale, atomistic simulations. The effects of temperature, surface terminations and coherency on the interfacial structure and energy were investigated. The efficiency of the molecular dynamics simulation allows for study of periodic systems oriented with minimal strain along the preferred relationship of $[10\bar{1}0]_{Al2O3} \parallel [\bar{1}10]_{Al}$ as well as secondary orientations along $[2\bar{1}\bar{1}2]_{Al2O3} \parallel [01\bar{1}]_{Al}$ and $[2\bar{1}\bar{1}2]_{Al2O3} \parallel [2\bar{3}1]_{Al}$. The results are compared to experimental data and to the results of density functional theory calculations. This work is supported by the National Science Foundation (DMR-0426870).

A novel ligand for hybrid frameworks

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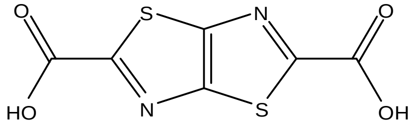
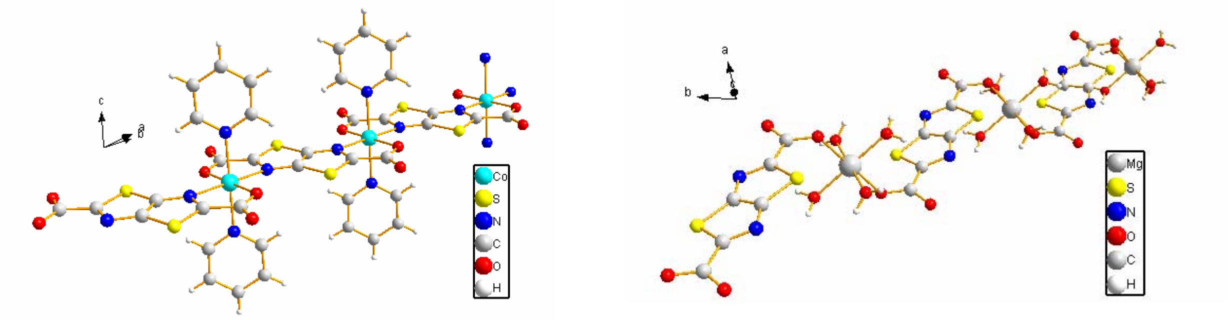
Hybrid frameworks offer promise in fields such as hydrogen storage, separations and catalysis. The nature of the metal cation, the organic linker and the three-dimensional architecture of the framework play crucial roles in determining the material's properties. In this work, we report the synthesis and structural characterization of compounds obtained by the reaction of 2,5-thiazolo[5,4-d]thiazoledicarboxylic acid (H_2-Thz) with several metals. This ligand features two carboxylate groups and the heteroatoms nitrogen and sulfur in fused 5-membered rings, offering additional linking sites for framework formation.



Although having very low solubility in most common solvents, the diacid can be dissolved in water at basic pH. Organic bases such as pyridine raise the pH enough to promote dissolution while not precipitating hydroxides of the metals used in this study. The reaction is carried out under hydrothermal conditions at temperatures around 100°C for 24 to 48 hours.

Reaction with the transition metals copper and cobalt yields linear chains in which two Thz units bind to the metal center through the oxygen and nitrogen, forming co-planar five-membered rings, while the remaining axial positions are occupied by two pyridine molecules. The chains are held together by inter-molecular forces, forming X-ray quality blue (Cu) and orange (Co) single crystals. A similar structure is obtained with zinc, but water molecules coordinate the axial positions instead of pyridine. Nickel promotes decomposition of H_2-Thz, and linear chains of Ni-oxalate result. Different structures are obtained when alkaline earths react with the diacid: with magnesium, for example, each Thz unit connects with the metal through one oxygen only, with water molecules occupying the four equatorial sites. A more complicated structure arises with strontium, in which seven-coordinated Sr ions are connected through bridging Thz, water and oxide units. Structural determination of the Ca and Ba products is currently being attempted.



The structures of $Co(Thz)(Pyr)_2$ (left) and $Mg(Thz)(H_2O)_4$ (right).

Polytypism, Homochirality, Interpenetration, and Hydrogen-Bonding in a New Family of Coordination Polymers

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We report the synthesis of five coordination polymers of divalent transition metals combined with *5*-hydroxyisophthalic acid ("HIP") and *4,4′*-bipyridyl ("bipy"). Mn forms two polytypic two-dimensional coordination polymers, Mn(HIP)(bipy) · 3 H_2O and Mn(HIP)(bipy) · ¼ bipy · 2 H_2O (**I** and **II**, with ABAB and ABC stacking sequences, respectively); Ni forms a homochiral hexagonal three-dimensional coordination polymer with two interpenetrating trigonal sublattices, Ni(HIP)(bipy)(H_2O) (**III**); Cu forms a one-dimensional coordination polymer containing arrays of infinite hydrogen-bonded molecular ribbons, $Cu(HIP)_2(bipy)$ **(IV);** and Zn forms a two-dimensional coordination polymer with a stair-stepped layered structure, $Zn_2(HIP)_2(bipy)(H_2O)_2$ · H_2O (**V**). The M-HIP-M connections are perpendicular to the M-bipy-M connections in all structures where they are present. Crystal data for **I**: *P*2/c, a = 10.1726(11) Å, b = 11.6397(13) Å, c = 16.2535(18) Å, β = 103.310(3)°, V = 1872.8(4) Å^3, Z = 4; for **II**: *P*2/n, a = 11.6900(8) Å, b = 10.1772(7) Å, c = 17.9098(12) Å, β = 102.326(2)°, V = 2081.6(2) Å^3, Z = 4; for **III**: $P6_1$, a = 11.2217(7) Å, c = 25.0290(16) Å, V = 2729.6(3) Å^3, Z = 6; for **IV**: *C*2/c, a = 10.118(3) Å, b = 11.051(3) Å, c = 21.051(5) Å, β = 99.029(5)°, V = 2324.5(10) Å^3, Z = 4; for **V**: *P*-1, a = 7.4720(14) Å, b = 9.6175(18) Å, c = 10.1060(19) Å, α = 100.587(3)°, β = 97.165(3)°, γ = 112.381(3)°, V = 644.8(2) Å^3, Z = 1.

