

SYMPOSIUM GG

Solid-State Chemistry of Inorganic Materials

November 27 – 30, 2000

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* Invited paper

SESSION GG1: CRYSTAL CHEMISTRY OF
COMPLEX SYSTEMS

Chairs: John P. Attfield and John D. Corbett
Monday Morning, November 27, 2000
Room 304 (Hynes)

8:30 AM GG1.1

STRUCTURAL STUDIES OF SILLEN AND AURIVILLIUS TYPE LAYERED BISMUTHATES. P. Lightfoot, C.H. Hervoches, School of Chemistry, Univ. of St Andrews, UNITED KINGDOM; P.S. Berdonosov, D.O. Charkin, A.M. Kusainova, S. Yu Stefanovich, V.A. Dolgikh, Moscow State Univ., Moscow, RUSSIA.

The Aurivillius phases are a well-known class of ferroelectric materials which have received considerable interest for applications in FRAM technology. Aurivillius phases adopt layered structures, consisting of intergrowths of fluorite-like and perovskite-like layers, typical examples being $\text{SrBi}_2\text{Ta}_2\text{O}_9$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. A related series is the Sillen family, which consist of analogous fluorite-like layers sandwiching halide rather than perovskite-like layers. We have recently prepared several new variants on these structure types, for example Sillen-Aurivillius phase intergrowths, Sillen-CsCl intergrowths and others. Several of these new materials have been found to display pyroelectric properties. The structural chemistry of these phases will be discussed, together with new insights into the behaviour of the Aurivillius phases themselves.

8:45 AM GG1.2

DEVELOPMENT OF BROWNMILLERITE-AURIVILLIUS INTERGROWTH PHASES BY A STRUCTURAL APPROACH USING IN-SITU DIFFRACTION TECHNIQUES. Scott A. Speakman and Scott T. Mixture, Alfred University, Alfred, NY.

Conducting ceramics based on brownmillerite phases, aurivillius phases, and intergrowths between the two have been studied. A fast-ion conducting brownmillerite-type material, $\text{Ba}_2\text{In}_2\text{O}_5$, was extensively studied using in-situ X-ray and neutron diffraction. This work established a thorough understanding of the relationship between structure and ionic conductivity in this material. Of particular interest is the order-disorder transformation that produces the transition from insulator to fast-ion conductor. A brief review of this work will be presented. This structural model has now been utilized in the development of brownmillerite-aurivillius intergrowth phases. Several Aurivillius-Brownmillerite phases have been prepared and the conductivity of the phases as a function of temperature was determined using AC impedance spectroscopy. Correlations of the ionic conductivity of $\text{Ba}_2\text{In}_2\text{O}_5$ and the modified Aurivillius phases will be presented, as well as strategies to disorder the oxygen vacancies in the modified Aurivillius phases. Comments on processing will also be included. Processing research has explored the use of molten salt and citrate methods as rapid synthesis routes. While the citrate method has not been successfully utilized, the molten salt method shows potential for producing some, but not all, intergrowth phases.

9:00 AM *GG1.3

STRUCTURAL MODEL IN THE SUPERSPACE FORMALISM OF COMPOSITE COMPOSITION FLEXIBLE PHASES $A_{1-x}(A'_x B_{1-x})O_3$ ($0 \leq x \leq 1/2$) (A=Ba, A', B = TRANSITION METAL). Jacques Darriet, Mirvat Zakhour, Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB-CNRS), Pessac, FRANCE; Ahmed El Abed, Mohamed I Univ, Faculté des Sciences, Oujda, MOROCCO; Hans-Conrad zur Loye, Univ of South Carolina, Dept of Chemistry and Biochemistry, Columbia, SC; Juan M. Perez-Mato, Univ del Pais Vasco, Dept de Fisica de la Material Condensada, Bilbao, SPAIN.

An idealized structural model is proposed for materials closely related to the 2H hexagonal perovskite structure having the general formula $A_{1-x}(A'_x B_{1-x})O_3$ ($0 \leq x \leq 1/2$). The structure of all these compounds can be considered as modulated composites with two subsystems and described, as a first approximation, by a unique structure in the superspace formalism with occupational Crenel functions and sawtooth displacive modulations along the trigonal axis. The structural modulation has only two adjustable parameters: the modulation wave vector or misfit parameter which is fixed by the compound composition, and the height difference between the octahedra and triangular prisms O_6 present in the trigonal $\{A', B\}O_3$ columns of the structure. By only varying these parameters, the basic structural features of any compound with arbitrary composition x in $A_{1-x}(A'_x B_{1-x})O_3$ are reproduced, including the two limiting cases ABO_3 (2H perovskite) $x=0$ and A_3A'/BO_6 $x=1/2$. For instance, the sequence of octahedra and prisms along the $\{A', B\}O_3$ columns follows a Farey-tree rule which is deduced directly from the model. A comparison with available experimental data and, in particular, with some fully determined structures in the systems $A=Ba$, $A'=Co$, Cu , $B=Co$, Ni , Rh , Ir demonstrate the soundness of the proposed scheme as the best starting point for their refinement. The model, although developed within the superspace formalism, is closely related with the

polytype layer picture in direct space. The present structural analysis constitutes new examples of the efficiency of the 4-dimensional superspace formalism for describing, in a unified fashion, the structures of so-called "composition flexible" systems.

10:00 AM GG1.4

NEW 2H-PEROVSKITE RELATED OXIDES: CRYSTAL GROWTH, STRUCTURES AND PROPERTIES. Mark D. Smith, Katharine E. Stitzer, Hans-Conrad zur Loye, Dept of Chemistry and Biochemistry, Univ of South Carolina, Columbia, SC; Mirvat Zakhour and Jacques Darriet, Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB-CNRS), Pessac Cedex, FRANCE.

The synthesis and structures of a perovskite-related family of oxides containing infinite chains of face-shared polyhedra will be presented. The structures of these oxides result from the stacking of A_3O_9 and A_3A/O_6 layers, and have the general composition $A_{3n3}A'_nB_{n3}O_{6n9}$. The exciting feature of this class of materials is its compositional and structural versatility. We have synthesized numerous members of this family, including $\text{Sr}_3\text{NiPtO}_6$, $\text{Sr}_6\text{Rh}_5\text{O}_{15}$, $\text{Sr}_3\text{PbNiO}_6$, Sr_3MCrO_6 ($M = \text{Sc}, \text{Y}, \text{In}, \text{Lu}, \text{Tb}, \text{Tm}, \text{Er}, \text{Ho}$), $\text{Ba}_{1-x}[(\text{Cu}_x\text{Rh}_{1-x})\text{O}_3]$ with $x = 0.1605$ and $x = 0.1695$ and $\text{Ba}_{1-x}[(\text{Cu}_x\text{Ir}_{1-x})\text{O}_3]$, $x = 0.2708$. The presentation will emphasize the underlying synthetic strategies, including single crystal growth, the structural versatility, including the observation of incommensurate structures, and the diverse magnetic properties of these materials. All compounds were structurally characterized by several techniques, including powder X-ray and neutron diffraction and single crystal X-ray diffraction.

10:15 AM GG1.5

SOLID STATE AND CRYSTAL CHEMISTRY OF THE INCOMMENSURATE $\text{Cu}_{2.33-x}\text{V}_4\text{O}_{11}$ VANADIUM OXIDE BRONZE. Patrick Rozier, Ray Withers, Jean Galy, CNRS/UPS, Toulouse, FRANCE.

Solid state chemistry reinvestigation of the Cu-V-O system allowed to define the existence domain of the vanadium oxide bronze (VOB) $\text{Cu}_{2.33-x}\text{V}_4\text{O}_{11}$ (upper limit $x=0$). Polycrystalline samples are prepared from CuO , V_2O_5 and V_2O_4 oxides in stoichiometric amounts. Single crystals were obtained via a reaction using SeO_2 as a transporting agent. Powders and crystals were analysed by XRD techniques (automatic diffractometers with $\text{CuK}\alpha$ and $\text{AgK}\alpha$ radiations and also Weissenberg photographs). $\text{Cu}_{2.33-x}\text{V}_4\text{O}_{11}$ with its average structure crystallises in the monoclinic system, space group Cm, with $a=15.309(1)\text{\AA}$, $b=3.610(1)\text{\AA}$, $c=7.335(2)\text{\AA}$ and $\beta=101.84(1)^\circ$ with $z=2$. The detected super-cell exhibits the following parameters : $a=30.639(7)\text{\AA}$, $b=28.908(6)\text{\AA}$, $c=7.358(2)\text{\AA}$ and $\beta=101.879(8)^\circ$, i.e. $2a;8b;c$. The atomic architecture shows a $[\text{V}_4\text{O}_{11}]_n$ zig-zag double layer of distorted VO_6 octahedra sharing corners and edges. Copper atoms, are situated on four different crystallographic sites between the layers, along two channels parallel to $[010]$. A temperature dependant electron diffraction study shows at low temperature two distinct incommensurate modulations associated with the three-dimensional ordering of Cu in each channel. The primary modulations wave vectors associated with the modulations $q_1 = \Omega c^* \sim 0.12b^*$ and $q_2 = \Omega a^* \sim 0.16b^*$ are associated with Cu ion ordering in the two kinds of channels. The second modulation appears to condense out at low temperature.

10:30 AM GG1.6

INCOMMENSURATE STRUCTURE OF ELECTRON-DOPED LAYERED $\text{La}_{2-2x}\text{Ca}_{12x}\text{Mn}_2\text{O}_7$ ($0.6 < x < 0.8$) COMPOUNDS. Leonid A. Bendersky, Metallurgy Division, NIST, Gaithersburg, MD; Ian D. Fawcett, Rongji Chen and Martha Greenblatt, Department of Chemistry, Rutgers, The State University of New Jersey, Piscataway, NJ.

A series of Ruddlesden-Popper compounds with $n = 2$ and stoichiometry $\text{La}_{2-2x}\text{Ca}_{12x}\text{Mn}_2\text{O}_7$ has been successfully synthesized by a citrate gel technique for $0.6 < x < 1.0$. Investigation of the magnetic and electric properties of the compounds indicated two distinct regions of different magnetic behavior: $0.6 < x < 0.8$ and $0.8 < x < 1.0$. These two regions were identified by our transmission electron microscopy (TEM) study as having very different sets of superlattice reflections. In particular, for the composition range $0.6 < x < 0.8$, analysis of reciprocal space identified two sets of incommensurate satellites (IC), each having two near-orthogonal k-vectors. High-resolution imaging showed the presence a two-dimensional near-square lattice with $a_{2D} = \sqrt{5}a_p$ (a_p - perovskite unit cell) and normal to a tetragonal c-axis. In-situ TEM experiments showed a possible IC-to-tetragonal phase transition around $300\text{-}400^\circ\text{C}$. We will discuss a possible model of the IC phase as having a previously unobserved type of charge/orbital ordering.

10:45 AM GG1.7

THE FORMATION OF ORDERED PHASES BY CHARGE LOCALIZATION IN VANADIUM PHOSPHATE LAYERED

COMPOUNDS. Ranko P. Bontchev, Junghwan Do, Allan J. Jacobson, Department of Chemistry, University of Houston, Houston, TX.

The layered mixed valent vanadium phosphates form an interesting series of systems with respect to the distribution of V(V) and V(IV) ions within the layers. All of the known compounds have close to equal amounts of V(V) and V(IV) but have very different structures. In the alkali metal series, the structures of $\text{Na}_{0.5}\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{M}_{0.5}\text{VOPO}_4 \cdot 1.5\text{H}_2\text{O}$ ($\text{M} = \text{K}, \text{Rb}$) contain a single inequivalent vanadium atom. In several other layered analogs, however, the V(IV) and V(V) atoms are ordered. This is apparent on inspection of the bond lengths or by calculation of bond valence sums. Several examples, including $(\text{NH}_4)\text{VOPO}_4 \cdot 1.5\text{H}_2\text{O}$ that form ordered phases with different periodicities will be described

11:00 AM GG1.8

THE STABILITY OF Mn_5Si_3 -TYPE COMPOUNDS OF SCANDIUM. THE EFFECTS OF SUBSTITUTION ON THE MAIN-GROUP ELEMENT SITE. Paul A. Maggard, Douglas A. Knight and John D. Corbett.