High Aspect Ratio Nanostructures of Conductive Vanadium Oxides

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Vanadium (IV) oxide is known to show a metal insulator transition slightly above room temperature. By dispersing high aspect ratio conductive oxides in a polymer we suggest it is possible to create an optically transparent conductor, despite their opaque bulk phase characteristics. Novel transparent conductors are anticipated to replace ITO as the transparent conductive electrode in display devices, and conductive polymers in flexible electronics. In this work we address the first phase of this process: the synthesis of high aspect ratio vanadium oxides and control of their oxidation state.

Vanadium oxide nanotubes are prepared using bulk V_2O_5 and long single chain amines as a templating agent under hydrothermal conditions. The amines are dissolved in ethanol and stirred with V_2O_5 and water, during which time a lamellar structure of oxide and amine forms. Samples were also doped with high valent metal cations such as niobium and tungsten to lower the phase transition temperature. The intercalated mixtures are then heated and the lamellar structure rolls up, forming hollow tubes. The vanadium tubes, as prepared, have an oxidation state somewhere between V(V) and V(IV). A post-synthesis annealing step removes any remaining amine, develops crystallinity and gives control over the oxidation state from V(III) to V(V) depending on the atmosphere. The morphology of the tubes is maintained through the annealing, as confirmed by SEM. Samples are also characterized by thermal XRD, and UV-VIS-IR spectroscopy. Optical measurements show a large increase in near-IR absorption in the reduced samples as compared to the as prepared samples, suggesting increase in conductivity.

Novel red phosphors based on vanadate garnets for solid state lighting applications

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Solid state lighting based on GaN LEDs has shown a significant potential for replacing conventional lighting sources such as incandescent and fluorescent lamps. White light is presently obtained using an InGaN chip that emits blue light in combination with a Ce-doped $Y_3Al_5O_{12}$ garnet yellow phosphor. The next generation of lighting devices is based on a near UV LED emitting at 400 nm in combination with blue, green and red phosphors. This approach has an advantage that the color is tunable and has a better color rendering. The success of this depends on the availability of efficient phosphors.

In our quest for red phosphors, we have synthesized a series of vanadate garnets with the composition $Bi_x Ln_y Eu_{1-x-y} Na_2 Mg_2 V_3 O_{12}$ (where *Ln*= Y, La, Gd; x=0-0.4 and y=0-0.2) and investigated their applications for solid state lighting. The phosphors show a broad charge transfer excitation that can be suitable tuned by the addition of Bi^{3+} to capture the UV radiation from a GaN LED. We have synthesized a range of compositions and performed structural and optical studies on the samples. In addition, the performance of the phosphors at higher temperatures has been evaluated and compared to commercial standards.

Epitaxial growth of metastable (110) layered perovskites using pulsed laser deposition

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Materials that exhibit multiple mechanisms of ferroelectricity in the same phase have recently attracted considerable interest. The $A_nB_nO_{3n+2}$ (typically n=4) compounds, also known as the (110) layered perovskites, can support both inbuilt structural frustrations, as in the so-called geometric ferroelectrics, and d^0-cations in octahedral coordination that are prone to cooperative off-centering (second order Jahn Teller) displacements, as those that occur in the well-known titanate and niobate perovskite ferroelectrics. Nevertheless, only a few chemistries are known to form in this crystal structure. In this work, we are interested in the synthesis of the $RE_4Ti_4O_{14}$ (*RE* = rare earth) family of compounds, to understand better the compositional flexibility that this structure can adopt. The larger rare earth cations (La-Nd) are stable in the (110) layered perovskite structure (space group: $P2_1$), while the smaller rare earth cations (Sm-Lu) are stable in the pyrochlore phase (space group: Fd3m). High pressure synthesis of smaller rare earth titanates in their (110) layered perovskite structure is not a viable synthesis approach, because the pyrochlore is the denser phase. Epitaxial stabilization offers an alternative route for the synthesis of these metastable phases in the form of thin films and is the main focus of this work.

We will present the synthesis of $La_4Ti_4O_{14}$, $Sm_4Ti_4O_{14}$, $Gd_4Ti_4O_{14}$, and $Dy_4Ti_4O_{14}$ in the (110) layered perovskite structure as epitaxial thin films. Special emphasis is placed on the attainment of $Gd_4Ti_4O_{14}$ and $Dy_4Ti_4O_{14}$ in this structure since their synthesis has never been reported before. All films were deposited on single crystal (110)-oriented $SrTiO_3$ substrates using pulsed laser deposition (PLD) and characterized using *ex-situ* X-ray diffraction. The metastable films (*RE* = Sm, Gd, and Dy) are epitaxial and adopt crystal structures that are essentially isostructural with $La_4Ti_4O_{14}$; the epitaxial relationship between the film and the substrate was determined to be $\{001\}_{Film} \parallel \{110\}_{Subs} : \langle 010\rangle_{Film} \parallel \langle 1\bar{1}0\rangle_{Subs}$.

The effects of several deposition parameters on the growth and structure of the metastable phases were also investigated. High quality crystalline films were obtained at a high substrate temperature (900°C), which provides thermal energy for diffusion to occur (both normal and parallel to the substrate surface) and for the epitaxial layers to align properly. The stoichiometry ($LaTiO_3$ or $La_4Ti_4O_{14}$) of the films is highly dependant on the ambient atmosphere (N_2 or O_2) used for deposition. The deposition rate is also found to have a critical influence on whether the stable pyrochlore or the metastable (110) layered perovskite phase is attained. This study paves the way for the synthesis of other similar metastable layered compounds having multiple mechanisms of ferroelectricity.

Synthesis and Characterisation of Perovskite Structures using Solid-State NMR

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Our current area of research aims to combine conventional solid-state techniques, such as X-ray and neutron powder diffraction, with solid-state Nuclear Magnetic Resonance (NMR). By combining two such complimentary approaches a variety of different perovskite based structures will be investigated and characterised in greater detail.

Scandium has various coordination capabilities in a variety of different compounds and our initial research has focused on a number of scandium based perovskites. The relative ease with which the well known perovskite structure can be distorted indicates the importance of such compounds in various areas of materials chemistry. Several scandium based materials have been synthesised and are currently undergoing solid-state NMR investigation, the findings of which will be presented. One compound in particular, $Ba_2Sc_2O_5$, is of significant interest owing to reports of unusually low scandium coordination number. Conformation of such a value cannot be determined by X-ray diffraction alone, therefore it is hoped ^{45}Sc NMR will offer further insight; the results of which will be presented.

An additional area of our research focuses on finding suitable replacements for currently the most extensively used piezoelectric and ferroelectric material, $PbZr_{1-x}Ti_xO_3$ (PZT). Using high pressure synthesis our research principally aims to investigate bismuth based perovskites as possible alternatives. In doing so it is hoped a material with either equivalent or enhanced piezoelectric and ferroelectric properties to PZT can be synthesised. One Bi based solid solution, $x\mathrm{Bi}(\mathrm{Zn}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3$–$(1-x)\mathrm{K}_{1/2}\mathrm{Bi}_{1/2}\mathrm{TiO}_3$, is currently being prepared and any significant findings will be presented and discussed.

Hybrid Frameworks of Chiral Magnesium Tartrate and their Racemic and *Meso* Analogues

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There has been an explosion of interest in hybrid inorganic-organic framework materials, with possible applications in separations, catalysis, and hydrogen storage. These hybrid frameworks exhibit both structural and chemical diversity such as nanoporosity and other chemical characteristics as a function of the bridging molecule.

One of the fascinating and interesting aspects of hybrid framework materials concerns those that have chiral structures. They represent a unique class of extended (i.e. non-molecular) solids that can be readily synthesized as chiral solids that may have potential applications in enantiomerically-selective catalysis and separations, as well as photoluminescence and non-linear optics. By contrast, purely inorganic materials, such as aluminosilicate zeolites, can only be obtained in chiral forms by physical separation of mixtures of enantiomers (conglomerates). The structural diversity of *chiral* framework structures is only just beginning to be explored.

Here, we present the synthesis and characterization of novel homochiral magnesium tartrate hybrid frameworks as well as their racemic and *meso* analogs prepared by hydrothermal method [1]. These new materials, formed under very similar conditions, exhibit a wide variety of different structures with varying dimensionalities, connectivities, and chemical compositions.

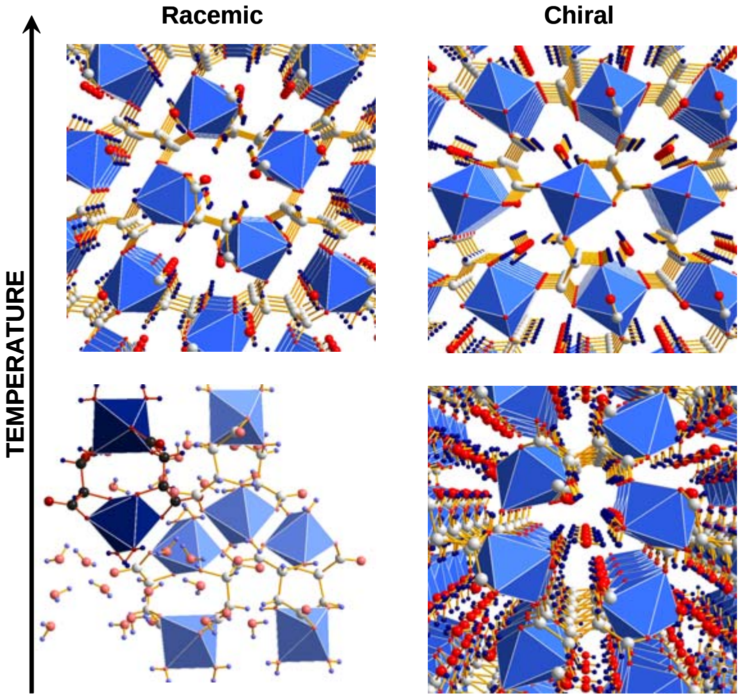

Figure: Some examples of magnesium tartrate hybrid frameworks

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[1] Kam, K.C.; Young, K. L. M.; Cheetham, A.K. *Cryst.Growth Des.* **2007**, *7*, 1522-1532.