The hexagonal Mn_5Si_3 -type structure ($\text{P6}_3/\text{mcm}$) is formed by a great many active metals (groups 2-5) combined with, mainly, main-group elements from the Al to As families (groups 13-15). All are evidently electron-rich and metallic. Our earlier studies of interstitial (Z) chemistry in a variety of hosts revealed that large numbers (15-20) of different Z may be incorporated. The electronic and geometric flexibility of compounds with this structure type is remarkable. We have now explored the stability of pseudo-binary $\text{Sc}_5(\text{B}_{3-x}\text{B}'_x)$ phases over the entire ranges of $\text{B} = \text{Al}$ or Ga together with one of the increasingly electron-rich and more stable anion formers $\text{B}' = \text{Sn}, \text{Sb},$ or Te . Crystal structures at the phase limits as well as data on lattice dimensions, resistivity and magnetic susceptibility over the homogeneity ranges have been determined. For systems annealed at 1100-1575°C, the phase widths of $\text{Sc}_5(\text{B}_{3-x}\text{B}'_x)$ extend over the ranges $x = 1.38(6) - 2.25(2), 0.83(1) - 0.96(1), 0 - 2.25(6), 0 - 1.25(3), \sim 1.2 - 3.0$ and $0.0 - 3.0$ for $(\text{B}/\text{B}') \text{ Al/Sb}, \text{Al/Te}, \text{Ga/Sb}, \text{Ga/Te}, \text{Al/Sn}$ and Ga/Sn , respectively. No interstitial effects were found. Many of the compounds display characteristics of poor metals, with positive temperature-dependence of resistivities and Pauli-like paramagnetic susceptibilities. Particularly novel are the stabilization of some intermediate compositions. Some effects of poor vs good anion formers and possible excess electron counts on stability will be considered.

11:15 AM GG1.9

B SITE DOPING IN MANGANATE RUDDLESDEN-POPPER PHASES. Peter Battle, Jonathan Burley, Nicola Jordan, Jeremy Sloan, Inorganic Chemistry Laboratory, Oxford University, UNITED KINGDOM; Liam Noailles, Matthew Rosseinsky, Chemistry Department, Liverpool University, UNITED KINGDOM; Clare Grey, Chemistry Department, SUNY, Stony Brook, NY.

Substitution of the A - site cation has been employed extensively as a means of controlling the magnetotransport properties of Ruddlesden - Popper manganates. However, the consequences of B - site doping are less well-known. In this paper we discuss the preparation and characterisation of some B-site doped Ruddlesden - Popper manganates, where the dopant ion B- is a diamagnetic non-transition metal ion; substitutions involving both isovalent and aliovalent B-dopant ions are reported. The effect of doping is marked, giving rise to magnetic behaviour which differs greatly from that of the parent "undoped" materials. It is clear that doping with an aliovalent B-cation in the electronically - active perovskite layers themselves opens up a wide range of possibilities for control of the transport properties of these phases, in addition to those which exist when substitutions are made in the AO rock-salt layers. Aliovalent B- ions can also induce cation ordering on the B - site, which in turn allows a large degree of control over the relative strengths of magnetic superexchange interactions between the manganese cations. The consequences of isovalent doping are also significant, although ordering of the B and B- cations is not observed. Li-, Ga- and In-doped perovskites and $n = 1, 2$ Ruddlesden - Popper phases have been studied and characterised by x-ray powder diffraction, neutron powder diffraction (including the collection of field-dependent data), SQUID magnetometry, solid-state magic-angle spinning NMR and electron microscopy (diffraction and high resolution imaging).

11:30 AM GG1.10

SYNTHESIS AND CRYSTAL CHEMISTRY OF NEW OF TRANSITION METAL TELLURIUM OXIDES IN COMPOUNDS CONTAINING LEAD AND BARIUM. Boris Wedel, DOWA Mining Co. Ltd., Central Research Laboratory, Hachioji, JAPAN; Katsuma Sugiyama, Kimio Itagaki, Tohoku University, Sendai JAPAN; Hanskarl Mueller-Buschbaum, Christian Albrechts University, Institute for Inorganic Chemistry, Kiel, GERMANY.

During the past decades the solid-state chemistry of tellurium oxides has been enriched by a series of quaternary metallates. Interest attaches not only to the chemical and physical properties of these compounds, but also to their structure, which been study by modern methods. The partial similarity in solid-state chemistry of earth alkaline metals to lead, and their relationships in oxides, opens a wide field of investigations.

Eight new compounds in the systems Ba-M-Te-O ($\text{M} = \text{Nb}, \text{Ta}$) and Pb-M-Te-O ($\text{M} = \text{Mn}, \text{Ni}, \text{Cu}, \text{Zn}$) were prepared and structurally characterized: $\text{Ba}_2\text{Nb}_2\text{TeO}_{10}$, $\text{Ba}_2\text{M}_6\text{Te}_2\text{O}_{21}$ ($\text{M} = \text{Nb}, \text{Ta}$) and the lead compounds PbMnTeO_3 , $\text{Pb}_3\text{Ni}_{4.5}\text{Te}_{2.5}\text{O}_{15}$, $\text{PbCu}_3\text{TeO}_7$, $\text{PbZn}_4\text{SiTeO}_{10}$ and the mixture compound $\text{PbMn}_2\text{Ni}_6\text{Te}_3\text{O}_{18}$. All compounds structure based on frameworks of edge and corner sharing octahedra between the transition metal and tellurium. Various different channel structures were observed and distinguished. The compounds are prepared by heating from mixtures of the oxides, and the single crystals were grown by flux method or solid-state reactions on air.

The interesting crystal structures adopted by many of these compounds raise the possibility that these materials may exhibit ionic conductivity, interesting optical and/or dielectric properties. Powder synthesis condition for purification and structural characterizations were carried out using a variety of tools including powder diffraction data and refinements of x-ray data. Relationships between lead transition metal tellurium oxides and the earth alkaline transition metals tellurium oxides are compared.

11:45 AM GG1.11

COMPOUND FORMATION, CRYSTAL CHEMISTRY, AND DIELECTRIC BEHAVIOR IN COMPLEX NIOBATES AND TITANATES. T.A. Vanderah, J.Y. Chan, I. Levin, R.S. Roth, NIST, Gaithersburg, MD; T.R. Lindsey, Appalachian State University, Boone, NC, V.L. Miller, Rider University, Lawrenceville, NJ; W. Febo, University of Puerto Rico, Cayey, PR; R.G. Geyer, NIST, Boulder, CO; S. Bell, TRAK Ceramics, Inc., Hagerstown, MD.

Dielectric oxides are used to fabricate a variety of components in cellular communications circuits that store, filter, and/or transfer electromagnetic energy with minimal loss (e.g., resonators, bandpass filters). Systematic phase equilibria studies of ceramic systems containing dielectric oxides were conducted to 1) reveal the existence of new, thermodynamically stable phases, 2) obtain quantitative information immediately useful for the preparation of controlled mixtures, and 3) provide systematic data for fundamental chemistry-structure-properties studies. Chemical systems of current interest include complex oxides featuring (Ti,M)-O and (Nb,M)-O octahedral matrices with larger A-cations such as Ca^{2+} , Sr^{2+} , or Ba^{2+} . The results of recent experimental studies of ternary systems will be presented. Trends in compound formation, crystal chemistry, and dielectric properties will be described.

SESSION GG2: SESSION IN HONOR OF J.M. HONIG

Chairs: Mercuri G. Kanatzidis, Susan M. Kauzlarich and Hans-Conrad zur Loye
Monday Afternoon, November 27, 2000
Room 304 (Hynes)

This session is dedicated to Professor J.M. Honig in recognition of his many contributions to the discipline of solid state chemistry and his stewardship of the Journal of Solid State Chemistry.

1:30 PM OPENING REMARKS

1:45 PM GG2.1

MAGNETORESISTANCE OF ELECTRON-DOPED $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$. M. Greenblatt, Z. Zeng, Rutgers Univ, Dept of Chemistry, Piscataway, NJ; M. Croft, Rutgers Univ, Dept of Physics, Piscataway, NJ.

$\text{Ca}_{1-x}\text{Ce}_x\text{MnO}_3$ ($0 < x \leq 0.2$) was prepared by the sol-gel method. The limit of Ce solubility is $x=0.20$. The orthorhombic lattice parameters increase with x consistent with the larger effective radius of Mn^{3+} compared to Mn^{4+} . X-ray absorption spectroscopy studies of the samples confirmed that the valence of Ce is 4, and the oxidation state of Mn decreases with increasing x. CaMnO_3 is antiferromagnetic, while $\text{Ca}_{1-x}\text{Ce}_x\text{MnO}_3$ for $x=0.025-0.05$, is ferromagnetic. However, for $x=0.075-0.2$, the samples show antiferromagnetic-like transitions with positive Weiss constants. Both the electrical and magnetic properties of $\text{Ca}_{1-x}\text{Ce}_x\text{MnO}_3$ for $0.075 \leq x \leq 0.2$ evidence charge ordering. All of the samples are n-type semiconductors. The

activation energies decrease below the Curie temperature for the ferromagnetic samples, and increase below the Neel temperature for those with antiferromagnetic-like transitions. Giant magnetoresistance, as high as -63 % is observed in $\text{Ca}_{0.975}\text{Ce}_{0.025}\text{MnO}_3$, which is attributed to inter-grain tunneling.

2:00 PM *GG2.2

ITINERANT VIBRONS AND HIGH-TEMPERATURE SUPERCONDUCTIVITY. John B. Goodenough, The University of Texas at Austin, Texas Materials Institute, Austin, TX.

The $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ phase diagram is interpreted within the framework of a transition from localized to itinerant electronic behavior. In the underdoped region $0 < x < 0.1$, holes in the $x^2 - y^2$ band are not small polarons; each occupies a mobile correlation bag of 5 to 6 copper centers at temperatures $T > T_F$. Within a bag the electrons are delocalized; outside they are localized. Below T_F , a spinodal phase segregation into the parent antiferromagnetic phase and a polaron liquid is accomplished by cooperative oxygen displacements. In the overdoped compositions $x > 0.25$, holes are excluded from strong-correlation fluctuations within a Fermi liquid. In the intermediate range $0.1 < x < 0.25$, the polaron liquid formed below room temperature changes character with increasing x and decreasing T . For $0.1 < x < 0.16$, mobile two-hole bags of 4 copper centers order with decreasing temperature into alternate (100) Cu-O-Cu rows. It is argued that hybridization of itinerant electrons with optical-mode phonons propagating along the Cu-O-Cu rows produces heavy electrons responsible for high-temperature superconductivity.

2:30 PM GG2.3

(Re/Li) TITANATES AND NIOBATES AS IONIC CONDUCTORS. A. Morata-Orrantia, S. Garcia-Martin, E. Moran, U. Amador and M.A. Alario-Franco, Laboratorio de Quimica del Estado Solido. Facultad de Ciencias Quimicas, Madrid, SPAIN; Universidad San Pablo/CEU, Montecprincipe, Madrid, SPAIN.

Besides the nowadays classical Lalitio, i.e. $\text{La}_{0.67-x}\text{Li}_{3x}\text{TiO}_3$, we have been working in different, closely related systems in trying to find new lithium ion conductors with perovskite-type structure, to be used as cathodes in electrochemical cells. In this sense, both Lanthanum/Lithium titanates and niobates of the types $\text{La}_{0.33-x}\text{Li}_{3x}\text{NbO}_3$ and $\text{La}_{0.67}\text{Li}_x\text{Ti}_{1-x}\text{Al}_x\text{O}_3$ have been synthesised. X-ray diffraction show that this compounds have as a basic structure a perovskite type cell with, more often than not, the so-called diagonal cell: $ap \div 2 \times ap \div 2 \times 2 \times ap$, where ap is the basic perovskite cell parameter. The microstructure observed, by selected area electron diffraction and high resolution electron microscopy is, however, much more elaborated. In the range of existence ($0.06 \pm x \pm 0.3$) of the above titano-aluminate; ionic conductivity has been measured as a function of composition and temperature. The maximum conductivity found at $T = 30^\circ\text{C}$ is $s = 3 \leq 1 \times 10^{-5} \text{ S cm}^{-1}$ for $x = 0.025$. The electrochemical window has been studied by potentiostatic discharge and charge showing that these materials are reduced (with Ti^4 to Ti^3) down to 1.5 V.