Structural and optical characterizations of polycrystalline wurtzites $Zn_{1-x}Mg_xO$

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The average and local crystal structures, optical properties, and phonon vibrations of polycrystalline wurtzites $Zn_{1-x}Mg_xO$ ($0 \le x \le 0.15$) have been studied. Rietveld and pair-distribution-function (PDF) analyses of synchrotron X-ray diffraction (XRD) patterns show that the increases in the Mg-concentration results in *c*-axis compression of the hexagonal lattice, and in diminution of the off-center cation displacement within each tetrahedral ZnO_4 unit. The size-strain line broadening analyses of XRD patterns reveal that the Mg-substitution decreases the crystallite size and also develops the lattice strain. The E_2^{high} Raman line of $Zn_{1-x}Mg_xO$ displays systematic changes in response to the evolution of the crystal lattice upon the Mg-substitution. The red-shift and broadening of the E_2^{high} mode are explained by the expansion of hexagonal *ab*-dimensions, and compositional disorder of Zn/Mg, respectively. On the other hand the E_2^{low} Raman mode shows an opposite behavior, blue-shift upon the increase of Mg content, which is explained by the change in the reduced-mass of (Zn,Mg)–O oscillators. The optical properties of the samples have been characterized by diffuse reflectance spectroscopy and fluorimetry. The band gap gradually increases with the Mg-concentration, from 3.24 (ZnO) to 3.35 eV ($Zn_{0.85}Mg_{0.15}O$).

Redox-driven Pd nanoparticles in and out of hexagonal $YFeO_3$ host

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The catalytic converter, a key component of modern automobiles, has been used to reduce air pollution caused by auto exhaust gases since the 1970's. The catalysts inside the catalytic converters are generally ceramic-supported precious metal fine particles. One of the drawbacks of these conventional catalysts is that their activity tends to decrease with time in use due to the sintering of the metal particles when exposed to heat. Recently, Nishihata and coworkers found that $LaFe_{0.57}Co_{0.38}Pd_{0.05}O_3$ is an "intelligent" catalyst because the sintering of metallic Pd particles seems to be suppressed by the self-regenerative process of the palladium and therefore the durability of the catalyst is improved. We have demonstrated, in our previous work, Pd-substituted perovskite $BaCeO_3$ is also an "intelligent" catalyst with extremely high catalytic activity for CO oxidation at low temperatures giving the surface area of only 1 m^2/g.

In present work, we have been successful in devising synthetic routes to macroporous nanocrystalline hexagonal $YFe_{1-x}Pd_xO_3$ ($0 \leq x \leq 0.1$) phases at low temperatures. The crystal structure of the metastable hexagonal $YFeO_3$ phase is reported for the first time. In situ X-ray diffraction shows that substitution of palladium helps to stabilize the hexagonal structure. The prepared materials were characterized using neutron and X-ray powder diffraction, N_2 absorption, scanning and transmission electron microscopy, and UV-Vis and X-ray photoelectron spectroscopy. Our XRD study clearly indicates that Pd^{2+} incorporates in the hexagonal host lattice as cations under oxidizing conditions, and that it is released as elemental *fcc*-Pd nanoparticles under reducing conditions. The regeneration of Pd is repeatable through many redox cycles. We have also monitored the same movement of Pd on the surface using core-level X-ray photoelectron spectroscopy. Scanning electron microscopy reveals highly porous nanostructures in these as-prepared and reduced samples. Palladium nanoparticles in reduced samples are detected by SEM backscattered electron imaging and HRTEM. It can be seen that these Pd nanoparticles disappear after reoxidation processes and nearly conserve their particle sizes after several redox cycles. Scanning transmission electron microscope (STEM) analysis, X-ray absorption, fine structure, and catalytic properties of these materials are currently under examination.

Effects of Potassium Content on the Structural, Magnetic, and Electronic Properties of K_xCoO_2

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Observations of numerous interesting electronic and magnetic properties (frustrated magnetism, high thermopower, superconductivity) in the sodium cobaltates Na_xCoO_2 and their hydrates have generated much interest in the recent literature. Several studies have investigated how the crystal structures and physical properties of these materials depend on the sodium content. However, no similar systematic study of the analogous potassium compounds has been reported. We have begun investigating the evolution of structural, magnetic, and electronic properties of the non-hydrated potassium cobaltate K_xCoO_2 as the potassium content x is varied. The materials are synthesized using a combination of solid state and solution chemistry techniques, and characterized by diffraction, magnetization, and electrical resistivity measurements. Correlations between the structural, electrical, and magnetic properties are examined, and comparisons to the well studied sodium cobaltates are made.

Coupling of magnetism and dielectric properties in transition metal spinels

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We have investigated the thermodynamic, magnetic, and dielectric properties of two ferrimagnetic insulating spinels $CoCr_2O_4$ and Mn_3O_4. Magnetocapacitive measurements show that the dielectric constant of $CoCr_2O_4$ couples to the spiral magnetic order parameter, but is insensitive to the ferrimagnetic spin component. Additionally the incommensurate magnetic transition in Mn_3O_4 produces no dielectric anomaly at zero magnetic field. However, with the application of modest magnetic fields an increase in dielectric constant at this transition has been found. We discuss our results in the framework of models for coupling the dielectric constant to non-collinear long-range magnetic order and spin-phonon coupling.

Chromium Ethylenediphosphonate: a 3D Hybrid Inorganic-Organic Framework with 1D Pores

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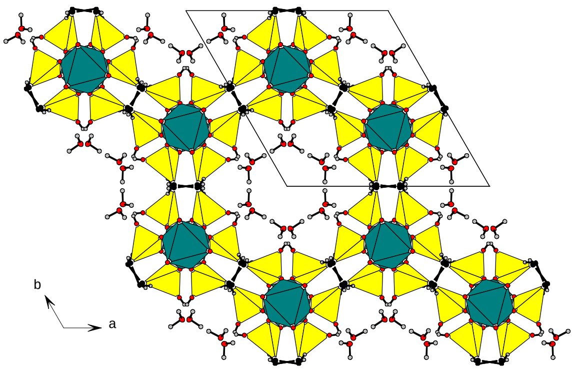
Poster Abstract

Interest in framework materials is due in part to structural similarities to zeolites and aluminum phosphates (AlPOs), both of which have huge industrial applications from petroleum cracking to ionic separation. Structures of phosphates (PO_4) led to phosphites (HPO_3), which led to phosphonates ($R\text{-}PO_3$). While most phosphonates are pillared layered structures, we have recently synthesized a new 3D chromium hybrid inorganic-organic framework with one dimensional pores. Not only is $Cr_2[HO_3PCH_2CH_2PO_3H]_3 \cdot 6H_2O$ one of the few phosphonates with accessible porosity (see Figure), it crystallizes in a space group that is rare for organic containing materials to crystallize in, the polar space group P6cc (*a* = 13.1098(11) Å, *b* = 9.2608(15) Å). The channels contain a unique hexamer of water molecules; a planar ring with the pendant hydrogens all pointing in a common direction along the *c*-axis.



SNAP - The High Pressure Beamline at SNS

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NSSD ORNL P.O. BOX 2008 MS-6475 OAK RIDGE TN 37831-6475

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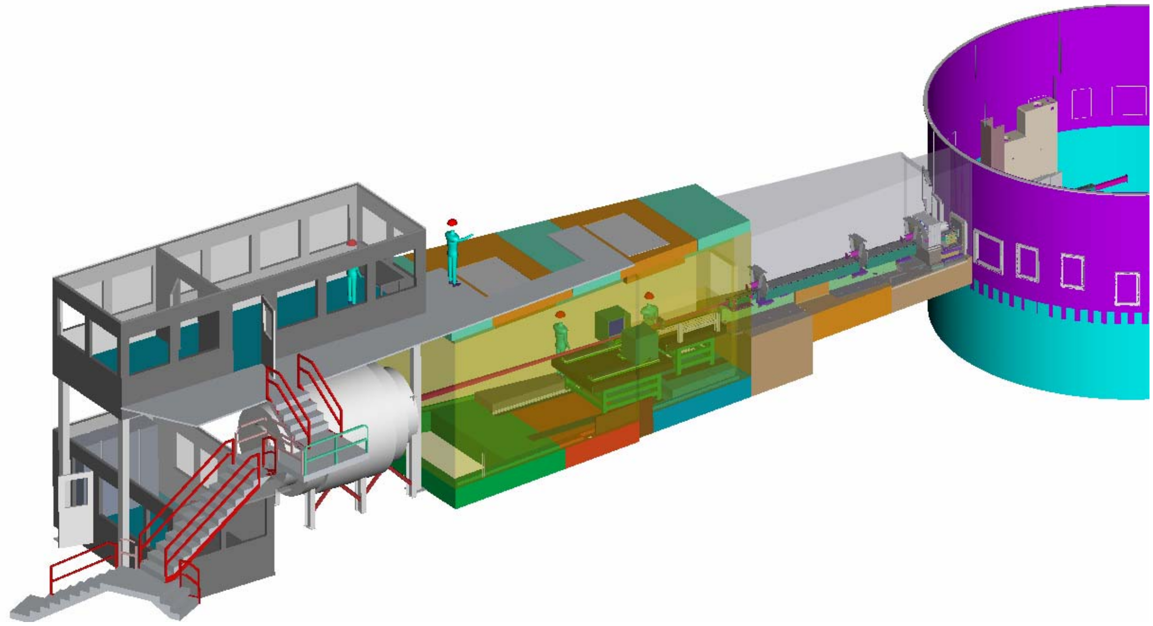
Designed to make a definitive contribution to the study of materials science under high pressure, the SNAP (**S**pallation **N**eutrons under **A**pplied **P**ressure) diffractometer at SNS, allows studies of a variety of powdered and single-crystal samples under extreme conditions of pressure and temperature. The increased neutron flux, coupled with large-volume pressure cells using large synthetic single-crystal opposed anvils, allows significant advances in the pressure range accessible to neutron diffraction. The pressure goal is 50 to 100 GPa on an ~1-mm^3 sample on a routine basis. In addition, recent advances in next–generation detectors will allow the incident beam-focusing optics, pressure chamber, and detector array to be highly integrated, thus providing a highly flexible facility for materials studies under extreme conditions.



Synthesis and Characterization of Technetium Oxides

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The oxide chemistry of technetium-99 ($t_{1/2} = 2.12 \times 10^5$ y) has not been investigated to any significant extent and presents an opportunity to explore new structural, electronic and magnetic regimes. The crystal structure of TcO_2, prepared from the careful thermal decomposition of freshly crystallized ammonium pertechnetate, has been determined using neutron powder diffraction data and will be presented and discussed. Based on the NPD data, TcO_2 has a distorted rutile-type structure with a Tc—Tc metal bond length of 2.622(1) Å, a value longer than anticipated from earlier studies. In addition, three new ternary oxides containing technetium and bismuth were prepared through the reaction of TcO_2 and Bi_2O_3 under different conditions. The products $Bi_2Tc_2O_7$, $Bi_3Tc_3O_{11}$, and Bi_3TcO_8 contain Tc in different oxidation states ranging from +4 to +7 and show a variety of structure-types as confirmed by X-ray and neutron powder diffraction data. Comparisons with other binary oxides and mixed-metal oxides of neighboring elements in the periodic table such as Mo, Ru, and Re will also be discussed.

Magnetoelectric coupling and interfacial multiferroism in transition metal oxide heterostructures

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We present results of density functional calculations of the dielectric and magnetic responses of $SrRuO_3/SrTiO_3/SrRuO_3$ and related oxide heterostructures. Our calculations indicate the spatial coexistence of magnetic and polar behavior at the metal-insulator interface, suggesting a route to a new type of *interfacial multiferroic*. We also find a linear magnetoelectric effect which arises from a novel carrier- mediated mechanism, and is a universal feature of the interface between dielectrics and spin-polarized metals. To formally quantify the magnetic response of these interfaces to an applied electric field, we introduce and define the concept of *spin-capacitance density*. In our calculations for SRO/STO/SRO, we find 37% of the capacitance density to be spin polarized. Comments on controlling this magnetoelectric effect as a means to realizing new devices and sensors are made, as we recognize that such devices should be feasible with the continued success in fabricating thin film oxide materials.