3:15 PM *GG2.4

SYNTHESIS, STRUCTURE AND PROPERTIES OF NEW PSEUDO-1D OXIDES. Peter Battle, Jonathan Burley, Edmund Cussen, Nicola Jordan, Caroline Moore, Jeremy Sloan, Inorganic Chemistry Laboratory, Oxford University, UNITED KINGDOM.

There are a number of aspects to the study of pseudo-1D mixed metal oxides having the general formula $\text{A}_{3n_3}\text{A}_n\text{B}_{n_3}\text{O}_{6n_9}$. First and foremost is the synthesis of new phases containing either chemical elements which have not previously been introduced into the system, or novel combinations of elements. In this way it should be possible to extend the range of physical properties observed within the structure type. Our strategy has been to attempt to induce metallic conductivity or other forms of itinerant electron behaviour in compounds in which the A- and B cations (occupying trigonal prismatic and octahedral sites respectively) are from the 2nd or 3rd transition series. The low-dimensional nature of the structure suggests that a range of electronic phenomena may be observable in such a system. Furthermore, we have attempted to induce a spontaneous magnetisation in compounds in which A- and B are both localised-electron, 1st row cations. In both cases, the known tendency of the A-cation to move away from the centre of the trigonal prism towards a four-coordinate site in one of the rectangular faces has strongly influenced the elements chosen for inclusion in the structure. In this paper we describe synthetic, diffraction (X-ray, neutron and electron), magnetic and conductivity studies of a number of systems including Sr/Mn/Co/O, Ba/Cu/Mn/O, Ba/Zn/Mn/O, Ba/Pt/Ir/O, and Ba/Pd/Ir/O. Our account of their crystal chemistry will include a discussion of the incommensurate phases discovered during the course of our work. Our attempts to extend the range of elements found in this structural family have recently focussed on Sb, and we shall report the results of a neutron diffraction study of $\text{Sr}_3\text{NaSbO}_6$.

3:45 PM GG2.5

V^5 - V^4 MIXED VALENCE AND V^4 OXIDES. SOLID STATE CHEMISTRY - STRUCTURES - MAGNETIC PROPERTIES. Jean Galy, Patrice Millet, Patrick Rozier CEMES/CNRS-Toulouse, FRANCE.

The family of V^5 - V^4 mixed valence oxides, particularly the vanadium oxide bronzes (VOB) $\text{M}_x\text{V}_y\text{O}_z$ (M = alkali, alkaline earth, metal) is extremely rich both for structural originality and electric and/or magnetic properties. The vanadates IV phases, because highly correlated electrons, exhibit unusual magnetic properties today deeply investigated at both experimental and theoretical levels. The aim of the lecture is, via selected choice of phases, to enlighten some particular aspects of this research field with its new results and questions: - Solid state chemistry and non-stoichiometric problems: * in the VOB phases β and β' $\text{M}_x\text{V}_2\text{O}_{5-y}$ (M = Li, Na), α' NaV_2O_5 which belong to the class of Spin-Peierls system and $\text{Cu}_{2.33-x}\text{V}_4\text{O}_{11}$ with its incommensurate modulations; * in the vanadates IV, MgVO_3 , a $s=1/2$ one-dimensional antiferro magnet, CaV_2O_5 alike MgV_2O_5 where the spins are arranged in planes made of coupled ladders and $\text{MV}_n\text{O}_{2n+1}$ (M = Ca, Sr) in which the member $n=4$, CaV_4O_9 , is the first of a quasi 2D spin system with a spin gap - New networks, based on VO_5 square pyramids, making: * ribbons in η $\text{Na}_x\text{V}_2\text{O}_5$ ($x = 1.286$); * and V_3O_7 nanotubes formed by an original association along a three-fold axis in the very new and unusual $\text{Na}_{2-x}\text{V}_3\text{O}_7$ crystal structures. Structure relationships and magnetic properties of some of these phases will be commented.

4:00 PM GG2.6

POWDER DIFFRACTION REFINEMENTS OF THE STRUCTURE OF MAGNETITE (Fe_3O_4) BELOW THE VERWEY TRANSITION. Jon P. Wright, J. Paul Attfield, Univ of Cambridge, Dept of Chemistry, Cambridge, UNITED KINGDOM; Paolo G. Radaelli, ISIS Facility, UNITED KINGDOM; J.M. Honig, Purdue Univ, Dept of Chemistry, Purdue, IN.

Magnetite is a classic example of a mixed valent transition metal oxide, in which electronic conductivity and ferromagnetism result from electron hopping between octahedrally coordinated Fe^{2+} and Fe^{3+} sites. Below the 122 K Verwey transition, magnetite becomes insulating and a complex monoclinic (or triclinic) superstructure of the high temperature cubic spinel arrangement is adopted. This is assumed to be the result of $\text{Fe}^{2+}/\text{Fe}^{3+}$ charge ordering on the octahedral sites, but this has not been confirmed crystallographically as single crystal refinements have been hampered by the extensive twinning that accompanies the Verwey transition. We have used very highly resolved powder diffraction data to attempt Rietveld refinements of the low temperature structure. The powder sample was prepared by grinding a single crystal of stoichiometric magnetite. Data were collected at 90 K on instruments HRPD at the ISIS neutron source, UK, and BM16 at the European Synchrotron Radiation Facility, France. The very high resolution of these data enables the monoclinic distortion to be observed, and the structure has been refined on the supercell proposed by Iizumi et al (Acta Cryst. B38, 2121 (1982)) using Pmca pseudosymmetry, giving parameters $a = 5.94443(1)$, $b = 5.92470(2)$, $c = 16.77518(4)$ Å, $\beta = 90.236(1)$ deg. The mean octahedral site Fe-O distances differ from each other significantly, but the maximum difference between values is only 30% of that expected for ideal $\text{Fe}^{2+}/\text{Fe}^{3+}$ ordering. Results of these refinements and interpretations in terms of possible charge ordered models will be presented.

4:15 PM *GG2.7

MICRO AND MESOPOROUS TITANIUM (IV) PHOSPHATES: SYNTHESIS, STRUCTURE AND MECHANISM OF FORMATION. Gérard Férey, Christian Serre, Institut Lavoisier, University, Versailles, FRANCE; Francis Taulelle, Solid State NMR Lab, University of Strasbourg, FRANCE.

The synthesis and structure of new microporous titanium fluorophosphates and phosphates will be presented. The analysis of their structural features according to the synthesis condition sheds some light on the chemistry of titanium in aqueous solutions, with progressive oligomerization as a function of pH. These results have been applied to the optimized synthesis of a mesoporous titanium fluorophosphate. During its aging, it transforms into a microporous solid, called π -TiP, whose structure was solved in the first part of the study. Therefore, a complete in situ and ex situ study was performed on both the mesophase and microporous π -TiP. The comparative study gives many informations on the behaviour of titanium(IV) phosphates in the solution, the species which exist, the competing role of fluoride and phosphates for the complexation of titanium but the main result of this work is the proof that whatever the meso or microporous solid, it is the same tetramer existing in the solution which gives rise to the solid. From NMR and X-ray diffraction studies, the geometry of the building unit is described. It contains two

titanium octahedra and two phosphorus tetrahedra linked in different ways to the titanium atoms.

4:45 PM GG2.8

THERMAL PROPERTIES OF FRAMEWORK MATERIALS.

Mary Anne White, Liyan Qiu, Dalhousie University, Department of Chemistry, Halifax, Nova Scotia, CANADA.

Results of our recent investigations of thermal properties of inorganic framework materials will be described. Particular emphasis will be placed on heat capacity models, and their role in advancing understanding of thermal conductivity and thermal stability.

SESSION GG3: POSTER SESSION DIELECTRICS, CRYSTAL CHEMISTRY, GLASSES, ELECTRICAL TRANSPORT

Chairs: Peter K. Davies and Terrell A. Vanderah
Monday Evening, November 27, 2000
8:00 PM

Exhibition Hall D (Hynes)

GG3.1

STRUCTURE AND MICROWAVE DIELECTRIC PROPERTIES OF THE PYROCHLORE SOLID SOLUTION x Y_2AlNbO_7 : $(1-x)$ $Y_2Ti_2O_7$. Julia Y. Chan, Department of Chemistry, Louisiana State University, Baton Rouge, LA; John Y. Li, S. Bell, T.A. Vanderah, MS&E Laboratory, National Institute of Standards and Technology, MSEL, Gaithersburg, MD.

The structure and dielectric properties of the x Y_2AlNbO_7 : $(1-x)$ $Y_2Ti_2O_7$ were studied. $Y_2Ti_2O_7$ is a cubic pyrochlore with $a = 10.0904(5)$ Å. Phase studies revealed a solid solution of the pyrochlore structure for up to $x = 0.3$ for x Y_2AlNbO_7 : $(1-x)$ $Y_2Ti_2O_7$ with lattice parameters $a = 10.0904(5)$ Å to $a = 10.1022(6)$ Å for $x = 0$ and $x = 0.3$, respectively. Materials in this system exhibit modest relative permittivities, with $30 < \epsilon_r < 48$ with $Q \times f$ near 10,000 for $x = 0.5$. All specimens show a positive coefficient of resonant frequency, with $\tau_f = 92$ ppm/°C for $x = 0.3$ and $\tau_f = 45$ ppm/°C for $x = 0.5$ with $\tan \delta \sim 10^{-3}$ to 10^{-4} at the GHz frequencies. Synthesis, structural characterization from powder X-ray diffraction and the dielectric properties of the phases will be described.

GG3.2

SUBSOLIDUS PHASE RELATIONS IN THE TERNARY SYSTEM $BaO-Al_2O_3-Nb_2O_5$. T.R. Lindsey, Appalachian State University, Boone, NC, T.A. Vanderah, R.S. Roth, NIST, Gaithersburg, MD.

Dielectric ceramic oxides are essential to the wireless communication industry because of their ability to be used as circulators, resonators, bandpass filters, etc. Oxides of particular interest include the system $BaO-Al_2O_3-Nb_2O_5$ which may contain potentially useful dielectric oxides. The subsolidus phase relations among the compounds that exist at equilibrium in the ternary system $BaO-Al_2O_3-Nb_2O_5$ have been studied. The phase diagram has revealed the existence of a new ternary phase with the tetragonal tungsten bronze structure. Moreover, single-phase regions and extensive solid solutions were discovered to exist in the system as well.

GG3.3

THERMODYNAMIC PROPERTIES OF SODIUM-LITHIUM NIOBATE SOLID SOLUTIONS. Irina Pozdnyakova and Alexandra Navrotsky, UC Davis, Thermochemistry Facility, Dept of Chemical Engineering and Material Science, Davis, CA; Lidia Shilkina and Larisa Reznichenko, Rostov State University, Physics Research Institute, Rostov-on-Don, RUSSIA.

In recent years there is increasing interest in niobate solid solutions as a new family of lead-free ferroactive materials. Among them the sodium-lithium niobate system provides a unique combination of electrophysical parameters for high-temperature piezoelectric applications. Although structural and electrical properties of this system were studied carefully, little attention was paid to their thermodynamic properties. In the present work the thermodynamics of the $NaNbO_3-LiNbO_3$ system was investigated by high-temperature drop-solution calorimetry in molten $3Na_2O-4MnO_3$ at 700°C. Both perovskite (rich in $NaNbO_3$) and lithium-niobate (rich in $LiNbO_3$) solid solutions were studied. The heats of formation from oxides and from elements and the heats of mixing were determined. The concentration dependence of the heat of mixing was compared with theoretical models.

GG3.4

NOVEL TUNABLE FERROELECTRIC COMPOSITIONS: $Ba_{1-x}Ln_xTi_{1-x}M_xO_3$ ($Ln=La, Sm, Gd, Dy, M=Al, Fe, Cr$).

Dong Li, M.A. Subramanian, DuPont Central Research and Development, Experimental Station, Wilmington, DE.

$Ba_{1-x}Ln_xTi_{1-x}M_xO_3$ -type solid solutions are prepared. $BaTiO_3$ remains as tetragonal phase up to about 5mol% $LaFeO_3$. For $x \geq 0.06$, the structure changes to cubic at room temperature. The phase change shifts the Curie temperature to lower value and increase the tunability at room temperature. Doping of other acceptor (Al, Cr) and donor (Sm, Gd, Dy) ions has the same effect although with varying levels of tuning. $BaTiO_3$: 4%LaFe has the highest tunability among the studied systems, which is even higher than the currently used $Ba_{0.6}Sr_{0.4}TiO_3$. Co-doping of La, Fe and La, Al in $Ba_{1-x}Sr_xTiO_3$ also lowers the Curie temperature. The results on structure/tuning relationships will be discussed.