IR to UV spectral ellipsometry investigation of the phonon-polaron interaction in electrochromic tungsten oxide thin films

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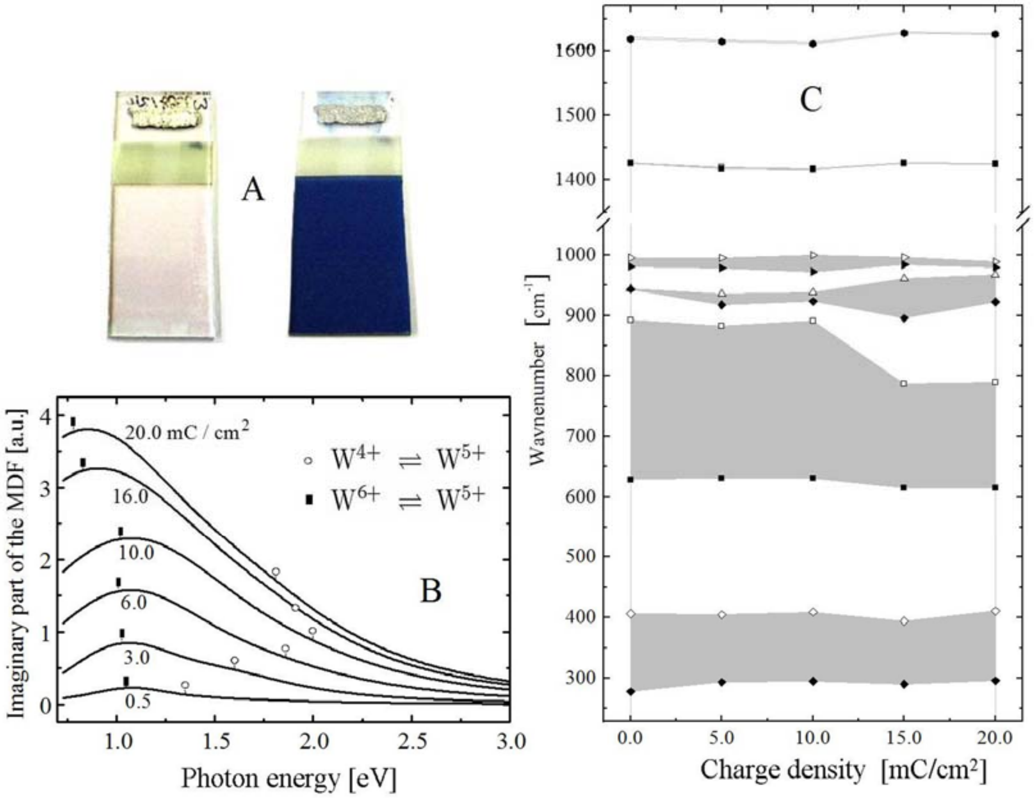
The polaron and phonon properties of amorphous tungsten oxide thin films were investigated as a function of the intercalated charge density with spectroscopic ellipsometry in the infrared to ultraviolet spectral range. We present a parametric model dielectric function which excelently describes the ellipsometry and optical density data over a large charge density range. Our model is congruent with the polaron-hopping theory, and corroborates conclusions from earlier infrared studies. Upon increased intercalated charge we observe a strong reduction of the W-O-W bond polarity, indicative for tungsten oxidation state reduction from W^{6+} to W^{5+}. A distinct vibration band located above the tungsten oxide phonon band is formed, whereas O-H related vibration frequencies remain unaffected, indicating that no hydrogen is incorporated upon charge intercalation. Furthermore, possible evidence for polaron formation by oxygen related defect generation is presented.



(A) Uncolored and colored tungsten oxide thin films. (B) Polaron contribution to $Im\{\varepsilon\}$ versus charge density, symbols correspond to the resonance energy position of the polaron transition. (C) IR reflection bands versus charge intercalation indicative for intercalation-induced bond reformation and polaron shift.

Synthesis and Investigation of Magnetic Oxide Nanoparticle Systems

Christina S. Schade, Katharine Page, and Ram Seshadri

June 28, 2007

Magnetic nanoparticles offer a wide range of applications such as high-density data storage, magnetic resonance imaging, drug targeting or innovative cancer treatments. We present the synthesis of a number of oxide nanoparticles, including core/shell architectures, based on high-temperature decomposition of metal precursors in the presence of capping agents (oleylamine and oleic acid). The size of the nanoparticles is controlled by using different amounts of surfactants and different reaction times. Samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and a Superconducting Quantum Interference Device (SQUID), whereas the SQUID measurements were acquired with pressed powders and diluted dispersions in paraffin wax. Purity and grain size were determined by diffracion data on the powder samples, subject to Rietveld refinement and Scherrer broadening. Size distribution and magnetization M as a function of field H_C and temperature T were obtained by TEM and SQUID magnetometer measurements respectively. The results provide insight to the magnetic properties of these oxide nanoparticles. In particular, we present the effect of size and interparticle interactions of nanoparticles as well as exchange bias behavior of core/shell structures.