GG3.5

MODIFICATION OF FERROELECTRIC PROPERTIES OF TGS CRYSTALS GROWN UNDER A DC ELECTRIC FIELD.

G. Arunmozhi, E. de Matos Gomes, S. Lanceros-Mendez, E. Nogueira, Departamento de Fisica, Universidade do Minho, Braga, PORTUGAL; A. Criado, M.J. Dianez, M.D. Estrada, S. Perez-Garrido, Departamento de Fisica de la Materia Condensada, Universidad de Sevilla, Sevilla, SPAIN; Joao F. Mano, Departamento de Engenharia de Polmeros, Universidade do Minho, Guimaraes, PORTUGAL.

Single crystals of triglycine sulphate (TGS) find wide application in pyroelectric detection. A second order phase transition from a ferroelectric (P_2) to a paraelectric ($P_{2/m}$) phase occurs at 49°C. Depolarization of the glycine molecule with time seriously affects the device performance. Several dopants were reported to stabilize the glycine molecule. Depolarization fields can be overcome if an internal bias field is created in the TGS lattice. A novel technique was used in stabilizing the glycine molecule by growing TGS crystals in the presence of an external dc electric field of the order of 10^6 V/m. It is presumed that the application of electric field during crystal growth causes poling, creating an internal bias field which prevents depolarization. The crystal habit of TGS grown under a dc electric field is similar to the TGS crystal. Dielectric studies show a significant decrease in the permittivity values compared to TGS grown under normal conditions and a shift in the transition temperature from 49°C to 53°C. The phase transition is less sharp in TGS-E indicating that the crystal is poled either partially or completely. Dielectric dispersion in TGS-E is explained on the basis of Cole-Cole plot. Internal bias field of 0.15kV/cm is created by the electric field. Dependence of spontaneous polarization with temperature was analyzed by tracing hysteresis at different temperatures. Specific heat measurements carried out on TGS and TGS-E agree well with the theoretically expected values. Structural changes were also observed in a powder diffraction pattern. Details about the structural, dielectric, hysteresis and specific heat measurements and comparison with theory will be presented and discussed.

GG3.6

CHEMICAL FORMULATION OF THE FABRICATION OF HELICAL LEAD ZIRCONATE TITANATE. Pramod K. Sharma, V.V. Varadan and V.K. Varadan, The Pennsylvania State University, University Park, PA.

Lead zirconate Titanate ($Pb(Zr_xTi_{1-x})O_3$) ceramics are widely used in transducer and other electromechanical devices. Further, its application in passive underwater acoustic damping (UAD) requires a special shape of the $Pb(Zr_xTi_{1-x})O_3$ which embedded in a passive material. Helical shape is highly desirable in this device because it reduces the acoustic echo from the submerged structure to avoid detection versus active sonar systems. Initially, $Pb(Zr_xTi_{1-x})O_3$ powder was prepared for $x=0.5$ by conventional method. A calcination profile was monitored for obtaining the pure phase of $Pb(Zr_xTi_{1-x})O_3$. The conditions are discussed in this work for the chemical formulation of the fabrication of helical $Pb(Zr_xTi_{1-x})O_3$. Slurry was optimized for the amount of calcined powder, concentration of binder, dispersant, plastisizer and solvent. A sintering profile was examined in detail so that a continuous helical could be prepared without cracks. Scanning electron microscopic study indicated a uniform spherical morphology of the particles in the helical $Pb(Zr_xTi_{1-x})O_3$.

GG3.7

OPTIMISATION AND CHEMICAL FORMULATION OF THE SLURRY FOR THE FABRICATION OF HELICAL PZT.

Pramod K. Sharma, V.V. Varadan and V.K. Varadan, The Pennsylvania State University, University Park, PA.

Lead zirconate Titanate ($Pb(Zr_xTi_{1-x})O_3$) ceramics are widely used in transducer and other electromechanical devices. Further, its application in passive underwater acoustic damping (UAD) requires a special shape of the $Pb(Zr_xTi_{1-x})O_3$ which embedded in a passive material. Helical shape is highly desirable in this device because it reduces the acoustic echo from the submerged structure to avoid

detection versus active sonar systems. Initially, $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ powder was prepared for $x=0.5$ by conventional method. A calcination profile was monitored for obtaining the pure phase of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$. The conditions are discussed in this work for the chemical formulation of the fabrication of helical $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$. Slurry was optimized for the amount of calcined powder, concentration of binder, dispersant, plastisizer and solvent. A sintering profile was examined in detail so that a continuous helical could be prepared without cracks. Scanning electron microscopic study indicated a uniform spherical morphology of the particles in the helical $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$.

GG3.8

MICROWAVE DIELECTRIC PROPERTIES OF $\text{Li}_{1-x-y}\text{M}_{1-x-3y}\text{Ti}_{x-4-y}\text{O}_3$ ($\text{M} = \text{Nb}, \text{Ta}$) SOLID SOLUTIONS. A. Borisevich and P.K. Davies, Dept. Materials Science, University of Pennsylvania, Philadelphia, PA.

As the utilization of wireless communications devices becomes increasingly widespread, novel dielectric materials combining good resonator properties (i.e. high temperature stable permittivities and high Q-factors) with low processing costs are in high demand. In this work we have examined a series of modulated $\text{Li}_{1-x-y}\text{Nb}_{1-x-3y}\text{Ti}_{x-4-y}\text{O}_3$ ($0.05 \leq x \leq 0.3, 0 \leq y \leq 0.175$) solid solutions in the $\text{Li}_2\text{O-Nb}_2\text{O}_5\text{-TiO}_2$ system. These oxides appear to be promising candidates for microwave applications. They can be sintered to full density below 1100°C , have relative permittivities as high as 70, microwave Q's up to 9000, and near-zero temperature coefficients. Similar solid solutions were also discovered in the corresponding tantalate system. Again they can be sintered at low temperature and exhibit good microwave properties. The structures of both systems are complex and consist of intergrowths of two different structural modules. The variations in the dielectric properties of both solid solution series can be attributed to bulk composition changes rather than more complicated structural effects.

GG3.9

CHEMICAL ORDER IN $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ RELAXOR FERROELECTRICS AND ITS IMPACT ON THE DIELECTRIC PROPERTIES. L. Farber¹, M.A. Akbas² and P.K. Davies¹. ¹Dept. of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA. ²Vishay Inc, Bridgeport, CT.

Thermal annealing treatments were used to induce long-range B-site cation order in the $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) - $(x)\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PSN) perovskite system for $x \geq 0.1$. The order-disorder transition boundary for the PMN-PSN system was mapped. It shows non-linear variation with x , with maximum at 1365°C for $x=0.5$. The chemical domain size in the annealed samples also shows a non-linear variation with x , being smaller for PMN- and PSN-rich compositions and larger for intermediate compositions. The well ordered, large chemical domain ceramics exhibit relaxor behavior up to $x \sim 0.5$, for higher values normal ferroelectric behavior was observed. Alterations in ordering had no significant effect on the properties of the lower x compositions, but induced a transition to relaxor behavior for $x > 0.5$. Disordered ceramics exhibit relaxor behavior in the whole compositional range studied. The structural changes and the associated modifications in the dielectric properties will be discussed in relation to the "random site" model for the chemical ordering in PMN.

GG3.10

STRUCTURE AND DIELECTRIC PROPERTIES OF THE $1-x\text{Pb}(\text{Sc}_{2/3}\text{W}_{1/3})\text{O}_3 - x\text{Pb}(\text{Ti/Zr})\text{O}_3$ RELAXOR SYSTEMS. Pavol Juhás, Dept. of Materials Science, Univ. of Pennsylvania, Philadelphia, PA; Mehmet A. Akbas, Vishay Vitramon, Inc.; Peter K. Davies, Dept. of Materials Science, Univ. of Pennsylvania, Philadelphia, PA.

The structural and dielectric properties of $(1-x)\text{Pb}(\text{Sc}_{2/3}\text{W}_{1/3})\text{O}_3 - (x)\text{PbMO}_3$, $\text{M} = \{\text{Ti}, \text{Zr}\}$ ceramics have been investigated in the substitution range $0 < x < 0.4$. All compositions can be indexed with a cubic perovskite structure; however, for $x < 0.25$ a doubled cell results from a 1:1 ordered distribution of the B-site cations. The chemical order in PSW can be described by a random site model where one cation site is occupied by Sc and the other by a random distribution of $(\text{Sc}_{1/3}\text{W}_{2/3})$. The stability of the ordering was found to be strongly enhanced by the incorporation of Ti, but reduced by Zr. The structure of the substituted samples was also influenced by the time and temperature of annealing. All of the solid solutions investigated showed relaxor ferroelectric behavior. For the substitution of PbTiO_3 the temperature of the relative permittivity maximum decreased up to $x = 0.15$ and then increased with a distinct onset at $x = 0.25$; for PbZrO_3 the maximum increased almost linearly with the Zr content. Maximum values of relative permittivity ($\epsilon_r \approx 7500$ at 1MHz) were achieved for the highest substitution ratios.

GG3.11

ORIGIN OF FERROELECTRICITY IN $\text{SrTi}^{(16}\text{O}_{1-x}\text{}^{18}\text{O}_x)_3$ INDUCED BY OXYGEN-ISOTOPE EXCHANGE. Mitsuru Itoh, Ruiping Wang, Mat and Structures Lab, Tokyo Inst Tech, Yokohama, JAPAN; Katsunori Iio, Kiyoko Morishita, Dept Phys, Tokyo Inst Tech, Tokyo, JAPAN; Yuji Tsujimi, Toshiro Yagi, Res Inst Electronic Sci, Hokkaido Univ, JAPAN.

Last 30 years, much effort has been devoted to elucidation of the mechanism for the evolution of the ferroelectricity in perovskite titanates. Among them, SrTiO_3 and KTaO_3 are called incipient ferroelectrics whose temperature dependence of dielectric constant increases with a decrease in T but does not show a maximum caused by the ferroelectric transition. For the quantum paraelectric SrTiO_3 and KTaO_3 the onset of a ferroelectric instability is suppressed by quantum fluctuations. Oxygen isotope exchange for quantum paraelectric SrTiO_3 induces ferroelectricity^{1,2}. Furthermore, $\text{SrTi}^{(16}\text{O}_{1-x}\text{}^{18}\text{O}_x)_3$ is a system with quenched random-field disorder and it can be regarded as a domain state. Similar behavior has been observed for Ca-doped SrTiO_3 ⁴. In this paper, many experimental data on dielectric constant, pyroelectricity, birefringence, first-Raman, and Brillouin scattering are conjugated and united, and possible model for the evolution of ferroelectricity of in $\text{SrTi}^{18}\text{O}_3$ is proposed.

1. M. Itoh et al, Phys. Rev. Lett., 82, 3540(1999).
2. M. Itoh and R. Wang, Appl. Phys. Lett., 76, 221(2000).
3. R. Wang and M. Itoh, Phys. Rev, B62, (2000), in press.
4. J.G. Bednorz and K. A. Müller, Phys. Rev. Lett., 52, 2289(1984).

GG3.12

DIELECTRIC PROPERTIES OF PFN CERAMICS MODIFIED BY MnO_2 . V.V. Bhat, A.M. Umarji, Materials Research Centre, Indian Institute of Science, Bangalore, INDIA.

The relaxor ferroelectric materials are of both academic and industrial importance because of their high dielectric constant, diffused phase transition (DPT) and frequency dependent transition. In the class of DPT materials Lead Iron Niobate (PFN) attracts much importance though it is a DPT material, it does not show frequency dependent transition and has sintering temperature less than 1000°C . PFN exhibits high loss due to the presence of Fe^{3+} and Fe^{2+} at the B' site. Aqueous manganese acetate was added to coat calcined PFN prior to sintering, composition with 1-4 wt% of the MnO_2 coated PFN were prepared and properties are studied. The dielectric constant and dissipation loss of this series is measured and found 1 wt% of MnO_2 gives high dielectric constant and low dissipation loss. The SEM and TEM studies of the samples are being carried out to understand the grain growth phenomenon and modified surface of PFN respectively. The density measurement is carried out for the understanding of the sinterability of PFN in the presence of MnO_2 .

GG3.13

PHASE EQUILIBRIA AND MICROWAVE DIELECTRIC PROPERTIES IN THE $\text{Ca}_2\text{AlNbO}_6\text{-CaTiO}_3$ SYSTEM. Igor Levin, Julia Chan, Terrell Vanderah, James Maslar, NIST, Gaithersburg, MD; Stephen Bell, Trak Ceramics, Inc., Hagerstown, MD.

Both CaTiO_3 and $\text{Ca}_2\text{AlNbO}_6$ crystallize in perovskite-related structures. The room-temperature forms of both compounds exhibit deviation from the ideal Pm-3m cubic perovskite symmetry due to tilting of BO_6 octahedra. Additionally, in $\text{Ca}_2\text{AlNbO}_6$, the Al and Nb cations are ordered on B-sites and occupy alternating 111 planes. Despite some structural similarities, the dielectric properties of CaTiO_3 and $\text{Ca}_2\text{AlNbO}_6$ are remarkably different; for example, the dielectric constants of CaTiO_3 and $\text{Ca}_2\text{AlNbO}_6$ are 170 and 25, respectively. In the present work we analyzed phase equilibria in the $\text{Ca}_2\text{AlNbO}_6\text{-CaTiO}_3$ system, in particular order/disorder transition, to correlate with dielectric properties at microwave frequencies.

GG3.14

MECHANISM OF QUALITY FACTOR COMPENSATION BY Nb_2O_5 ADDITION FOR DIELECTRIC PROPERTIES OF LOW-T SINTERED ZST MICROWAVE CERAMICS. Yong H. Park, Moo Y. Shin, Hyung H. Kim, Kyung H. Ko, Dept of MS&E, Ajou Univ., Suwon, KOREA.

It has been known that some additives such as Nb_2O_5 are efficient quality factor compensator to ZnO , a potential additives for low-T sintering of $(\text{Zr}_{0.8}\text{Sn}_{0.2})\text{TiO}_4$. The compensation mechanism of Nb_2O_5 was analyzed in the light of its effects on the Zn incorporation in grain. ZST ceramics was prepared by conventional mixed oxide method and their microwave dielectric properties including quality factor, permittivity and temperature coefficient frequency (TCF) were measured at X-band. After sintered at 1350 and 1400°C , samples were annealed at $900 \sim 1100^\circ\text{C}$. It was found that as Nb_2O_5 was added, quality factor of specimens 6 mol% ZnO-ZST increased from 24000 to 44000 without any sacrificing of other dielectric properties such as permittivity and TCF. According to TEM and XRD, Nb addition

tends to enhance Zn diffusion toward grain boundaries while they moved in opposite direction. Due to no second phase formation was detected, it was assumed that the redistribution of Zn and Nb could play a major role to the compensation mechanism of quality factor. Post-annealing can also be a remedy for the side effect of ZnO addition as previously reported. After annealing at 900 ~ 1100°C, quality factor of specimen added ZnO/Nb₂O₅, increased to 48000. In annealed samples, out-diffusion of Zn toward grain boundary proceeded thoroughly. Therefore, it is conceivable that co-addition of Nb with Zn could also enhance the post-annealing effects.

GG3.15
INTERSTITIAL DEFECT FORMATION AND MIGRATION ENERGIES IN STRONTIUM TITANATE. R.E. Williford, W.J. Weber, Pacific Northwest National Laboratory, Richland, WA.

Ion implantation in SrTiO₃ results in the formation of interstitial and vacancy defects. While the behavior of vacancies in SrTiO₃ is somewhat understood, there is almost no understanding of interstitial behavior, particularly the migration energies that control dynamic recovery processes during irradiation or during post-irradiation annealing. This paper presents new computational results on the formation and migration energies of interstitials in SrTiO₃. Atomistic simulations show that split interstitials are more stable than single interstitials for Sr and O, but the reverse is true for Ti. The lowest energy pathway for migration of the Ti interstitial is by an interstitialcy mechanism along the <110> directions with an activation energy of 2.64 eV. The stable Sr and O split interstitials migrate by an interstitialcy-like mechanism along <100> directions, with activation energies of 1.67 and 0.83 eV, respectively. The metastable O single interstitial migrates along <110> directions by successive jumps with an activation energy of 0.16 eV; however, the energy barrier for decaying to a split configuration is 0.09 eV. The effects of using alternative interatomic potentials will be discussed, and the results will be compared to data from ion-channeling experiments.

GG3.16
ENERGETICS OF PU INCORPORATION AND ORDER-DISORDER TRANSFORMATIONS IN GADOLINIUM ZIRCONATE AND TITANATE. R.E. Williford and W.J. Weber, Pacific Northwest National Laboratory, Richland, WA.

Pyrochlore structured Gd₂Ti₂O₇ and Gd₂Zr₂O₇ are candidate materials for immobilization of Pu. Radiation-induced disordering results in the transformation from pyrochlore to fluorite, and in the case of Gd₂Ti₂O₇, eventual amorphization. Atomistic computer simulations were used to quantify the energetics of Pu₃ and Pu₄ substitutions and interstitials in the Gd₂Ti₂O₇ and Gd₂Zr₂O₇ pyrochlore and fluorite lattices, so that processing and stability issues may be better understood. The lowest energies were found for Pu₃ substitutions on Gd sites in the pyrochlore (-1.42 and -0.86 eV/Pu for the titanate and zirconate, respectively), and Pu₄ substitutions on Ti or Zr sites in the fluorite (-0.23 and -0.26 eV/Pu for the titanate and zirconate, respectively). Lattice energies are higher for the fluorite in both materials, but the pyrochlore-to-fluorite transformation energy is lower for the zirconate. Volume changes due to the pyrochlore-to-fluorite phase transformation were minimized by Pu₄ substitutions.

GG3.17
GRAIN ORIENTATION OF ALUMINUM TITANATE CERAMICS DURING FORMATION REACTION. Yutaka Ohya, Gifu Univ, Dept of Chemistry, Gifu, JAPAN; Zenbe-e Nakagawa, Akita Univ, Akita, JAPAN; Kenya Hamano, Professor Emeritus, Tokyo Inst Tech, JAPAN; Hiroshi Kawamoto, Satoshi Kitaoka, JFCC, Nagoya, JAPAN.

A microstructural change during formation reaction of aluminum titanate from a mixture of rutile and corundum powders and the resultant structure of ceramics has been studied. The characterization was carried out using a polarization microscope, a scanning electron microscope and an X-ray diffractometer. A formation rate of aluminum titanate was controlled by a nucleation step. The formation reaction proceeded to form spherical oriented regions of aluminum titanate grains in the matrix of rutile and corundum. At the end of the reaction, the specimen was entirely filled with the oriented region of several hundred micrometers. Size of the oriented regions was reduced by an addition of fine aluminum titanate powder as nuclei. The oriented region was composed of primary aluminum titanate grains of several micrometers and pores. Large cracks due to a thermal expansion anisotropy were formed at the boundaries of the orientated regions. The addition of MgO and Fe₂O₃ resulted in the small oriented regions.

GG3.18
DIELECTRIC PROPERTIES OF SUBMICRON BARIUM TITANATE SYNTHESIZED BY HYDROTHERMAL METHOD.

Pramod K. Sharma, V.V. Varadan and V.K. Varadan, Earth and Engineering Science Dept, Pennsylvania State University, University Park, PA.

Barium titanate (BaTiO₃) is a ferroelectric material with a high room temperature permittivity and is used in the manufacture of multilayer capacitors. The increasing demands of multilayer capacitors are requiring improvements in the processing techniques of the fabrication of ultra fine ceramic powders. In this study, BaTiO₃ based ceramic has been synthesized by hydrothermal method. The lowering processing temperature has its advantages in producing finer and uniform particles. This method avoids the calcination step that is essential for BaTiO₃ preparation via conventional method. As hydrothermal reaction takes place at ambient temperature therefore the crystallization of the BaTiO₃ powder in a single phase under different hydrothermal conditions that is a critical feature of this processing, are discussed in detail. Optimisation of BaTiO₃ particle size and electrical properties can be achieved by altering the hydrothermal conditions. X-ray powder diffraction was used to study the phase in the final powder. The particle size of as received powder measured by laser particle size analyser was observed to be <200nm. In this study the electrical properties e.g. dielectric permittivity and loss, of the as received powders were discussed in detail with respect of hydrothermal conditions.

GG3.19
EFFECT OF CATION ORDERING ON THE DIELECTRIC PROPERTIES OF Ba(Co_{1/3}Nb_{2/3})O₃ AND Ba(Zn_{1/3}Nb_{2/3})O₃ NIOBATE PEROVSKITES. Irina Molodetsky, Peter Davies, University of Pennsylvania, Dept of Materials Science and Engineering, Philadelphia, PA.

Barium based tantalate perovskites such as Ba(Zn_{1/3}Ta_{2/3})O₃ (BZT) are important components in several microwave communications systems. The type and degree of B-site cation order in the tantalates is a critical parameter in optimizing their properties for commercial application. In this work we have examined the effect of different thermal treatments and chemical substitutions on the B-site cation order and the dielectric properties of Ba(Co_{1/3}Nb_{2/3})O₃ and Ba(Zn_{1/3}Nb_{2/3})O₃ niobate based perovskites. While both systems have previously been shown to exhibit promising microwave responses, improvements in their loss properties are necessary before they could replace their more expensive tantalate counterparts. Both of the parent systems undergo a B-site order/disorder transition at temperatures close to 1400C. Additional alterations in the ordering, in particular a transition to a 1:1 ordered doubled perovskite structure, can be induced through substitution of BaZrO₃ or Ba(Y_{1/2}Nb_{1/2})O₃. The alterations in the degree and type of ordering have significant effects on the dielectric loss properties and on the temperature coefficient of the relative permittivity. By manipulating the ordering and chemical composition new dielectrics have been developed with properties that approach those of the tantalate systems. The relationships between the composition, ordering, and dielectric response will be discussed.

This work is supported by Ericsson Radio Access AB.

GG3.20
SOLID-STATE NMR INVESTIGATION OF MIXED-ALKALI DISTRIBUTION IN PHOSPHATE GLASSES. S. Prabakar and K.T. Mueller, Department of Chemistry, The Pennsylvania State University, University Park, PA.

Solid-state NMR spectroscopy has been widely employed to investigate the local structural order in amorphous materials. Magic-angle-spinning (MAS) NMR, along with radio-frequency pulse sequences that recouple the dipolar interaction between nuclei, has provided new information about the spatial distribution of different nuclei in glasses. We have investigated a series of mixed-alkali sodium-cesium phosphate glasses by both MAS NMR and heteronuclear correlation experiments such as cross polarization and TRAPDOR (transfer of populations by double resonance) techniques. A wide range of compositions in the system x Na₂O: (50-x) Cs₂O: 50 P₂O₅ (series I) and x Na₂O: (57-x) Cs₂O: 43 P₂O₅ (series II), where x = 0 - 40, have been investigated by ¹³³Cs, ²³Na, ³¹P MAS NMR, and ³¹P₂₃Na or ¹³³Cs TRAPDOR NMR. ³¹P MAS NMR of glasses in series I show only one resonance due to phosphorus bonded to two bridging oxygens, and series II glasses show two resonances due to phosphorus bonded to one and two bridging oxygen respectively. TRAPDOR data show both the alkali ions are correlated to phosphate units, and the TRAPDOR fraction as a function of composition gives new insights into the distribution of sodium and cesium ions in these glasses.

GG3.21
NMR DETERMINATION OF DIVALENT ION DISTRIBUTIONS IN Pb Sr - (NO₃)₂. Xin-Gang Zhao, David Bussian, Gerard S. Harbison, Department of Chemistry, UNL, Lincoln, NE.

The NMR chemical shifts of heavy atoms includes a substantial contribution from dispersion effects. These dispersion shifts can be as large as hundreds of ppm, and are proportional to the polarizabilities of nearby ions and to the inverse sixth power of their distances. We have used these shifts to quantitate the distribution of lead and strontium ions in lead strontium titanates prepared by sintering. At low lead mole fractions, these solid solutions are cubic, and the NMR spectrum shows a series of resolved lines arising from lead ions with three, four, five or six strontium nearest neighbors, shifted by approximately 70 ppm for each additional strontium neighbor. Each individual resonance is further split by next-nearest neighbor effects, which are considerably smaller and of opposite sign. The intensities of the resonances can be integrated and used to model the distribution of lead and strontium ions in the solid solution; these distributions appear to be anti-clustered, possibly a response to lattice strain in these crystals.