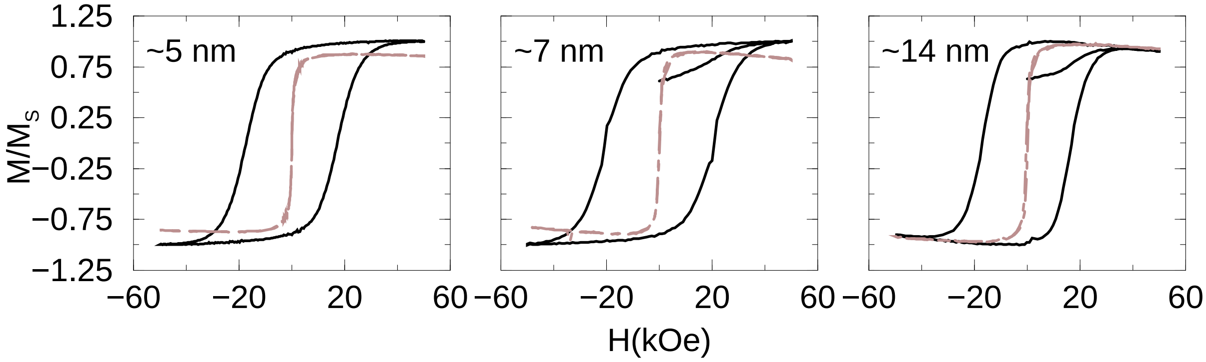


Figure 1: Hysteresis loops of three different sizes of $CoFe_2O_4$ nanoparticles diluted in paraffin wax: the data was collected at 5 K (solid black line) and at 300 K (dashed grey line).

Spontaneous Phase Separation of Exchange Biased Nanoparticle–Monolith Composites

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In this work we demonstrate the spontaneous conversion of a homogeneous, single-phase oxide into a magnetically functional nanocomposite. Traditional ceramic processing is used to create dense $\mathrm{Ni}_x\mathrm{Mn}_{3-x}\mathrm{O}_4$ ($0.15 \leq x \leq 0.60$), which is transformed by hydrogen reduction into ~ 20 nm ferromagnetic Ni nanoparticles embedded within a porous antiferromagnetic MnO monolith. Due to the common oxygen sublattice shared by the spinel and rocksalt structures, the oxide grain size and orientation remain unchanged during the reduction process, and intragranular pores display isoaligned edges over the extent of the grains. The MnO lattice parameter determined by Rietveld refinement and the saturation magnetization of the composites are monitored to ensure complete Ni reduction. Analysis of cross-sectional focused ion beam micrographs reveal that approximately 20% of the Ni nanoparticles are attached to the monolith surface or intragranular pores, and the remainder are completely encased in MnO. We observe exchange bias fields of $H_E \approx 40 - 100$ Oe at 5 K at the Ni–MnO interface, while coercivity ranges from $H_C \approx 400 - 1300$ Oe, depending on Ni content and reduction conditions. Our reduction process affords an elegant route to controlling magnetic, electric, or elastic responses at the interface between nanoscale precipitates in metal–oxide or oxide–oxide composites.

Porous Silicon Dioxide as a Template for Nanoconfinement of Responsive Hydrogels

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Current research efforts have been focused on the use of templates and matrices for the fabrication of stimuli-responsive hydrogels. In this work, temperature/pH sensitive hydrogels are synthesized in situ within nanostructured silicon dioxide templates. Oxidized porous Si is an attractive material for use as a nanoscale template because its porosity and the average pore diameter can be easily tuned by adjusting the electrochemical preparation conditions. The resulting composite is a hybrid of the two materials, combining the unique optical properties of the oxidized porous Si template and the thermal responsiveness of the hydrogel.

The hydrogels were prepared by copolymerizing N-isopropylacrylamide (NIPAM) and acrylic acid (AAc) at different ratios, to create poly(NIPAM-co-AAc). Poly(NIPAM) and poly(acrylic acid) have characteristic temperature and pH sensitivity, respectively. Therefore, the resulting poly(NIPAM-co-AAc) hydrogels exhibit both, temperature- and pH-sensitivity. Infiltration of the hydrogel into the interconnecting nanoscale pores of the porous SiO_2 host is confirmed by scanning electron microscopy. The optical reflectivity spectrum of the nanocomposite hybrid displays Fabry–Pérot fringes characteristic of thin film interference, enabling direct, real-time observation of the volume changes of the confined poly(NIPAM-co-AAc) hydrogel. Optical reflectivity changes were quantified to correlate with hydrogel pH-sensitive volume changes. Reversibility was shown by repeated cycling between two pH solutions. The changes were found to be dependent on the composition of the hydrogel and the initial pH condition of the composite. The nanoscale composite system allows for almost immediate pH response, significantly faster than the bulk hydrogels.

Electric and Electrooptic investigation of spontaneous polarization coupling in PLD-grown ZnO-$BaTiO_3$ heterostructures.

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Spontaneous wurtzite-structure polarisation is inherently tied to one distinct lattice direction and orientation (ZnO), the perovskite-structure polarization can be reversed and switched by external electric potentials ($BaTiO_3$). Here we investigate wurtzite-perovskite-structure interfaces between ZnO and $BaTiO_3$ piezoelectric thin films by electric methods and by electrooptic ellipsometry. Our heterostructures were grown by pulsed laser deposition on (001) Si without breaking the vacuum using a switchable target holder [1],[2] and thereby ensuring high quality interface properties. We provide first evidence for coupling effects between the ZnO and $BaTiO_3$ spontaneous polarization charges by asymmetric electric and electrooptic hysteresis. We observe rectifying behavior due to depletion-region dominated resistance with strong asymmetric hysteresis caused by perovskite polarization coupling with the ZnO polarization [3]. NIR-VIS-UV electroopic ellipsometry findings corroborate the asymmetric depletion region formation and hysteresis and further reveals asymmetric piezoelectric strain fields (effective thickness hysteresis).