GG3.22

INVESTIGATION OF LEAD BOROSILICATE GLASS STRUCTURE WITH ^{207}Pb AND ^{11}B SOLID-STATE NMR.

James M. Gibson, Frederick G. Vogt, Amy S. Barnes, Karl T. Mueller, Dept of Chemistry, Pennsylvania State University, University Park, PA.

Questions about the structure of lead borosilicate glass include whether the lead takes the role of a network former or a network modifier, and whether BO_3^- units exist at different compositions of the glass. Using phase-adjusted-spinning-sieband (PASS) NMR experiments on the ^{207}Pb nucleus and multiple-quantum-magic-angle-spinning (MQMAS) NMR experiments on the ^{11}B nucleus, both of these structural questions are investigated. A series of lead borosilicate glass compounds are synthesized with the melt-quench technique, primarily around the transition point for lead as a network former or modifier. Previous NMR experiments by Kim, Bray and Merrin (1) suggest that the transition is around 50% PbO by mole percentage, although they note that their ^{207}Pb spectra do not present a clear separation between the ionic and covalent peaks. ^{207}Pb PASS NMR helps to clarify this situation. Kim, Bray and Merrin also stated that were probably some (less than 10%) BO_3^- units, but they were not detectable with their wide-line ^{11}B NMR experiments. The ^{11}B MQMAS data reveals a peak that can be assigned to the BO_3^- ion, although MQMAS is not a quantitative technique. In addition, the MQMAS data can be used to show that both BO_3 and BO_4 units are present.

GG3.23

THERMOCHEMICAL STUDY OF GLASSES IN THE SYSTEM $2\text{YAlO}_3\text{-}3\text{SiO}_2$. Yahong Zhang, Alexandra Navrotsky, Thermo-Chemical Facility, Department of Chemical Engineering and Materials Science, University of California, Davis, CA.

Yttrium aluminosilicate glasses are important for technical use due to their extraordinary physico-chemical properties such as high glass transformation temperature, very low electrical conductivities, and excellent chemical stability. In addition, this system is important because it contains the most widely used additives for sintering of Si_3N_4 , SiAlON and SiC ceramics. Quantification of the thermochemical and physical properties, as well as the structure, of yttrium aluminosilicate glasses is necessary for a more complete understanding of processes occurring in this system. In this study, four yttrium aluminosilicate glasses along the $2\text{YAlO}_3\text{-}3\text{SiO}_2$ join were synthesized with 40, 50, 60 and 70 mol% 3SiO_2 content. High temperature oxide melt reaction calorimetry using $2\text{PbO}\cdot\text{B}_2\text{O}_3$ solvent at 800°C of these glasses resulted in enthalpies of drop solution of 12.40 ± 0.28 kJ/mol, 12.34 ± 0.12 kJ/mol, 11.96 ± 0.26 kJ/mol and 11.84 ± 0.25 kJ/mol, respectively. Thermochemical measurements on the end members, YAlO_3 and SiO_2 , are underway and will constrain the enthalpies of mixing and of vitrification and fusion in yttrium aluminosilicate system. Differential scanning calorimetry (DSC) is being employed to measure the heat capacities of the supercooled liquids, to determine their glass transition temperature and assess their fragility.

GG3.24

SYNTHESIS AND CHARACTERIZATION OF VANADIUM OXIDE FILMS. Khoi Le, R. Dillon and N. Ianno, University of Nebraska, Dept of Electrical Engineering, Lincoln, NE.

The objective of this work is to make and characterize films containing the VO_2 phase. This phase undergoes a semiconductor to metal transition at about 68°C and thus experiences a large change in electrical and optical properties. This work is focused on the change in optical properties in the infrared near 10 microns that can be used for satellite thermal control. However, it is also known that the transition temperature can be reduced to ambient by doping so that this material has applications in smart windows as well. Due to the narrow phase-range associated with VO_2 and its large free energy of

reaction with oxygen it is very difficult to reproducibly deposit this phase. To aid in the process control of sputter-depositing these films we measured the optical emission of V and O lines in the plasma, and maintained the ratio constant via feedback to the oxygen flowmeter. Typical deposition parameters for the dc magnetron sputtering were a power of 200 W, substrate temperature of $450\text{-}500^\circ\text{C}$, a total argon plus oxygen flow rate of 50 sccm with the oxygen percent varying from 1 to 5%, and a deposition time of one hour. We will report on our use of IR Variable Angle Spectroscopic Ellipsometry with a heated stage to characterize the changes that occur in the refractive index and extinction coefficient due to the transition. We thank NASA for support of this work under grant NAGW-4414.

GG3.25

INTERFERENCE EFFECT BETWEEN ELECTRON AND ION FLOWS IN SEMICONDUCTING Fe_3O_4 . Han-Il Yoo, Jeong-Oh Hong, Seoul National Univ, School of MS&E, Solid State Ionics Research Lab, Seoul, KOREA.

In the treatment of charge/mass transport phenomena in a mixed ionic electronic conductor compound, independent migration of charge carrier electrons and mobile ions, has routinely been assumed. It has, however, been found on the system of CoO [Yoo and Lee., *J. Phys. Chem. Solids* 57 (1996) 65] that the interference between ionic and electronic flows is large enough to reduce the effective valence of cation, Co^{2+} , appreciably from its formal value, 2. This work is aimed to examine the interference effect in the system of magnetite Fe_3O_4 , another semiconducting oxide. We performed Tubandt-like electrotransport experiments on single crystal Fe_3O_4 in both vacancy-dominating and interstitial-dominating regions at elevated temperatures to evaluate the effective valence of Fe-ions. It has been found that the effective valence of the mobile Fe-cations takes a value from below 2 up to 3 depending on the defect concentration in each defect regime. From the fact that the effective valence becomes even smaller than 2, we have concluded that contrary to the routine practice, the interference effect between the mobile cations and electrons is neither negligible in Fe_3O_4 .

GG3.26

ELECTRICAL AND OPTICAL PROPERTIES OF Ta-DOPED SnO_2 THIN FILMS PREPARED BY MOCVD METHOD. Sang woo Lee, Young-Woon Kim, and Haydn Chen, Department of Materials Science and Engineering and Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, IL.

Undoped and Ta-doped SnO_2 thin films have been deposited on glass substrates using metal organic chemical vapor deposition method with the film thickness of $0.2 \mu\text{m}$. The deposited films were characterized by XRD, TEM, SIMS, four-point probe, and Hall measurement. The films followed a columnar growth pattern verified by XTEM. The relative doping amount of Ta was up to 7.13%. The undoped film showed a typical n-type semiconductor behavior where carrier freezing upon cooling became dominant. At low temperature region below 80K , the electrical conductivity increased upon further cooling and was weakly temperature dependent. It is believed that this is due to hopping conduction through impurity states at the Fermi level. Once Ta was introduced, the films became degenerate semiconductor and metallic conduction was the main mechanism. The electrical resistivity varies from 1.7×10^{-1} to $2 \times 10^{-4} \Omega\text{-cm}$ depending upon the Ta contents and the minimum room temperature resistivity was observed when relative Ta concentration was 3.75% with the carrier concentration and the mobility of $1.27 \times 10^{21} \text{cm}^{-3}$ and $24.5 \text{cm}^2/\text{Vs}$, respectively. The average optical transmittance in the visible spectrum was about 89%. As the Ta doping increased, the fundamental absorption edge was shifted toward shorter wavelength region, which can be explained as Burstein-Moss effect. The change in the resistivity in conjunction with the carrier density and the mobility as well as the optical property will be explained in terms of the chemical effects induced from Ta doping in the thin films. Work supported by the U.S. Department of Energy.

GG3.27

STRUCTURE AND PROPERTIES OF RARE-EARTH NICKELATES AS EPITAXIAL THIN FILMS GROWN BY PULSED LASER DEPOSITION. Trong-Duc Doan, Cobey Abramowski, Paul A. Salvador, Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh PA.

Thin film techniques allow for the growth of materials that are otherwise only stabilized using high-pressure synthesis. Because of the structural mismatch across the film-substrate interface, large residual strains that can be exploited to tailor specific properties can exist in these metastable films. The rare-earth nickelates, LnNiO_3 , that adopt the perovskite structure are one example of a metastable family of compounds that can be made in a straightforward manner as thin epitaxial films. Using pulsed laser deposition we synthesized thin films of NdNiO_3 and YNiO_3 in as a function of temperature and pressure

on various substrates. The structural characteristics of as-grown and in-situ annealed films were investigated by X-ray diffraction allowing us to determine their epitaxial relationships to the underlying substrates, as well as the difference between the strained films and known bulk materials. In a second step, these strained metastable films were annealed ex-situ at various temperatures and under different reducing atmospheres to determine their reduction pathways and overall stabilities. Electrical properties were studied by resistivity measurements and were observed to be a strong function of the substrate type, film thickness, and reducing conditions. These differences are explained by both the different strain states and oxygen contents of the various films.

GG3.28

REDUCTIVE INTERCALATION OF (CuCl)LaNb₂O₇. Marilena L. Viciu, Thomas A. Kodenkandath, Leonard Spinu, Weilie L. Zhou, Jean-Noel Chotard, John B. Wiley Dept. of Chemistry and the Advanced Materials Research Institute, University of New Orleans, New Orleans, LA.

Topotactic methods can be used to construct metal-anion arrays within host compounds as well as to alter the charge of the host itself. Currently we are working to develop new strategies based on ion exchange and intercalation for the manipulation of structure and properties of perovskite-related compounds. Here we examine the reductive intercalation chemistry of the topochemically prepared copper-oxylhalide, (CuCl)LaNb₂O₇. A simple room-temperature reaction was used to insert lithium into this system. The resulting compound shows a significant structural change on intercalation as well as unusual transport behavior. Rietveld refinement results on this new compound will be presented along with transport and magnetic data.

GG3.29

ELECTRICAL RESISTIVITY AND SEEBECK COEFFICIENT OF RARE-EARTH DOPED CaMnO₃. Hideki Taguchi, Faculty of Science, Okayama University, Okayama, JAPAN.

Orthorhombic perovskite-type CaMnO₃ exhibits an n-type semiconductor. The electrical resistivity is $\approx 1 \Omega\text{-cm}$ and the Seebeck coefficient is $\approx 0.30 \text{ mV}\cdot\text{K}^{-1}$ at 773 K. In order to use CaMnO₃ for the thermoelectric conversion material, it is necessary to lower the electrical resistivity in keeping the Seebeck coefficient high. In the present study, the electrical properties of Ca_{1-x}(RE)_xMnO₃ (RE = La, Nd, Gd) were measured. CaCO₃, RE₂O₃, and MnO₂ were used as the starting material. They were weighed in the appropriate proportion and milled with acetone. The mixed powder was calcined and fired at 1623 K in a flow of pure oxygen gas. The X-ray diffraction patterns of all samples were completely indexed as the orthorhombic perovskite-type structure. The electrical resistivity at room temperature decreases abruptly with increasing the RE content. The Seebeck coefficient of Ca_{0.99}La_{0.01}MnO₃ is $\approx 0.20 \text{ mV}\cdot\text{K}^{-1}$ at 773 K and independent of temperature. The relationship between the electrical resistivity and the Seebeck coefficient of Ca_{1-x}(RE)_xMnO₃ will be reported.

GG3.30

CRACKING OPEN THE BLACK BOX: PROBING HIGH TEMPERATURE REACTIONS USING TIME-RESOLVED, ENERGY-DISPERSIVE X-RAY DIFFRACTION. Margret J. Geselbracht, Dept of Chemistry, Reed College, Portland, OR; Richard I. Walton, E. Sarah Cowell, Franck Millange, and Dermot O'Hare, Inorganic Chemistry Laboratory, Oxford, UNITED KINGDOM.

Many inorganic materials are commonly prepared by high temperature reactions, carried out in large furnaces and in some cases, within sealed vessels. Because of this, the availability of mechanistic and kinetic information for these reactions has historically been limited. The reaction occurs inside a "black box", and researchers are left to determine the optimal conditions by trial and error rather than based on any knowledge of the chemistry involved. We have recently constructed a furnace designed for monitoring high temperature reactions using in-situ synchrotron X-ray diffraction. The use of this furnace is described for laboratory-scale preparations of complex transition metal oxides by both solid state and molten salt flux synthesis methods.

GG3.31

CHALLENGING RIETVELD REFINEMENTS: ISOTOPIC SUBSTITUTION FOR THE INVESTIGATION OF PHASE TRANSITIONS IN INORGANIC MATERIALS. Paul F. Henry, Mark T. Weller, Southampton University, Chemistry Department, UNITED KINGDOM; Chick C. Wilson, Rutherford Appleton Laboratory, ISIS Pulsed Neutron Source, UNITED KINGDOM.

Neutron diffraction is a key technique in the characterisation of inorganic materials, often providing information unobtainable with

any other method. Its importance has been amply demonstrated in recent years with investigations of high temperature superconductors, zeolites, compounds displaying colossal magneto-resistance, ferroelectrics and zero and negative co-efficient of thermal expansion materials. Despite this widespread use, the method still has limitations deriving from the fundamental neutron scattering properties of many systems, coupled with (until now) relatively weak neutron count-rates, leading to the requirement for large sample sizes. With the advent of very high count-rate neutron diffraction instrumentation, such as GEM at ISIS, D20 at the ILL and the planned instrument at the SNS at Oakridge, incorporating large detector areas, sample sizes can be reduced dramatically whilst maintaining good data statistics. Our work addresses an aspect of structural determinations using powder neutron diffraction that will become possible with much smaller sample sizes, namely the use of otherwise prohibitively expensive isotopes. By using isotopically pure materials with strongly contrasting scattering lengths for the elements present and multiple data-set analysis techniques, a new generation of powder neutron diffraction experiments producing much higher quality structural information and structural data on systems has become possible. The technique has been employed successfully to study several systems. Using a combination of Sm and Ni isotopes, the metal-insulator transition in SmNiO₃ has been fully investigated. The Ti distribution in the important oxidation catalyst titanium silicalite-1 (TS-1) has been elucidated using Ti isotopes. 123 superconductors have been studied using Er, Ba and Cu isotopes to investigate subtle structural distortions that occur at T_c in order to understand the mechanism of high-temperature superconductivity. The location of dopant ions such as Ni, Fe and Zn in doped 123 superconductors, also important in determining the mechanism of high-temperature superconductivity.

GG3.32

Pb₂SnF₆: THE FIRST TIN(II)-LEAD(II) FLUORIDE THAT IS A SUPERSTRUCTURE OF α -PbF₂ - THE MYSTERIES OF ITS PREPARATION. Raimondo Calandrino, Anthony Collin, Georges Dénès, Morgane Logiou, M. Cecilia Madamba and Josselin Vogel, Concordia University, Dept. of Chemistry and Biochemistry, Laboratory of Solid State Chemistry and Mössbauer Spectroscopy, and Laboratories for Inorganic Materials, Montréal, Québec, CANADA.

Many tin(II)-metal(II) fluorides are known, several of which were discovered and studied in our laboratory. When the M²⁺ cation is large (M = Ca, Sr, Ba and Pb), the structure of the tin(II)-metal(II) fluoride is often related to the CaF₂ fluorite-type structure. This is the case of the MSnF₄ (Sr, Ba and Pb), PbSn₄F₁₀, and the M_{1-x}Sn_xF₂ (M = Ca and Pb). The relationship with the fluorite-type can occur according to two different mechanisms: (i) unit-cell distortion and superstructure in fully or partially ordered structures (cases of α -PbSnF₄, SrSnF₄, BaSnF₄, o-PbSnF₄, β -PbSnF₄ and the Pb_{1-x}Sn_xF₂ solid solution (x = 0.31 to 0.50)), (ii) no cell distortion or superstructure in fully disordered systems (PbSn₄F₁₀, γ -PbSnF₄, $\mu\gamma$ -PbSnF₄, Ca_{1-x}Sn_xF₂, and Pb_{1-x}Sn_xF₂ (x = 0 to 0.30)). In other cases, the crystal structure is unknown, however, its diffraction pattern shows no obvious relation to the fluorite-type structure (cases of MSn₂F₆ (M = Ca, Sr and Ba) and BaSn₄F₁₀). PbF₂ is known to exist in two different polymorphs: low temperature α -PbF₂, and high temperature β -PbF₂ obtained when α -PbF₂ is heated above ca. 300°C. β -PbF₂ is quenchable to ambient temperature where it seems to be stable indefinitely in the metastable state. We discovered recently that solid α -PbF₂ reacts under appropriate conditions with an aqueous solution of SnF₂ to give a new material. This material has been analyzed to have the Pb₂SnF₆ stoichiometry, and its X-ray diffraction pattern shows it is a superstructure of the α -PbF₂ structure. This is the first tin(II)-metal(II) compound, the structure of which is related to that of α -PbF₂. Recently, we discovered unexpected complications regarding the preparation of Pb₂SnF₆. The material preparation and characterization will be addressed in this presentation.

GG3.33

TiN RATTTLING IN THE Ba_{1-x}Sn_xCl_{1-y}F_{1-y} SOLID SOLUTION, VERSUS BINDING AND STOICHIOMETRY. Georges Dénès and Abdualhfeed Muntasar, Concordia University, Dept. of Chemistry and Biochemistry, Laboratory of Solid State Chemistry and Mössbauer Spectroscopy, and Laboratories for Inorganic Materials, Montréal, Québec, CANADA.

We have studied many cases of partial substitution of metal(II) by tin(II) in fluorides to give new ordered or disordered metal(II)-tin(II) fluoride materials possessing unique properties, particularly exceptionally high fluoride-ion conductivity. Until our recent discovery of the Ba_{1-x}Sn_xCl_{1-y}F_{1-y} solid solution, no such partial metal(II)/tin(II) substitution was known to occur in chloride fluorides. We have discovered that at high X = Ba/(Ba Sn) molar ratios in the reaction mixture, mixing aqueous solutions of SnF₂ and BaCl₂·2H₂O results in the precipitation of a material that has the

same X-ray diffraction pattern as BaClF, however with a small line shift. Chemical analysis shows that some of the barium has been replaced by tin, and some of the fluorine by chlorine, or vice-versa. These substitutions result in Ba/Sn disorder, and in F/Cl disorder on the F site ($y > 0$) or on the Cl site ($y < 0$), while the F/Cl order characteristic of the BaClF structure (PbClF type) is preserved. A similar wide range of $Ba_{1-x}Sn_xCl_{1-y}F_{1-y}$ solid solution ($0 < x < 0.26$, $-0.16 < y < 0.26$) can be prepared by direct reaction of appropriate amounts of SnF_2 , BaF_2 and $BaCl_2$ at high temperature. Tin-119 Mössbauer spectroscopy has been used to investigate tin bonding versus the composition of the solid solution. It was found that in precipitated materials, all the tin(II) is present in the form of the Sn^{2+} stannous ion, a situation unheard of in fluorides or in chlorides. For the materials prepared by direct reaction, a mixture of Sn^{2+} and of covalently bonded tin(II) is observed for negative and weakly positive y values, i.e. mostly when the F/Cl value is larger or close to one, and the relative amount of covalently bonded tin(II) decreases when y increases. For $y > 0$, there is little covalent tin(II) present, and none at higher positive y values. When y increases further, the intensity of the Mössbauer signal for ionic Sn^{2+} decreases drastically, and becomes nearly undetectable at the highest values ($Y > 0.15$). The high sensitivity of the Mössbauer probe to lattice strength has been used to analyze the strength of the bonding of tin to the BaClF type lattice, and it is obvious that bonding becomes very weak such that the stannous ion is probably smaller than its site, and therefore it rattles in its oversized box.

GG3.34

A MODEL OF IONIC CONFIGURATION OF SiO_2 -CaO BINARY GLASS ON THE BASIS OF THE MEASUREMENT OF $O K_{\alpha}$ X-RAY EMISSION SPECTRUM AND ITS MOLECULAR ORBITAL CALCULATION. Masao Morishita, Koichiro Koyama and Tadayoshi Kikko, Dept of Materials Science and Engineering, Himeji Institute of Technology, Himeji, JAPAN.

A method has been developed to simulate $O K_{\alpha}$ X-ray Emission Spectrum of SiO_2 -CaO binary glasses using the DV- X_{α} molecular orbital calculation. The composition of the glasses has been incorporated in the calculation of the O_{2p} partial density of states (PDOS). The calculated O_{2p} PDOS as a function of the CaO content agreed well with the experimental $O K_{\alpha}$ EPMA Spectra of the 62.4mol% SiO_2 -37.6mol%CaO and 43.3mol% SiO_2 -56.7mol%CaO binary glasses. The present method was found to provide a very useful means of clarifying the change in shape of the X-ray emission spectrum of the glasses with the metal oxide content.

GG3.35

INVESTIGATION OF PHASE FORMATION IN ELECTRICAL INSULATOR PORCELAIN BODIES. Scott Misture, David Seymour, William Carty, Alfred University, NYS College of Ceramics, Alfred, NY.

Both conventional quantitative X-ray Diffraction (XRD) and in-situ XRD analysis were used to study the formation of phases in electrical insulator porcelain bodies. An intensive investigation was conducted to optimize internal-standard quantitative XRD analysis of porcelains. Samples of ballclays that are used in the porcelain bodies were studied individually to better understand the formation of primary mullite. In addition, porcelain bodies were studied to determine the phase evolution sequence during firing, with particular emphasis on mullite formation and quartz dissolution. Both in-situ XRD and post-situ quantitative analysis were applied to determine the time/temperature profiles required to crystallize mullite and dissolve quartz. Quantitative XRD analysis showed that the mullite level remained constant from 1150°C to 1260°C but the quartz crystals continued to dissolve. These results show that the kinetics of mullite formation is not the limiting factor for producing a fast firing schedule for porcelain.

GG3.36

CRYSTAL CHEMISTRY OF COLLOIDS OBTAINED BY HYDROLYSIS OF FE(III) IN THE PRESENCE OF SiO_4 LIGANDS. Emmanuel Doelsch, Armand Masion, Jerome Rose, Jean-Yves Bottero, William Stone, CEREGE, Aix-en-Provence, FRANCE; Paul M. Bertsch, AACES, University of Georgia, Aiken, SC.

Fe and Si are two of the most abundant elements of the earth's crust. However, surprisingly little is known about the crystal chemistry of Fe-Si systems. We investigated Fe-Si systems over a wide range of Si/Fe molar ratios (0 to 4) and pH values (3 to 10) by combining Fe and Si K-edge EXAFS, Si-29 NMR, FT-IR, SAXS and computational molecular dynamics. The formed solid phases were all either poorly crystalline or amorphous. The iron within the precipitates is poorly polymerized. At low Si/Fe (<1), the growth of Fe species occurs by edge and corner linkages whereas at higher Si/Fe (>1) mainly edge linkages between Fe atoms were observed. Si/Fe=1 represent a crossover between the two growth regimes characterized by very poor

Fe polymerization. The speciation of Si was not only very dependent on the Si/Fe ratio but also on the pH. The size of Si clusters in the solid phase regularly decreased with increasing pH. The fractal dimensions ranging from 2.0 to 2.7 show that the aggregates are dense. However the evolution of the structure of the formed Fe-Si aggregates does not follow a clear trend. At low and high Si/Fe, the fractal dimensions tend to increase with increasing pH, which is well correlated with a decrease of the Si cluster size. However, at Si/Fe=1, the opposite trend is observed. Attempts to explain this difference were made using molecular dynamics and subsequent recalculation of EXAFS spectra.

GG3.37

PHASE EQUILIBRIA IN THE ALUMINA-DYSPROSIA-SILICA SYSTEM. Zhengping Zhang, Arun Varshneya and Scott Misture, Alfred Univ., Alfred, NY.

Phase equilibria in the dysprosia - alumina - silica system has been revisited. Portions of the phase diagram at and near primary phase boundaries have been investigated. The primary binary phases were studied as a function of temperature and equilibration time. Solid state reactions were used to prepare specimens during the study. The literature is lacking detailed crystal structures of several of the primary phases, hence the structures of several phases were refined using the Rietveld whole pattern fitting method.

GG3.38

THERMODYNAMIC INVESTIGATION OF CHARGE ORDERING AND CMR PHENOMENA IN RARE EARTH MANGANATES. Manisha V. Rane, Alexandra Navrotsky, University of California at Davis, Thermochemistry Facility, Dept of Chemical Engineering and Materials Science, CA.