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Synthesis of Doped TiO_2 by the Hydrothermal Pouch Method

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Titanium dioxide is a well known photocatalytic material. When illuminated with UV light, an electron is excited within the TiO_2, creating an electron – hole pair that can participate in catalytic reactions. In the pure anatase phase of TiO_2, this phenomenon is limited to the use of UV wavelength light. Using controlled hydrolysis through moderate temperature hydrothermal synthesis, TiO_2 doped with carbon, nitrogen, copper, erbium and yttrium has been synthesized. The synthesis can be modified to produce exclusively the rutile or the anatase form of TiO_2. In this method, the properties of the polymer pouch are exploited to achieve controlled hydrolysis at elevated temperatures and pressures. For comparison, syntheses of anatase C-doped TiO_2 were carried out at five different temperatures ranging from 100 to 200 °C. Agglomerates of C-doped TiO_2 crystallites are visible by SEM. Average particle size as calculated from the powder x-ray diffraction ranges from 10 to 20 nm; the largest average particle size was found for the C-doped TiO_2 synthesized at 200°C. The highest dopant levels of carbon (0.12%) and nitrogen (0.15 %) occur at a reaction temperature of 125° C, while for yttrium, the maximum (13.3%) occurs at 200°C. Doping the material shifts the adsorption edge from the UV (385 nm) to the visible light spectrum (410nm). Testing of the oxidative ability of C-doped TiO_2 versus pure TiO_2 reveals that methyl orange, a test dye molecule is degraded by the C-doped TiO_2 in less than half the time of pure anatase TiO_2.

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$SrTiO_3$ Thin Film Deposition: A Computational Study

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Thin film deposition of $SrTiO_3$ is currently a popular area of research due to its widespread use in electronic applications. Pulsed laser deposition (PLD) is an effective deposition process yielding dense, homogeneous thin films. Here, classical molecular dynamics simulations are used to determine the mechanisms involved in PLD. In particular, these simulations consider the deposition of SrO and TiO_2 molecules and stoichiometric $SrTiO_3$ clusters with a kinetic energy between 0.1 and 1 eV/atom on a (001) surface of $SrTiO_3$. The simulations show that collisions between the incident particles and the substrate can induce chemical reactions. It is also found that the composition and size of the deposition species have an important impact on film growth. The effects of impact energy, orientation of incident particles, cluster size and surface termination layer (SrO vs. TiO_2) are examined. The main surface phenomenon of interest is chemical changes that occur at the oxide surface due to the ablating particles. The simulation results are compared to experimental data. This work is supported by the National Science Foundation (DMR-0426870).

A Low Temperature Dehydration Method for the Carbon Coating of Transition Metal Oxides

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We have developed a novel soft-chemical carbon coating method and demonstrated its usefulness through the carbon coating of spinel lithium manganate. The present method is based on the low temperature dehydration of sucrose molecules assisted by sulfuric acid. Electron microscopy, elemental analysis, and N_2 adsorption–desorption isotherm measurements clearly demonstrate that porous carbon nanolayer is successfully coated by the dehydration reaction of sucrose-adsorbed lithium manganese oxide at 90 °C. According to power X-ray diffraction, Mn K-edge X-ray absorption, and Micro-Raman spectroscopic analyses, the carbon coating does not modify the cubic spinel-type atomic arrangement of lithium manganate and the coated carbon layer is composed of disordered amorphous carbon and polycyclic aromatic hydrocarbons. Of special importance is that the carbon coating can improve the electrode performance of spinel lithium manganate. In this regard, one can conclude that the present method provides a novel less energy-consuming route not only the carbon coating of metal oxides but also to the improvement of electrode performance.

Exfoliation and Reassembling Route to TiO_2-pillared MnO_2 with microporosity

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Pillared architecture of colloidal manganate nanosheets with titania nanoparticles has been accomplished via exfoliation and reassembling route. At first, the layered protonic manganese oxide, $H_{0.13}MnO_2 \cdot 0.7H_2O$, was exfoliated in a solution of tetrabutylammonium (TBA) hydroxide, and then the exfoliated nanosheets were reassembled in the presence of titania nanoparticles in an aqueous solution, which resulted in microporous nanohybrid. X-ray diffraction and cross-sectional transmission electron microscopy (TEM) analyses clearly showed that the titania nanoparticles with a diameter of 1 nm were successfully intercalated into two dimensional manganate lattice to form highly ordered pillared structure along the crystallographic *c*-axis. According to the Mn K-edge X-ray adsorption near edge structure (XANES) analysis, the absorption edge energy corresponding to the transition from the core 1s to unoccupied 3d or 4p was found to be unchanged, indicating that the electronic structure and local symmetry of Mn ion were maintained even after exfoliation-reassembling reaction. From the preliminary electrochemical charge-discharge measurements indicated that the present nanohybrid showed the enhanced discharge capacity compared to the theoretical value of the physical mixture between TiO_2 and MnO_2. It is, therefore, concluded that the present nanohybrid with high porosity fabricated by pillaring reaction could be useful as a cathode material for lithium secondary batteries.

One-pot Hydrothermal Synthesis of 1D/3D Nanostructured Cobalt-substituted Manganese Oxides with Electrochemical and Catalytic Activity

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We have successfully synthesized cobalt-substituted manganese oxide 1D nanowires and their 3D hierarchically assembled microspheres through one-pot hydrothermal treatment. The use of the ion-pair solution of Co^{2+} and MnO_4^- makes it possible to incorporate cobalt ion into the manganese sites of α- and δ-MnO_2 structures. The chemical composition, crystal structure, and morphology of the resultant nanostructures can be easily tailored through the control of reaction condition and precursor composition. We have found that the partial Co substitution for the nanostructured manganese oxides causes the improvement of their catalytic activity with respect to olefin oxidation as well as affects significantly their electrode performances. The present study provides an effective way of controlling the chemical properties and functionalities of nanostructured manganese oxides through cation substitution.

Abstract Index