Interest in rare earth manganates of the composition $Ln_{1-x}A_xMnO_3$ ($Ln = La, Nd, Y$ and $A = Ca, Sr$) has been renewed due to their colossal magnetoresistance (CMR) and charge ordering (CO). These properties vary with $\langle r_d \rangle$, the weighted average radius of cations on A site, and the cation size mismatch at the A site. Four different regions of CO behaviour have been delineated on the basis of this. Crystallographically speaking, charge ordering is basically the ordering of Mn^{3+} and Mn^{4+} on the B site, and is governed by the mixing of cations at A and B sites. The sensitivity of the charge ordered state to magnetic field is strongly dependent on $\langle r_d \rangle$. The compositions investigated namely, $Ln_{0.5}Ca_{0.5}MnO_3$ ($Ln = La, Nd, Y$) and $La_{1-x}Sr_xMnO_3$ ($x = 0.1$ and 0.3) encompass the $\langle r_d \rangle$ range from 1.127 to 1.263 Å. Preliminary studies by transposed temperature drop calorimetry and drop solution calorimetry in molten oxide solvents shows that the heat of formation of the compounds decrease with increasing $\langle r_d \rangle$ [1]. Moreover, the variation of heat of solution with $\langle r_d \rangle$ is found to be similar to the variation of Mn-O bond lengths and one electron bandwidth, W_a , with $\langle r_d \rangle$. This strongly suggests a correlation between CO and the associated magnetic behaviour with the heat of mixing and entropy. This work aims to investigate the energetics and entropy involved with mixing of cations at A and B sites and explain the resulting interplay between Jahn-Teller distortion, lattice and spin effects in different CO states. [1] C. Laberty, A. Navrotsky, C.N.R. Rao and P. Alphonse, J. Solid State. Chem., 145, 77-87, 1999.

SESSION GG4: TRANSPORT
PROPERTIES/METAL-INSULATOR SYSTEMS
Chairs: Martha Greenblatt and John B. Goodenough
Tuesday Morning, November 28, 2000
Room 304 (Hynes)

8:30 AM GG4.1

ELECTRICAL AND MAGNETIC PROPERTIES OF d^1 PNICTIDE-OXIDES: $Na_2Ti_2Pn_2O$ ($Pn = As, Sb$). Tadashi C. Ozawa, Univ of California, Dept of Chemistry, Davis, CA; Mario Bieringer, BIMR, McMaster Univ, Ontario, CANADA; John E. Greedan, BIMR, McMaster University, Ontario, CANADA; Susan M. Kauzlarich, Univ of California, Dept of Chemistry, Davis, CA.

$Na_2Ti_2Pn_2O$ ($Pn = As, Sb$) is a member of a small and unique class of compounds known as pnictide-oxide. The structure of $Na_2Ti_2Pn_2O$ is very similar to that of a High Tc superconductor, $La_{2-x}Sr_xCuO_4$; however, $Ti_2Pn_2O^{2-}$ layer in $Na_2Ti_2Pn_2O$ is anti configuration to CuO_2^{2-} layer in $La_{2-x}Sr_xCuO_4$. Recently, we have measured magnetic and electronic properties of $Na_2Ti_2Pn_2O$, and found the anomalous behavior, reminiscence of charge-density wave / spin-density wave materials, of these compounds. Results from these physical properties and further characterization will be presented.

8:45 AM GG4.2

FINE-TUNING THE PHYSICAL PROPERTIES OF PEROVSKITE

RELATED; LAYERED La-Ti- AND Sr/Ca-Nb-OXIDES BY MERE ALTERATION OF THE OXYGEN STOICHIOMETRY. Olav Becker, Stefan Ebbinghaus, Armin Reller, Bernd Renner, University of Augsburg, Solid State Chemistry, Augsburg, GERMANY; Michael Fröba, University of Erlangen-Nürnberg, Erlangen, GERMANY.

The isostructural oxides $\text{La}_2\text{Ti}_2\text{O}_7$ as well as $\text{Sr}_2\text{Nb}_2\text{O}_7$ and $\text{Ca}_2\text{Nb}_2\text{O}_7$ adopt layered structures made up of perovskite related slabs intermitted by layers of non-linking BO_6 -octahedra (B = Ti, Nb). In these phases the transition metals Ti and Nb are in their highest oxidation states IV and V respectively. They are insulators, in the case of the Ti phase a ferroelectric insulator with the highest known T_c of above 1700°C. By changing the oxygen stoichiometry, i.e. by controlled reduction or re-oxidation processes in the range of $\text{A}_2\text{B}_2\text{O}_7 \rightleftharpoons 2\text{ABO}_3 \frac{1}{2} \text{O}_2$ (A = La, Ca or Sr, B = Ti or Nb) mixed valence phases are obtained. Accordingly, the physical properties of the different phases alter from insulating to semiconducting or to conducting state. Detailed studies on the structural changes reveal however, that the sublattice of the metal cations is basically conserved. In principle the reduction corresponds to a condensation of the perovskitic layers leading to intermediate phases such as semiconducting $\text{La}_5\text{Ti}_5\text{O}_{17}$, where five TiO_6 -octahedra thick perovskitic slabs constitute the structural framework and 20% of the Ti^{IV} cations are reduced to Ti^{III} . Conductivity measurements using single crystals of the corresponding Ti and Nb phases reveal that these mixed valence oxides must be considered as one-dimensional conductors. The localisation of the reduced cations, i.e. of the Ti^{III} O_6 -octahedra (or the Nb^{IV} O_6 -octahedra) has been performed using XAS spectroscopy. The fully reduced phases $\text{La}^{\text{III}}\text{Ti}^{\text{III}}\text{O}_3$ and $\text{Sr}^{\text{II}}\text{Nb}^{\text{IV}}\text{O}_3$ adopt distorted perovskite structures. Extensive high resolution electron microscopic and light microscopic investigations have been carried out in order to characterise the structural mechanism of the reversible, highly topotactic reduction and re-oxidation processes. Thermogravimetric measurements in reducing and oxidising atmospheres have been performed for the identification of the temperature ranges wherein the decisive mass changes take place. The results of the described experiments support that the properties of such metal oxides can be finely and reversibly tuned by merely changing the oxygen stoichiometries.

9:00 AM *GG4.3

$\text{NiS}_{2-x}\text{Se}_x$ AS A PARADIGM FOR THE MANIPULATION OF ELECTRON CORRELATION EFFECTS. J.M. Honig, Department of Chemistry, Purdue University, West Lafayette, IN.

The $\text{NiS}_{2-x}\text{Se}_x$ system is an excellent candidate for studying electron correlation effects. One alters the electron interactions by progressive substitution of Se for S. This process leaves the cation sublattice intact and the electron count constant but changes the energy band structure of the alloy. Electrical conductivity measurements on single crystal specimens show a changeover from insulator, at $x \sim 0.3$, to metal, at $x \sim 0.55$. At intermediate Se concentrations the alloy is metallic at low temperature (T) and insulating at higher T. This peculiar result is rationalized by a simple thermodynamic argument involving electron correlation effects. Thermopower measurements are used to argue that for low x the half-filled narrow band of primarily e character is split as prescribed by the Hubbard-Mott model; this leads to the equal participation of holes and electrons in electron transport. At higher T carriers are thermally excited from the wider oxygen p band of slightly lower energy to the e states, so that the material then effectively becomes a one-band, p type semiconductor. These effects are gradually attenuated; the materials are converted to a poor metal for $x > 0.55$. Magnetic susceptibility and heat capacity measurements substantiate the above model. Finally, measurements by T. Rosenbaum, University of Chicago, of alloys with $x = 0.44$ show that one can induce a change from insulator to metallic characteristics by applying hydrostatic pressure. This permits exploration of the critical phenomena that occur near the transition point. The data are rationalized in terms of scaling theories, but the numerical values of the critical exponents require further explanation.

9:30 AM GG4.4

SLATER TRANSITION IN THE PYROCHLORE $\text{Cd}_2\text{Os}_2\text{O}_7$. D. Mandrus and J.R. Thompson, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN, and Dept. of Physics, The Univ. of Tennessee, Knoxville, TN.

The pyrochlore $\text{Cd}_2\text{Os}_2\text{O}_7$ undergoes a continuous, purely electronic metal-insulator transition (MIT) at 226 K as first discovered by Sleight et al. [1] in 1974. Here we present heat capacity and magnetization results on single- and poly-crystalline samples of $\text{Cd}_2\text{Os}_2\text{O}_7$. We interpret these results in the framework of a split-band model of antiferromagnetism originally put forward by Slater [2]. In Slater's model, the exchange field favors up spins on one sublattice and down spins on another sublattice. When the material orders magnetically, the additional periodicity doubles the unit cell and produces a MIT. The only other material thought to undergo a

pure Slater transition is V_2O_3 under pressure.

[1] A.W. Sleight et al., Solid State Comm. 14, 357(1974).

[2] J.C. Slater, Phys. Rev. 82, 538 (1951).

10:15 AM GG4.5

STRUCTURE AND ELECTRONIC PROPERTIES OF MONOCLINIC $\text{Nb}_{12}\text{O}_{29}$. J.E.L. Waldron and M.A. Green, Royal Institution of Great Britain, London, UNITED KINGDOM.

Monoclinic $\text{Nb}_{12}\text{O}_{29}$, which is a crystallographic shear plane structure with 4 x 3 blocks of NBO_6 octahedra, is synthesised as a bulk sample and its structure, magnetism and conductivity investigated using a number of techniques. The origin of its metallic and magnetic (anti-ferromagnetic, $T_N=12\text{K}$) characteristics are discussed in detail.

10:30 AM *GG4.6

SrFeO_3 AND CaFeO_3 DOMINATED BY STRONG OXYGEN-HOLE CHARACTER. Mikio Takano, Naoaki Hayashi, Takahito Terashima, Kyoto Univ, Institute for Chemical Research, Uji, Kyoto-fu, JAPAN.

SrFeO_3 (SFO, cubic) and CaFeO_3 (CFO, orthorhombic) contain iron in a rare oxidation state of 4. Fe^4 is isoelectronic with Mn^3 , but their oxides show remarkably different properties because the d levels are considerably deeper for Fe^4 than for Mn^3 . According to photoelectron spectroscopy, the Fe^4 ion should be regarded as a ferric ion accompanied by a ligand hole, $\text{Fe}^3\bar{L}$. The oxygen holes remain delocalized in metallic SFO, while those in CFO begin to be localized below 290 K as suggested from a gradual increase of resistivity. The low-T phase is monoclinic, with two kinds of Fe-O octahedra, which are both almost regular but different in size from each other, being contained. These and Mössbauer data also have strongly suggested that the oxygen holes tend to be concentrated in the smaller octahedra as $2\text{Fe}^3\bar{L} \leftrightarrow \text{Fe}^3\text{Fe}^3\bar{L}^2$. Another point is that the substitution of Co for Fe induces ferromagnetism with relatively high T_C 's: $\text{Sr}_2\text{FeCoO}_6$ (SFCO) has a high T_C of 340 K and a large moment of $4 \mu_B/\text{Fe}$ and $1.8 \mu_B/\text{Co}$ though SFO itself is an antiferromagnet with a T_N of 134 K. And SFCO is a better metal than SFO. Very recently we succeeded in preparing 40 nm-thick epitaxial films of SFO and CFO at a very low P_{O_2} of 10^{-2} atm though P_{O_2} of 10^4 atm, typically, is needed for bulky samples. The film quality was found to be excellent by the four-circle X-ray diffractometry. The SFO film was found to be metallic, and the hole concentration was estimated at 1.7/molecule. In summary, the various electronic states ranging from the AF insulator (CFO) to the ferromagnetic metal (SFCO) can be lined up in order of increasing oxygen-hole band width, and single crystals are now available in the form of film.

11:00 AM GG4.7

TRANSPORT PROPERTIES AND CRYSTAL CHEMISTRY OF Ba-Sr-Bi OXIDES. Oya A. Gökçen, James K. Meen, Allan J. Jacobson, University of Houston, Dept of Chemistry, Texas Center for Superconductivity, and Materials Research Science and Engineering Center, Houston, TX.

Rhombohedral phases of the binary systems AE-Bi-O (AE = Ca, Sr, Ba) have low temperature (β_2) and high temperature (β_1) polymorphs and the (β_1) polymorph is a good oxygen ion conductor. In a previous study, we showed that in the ternary system Ba-Sr-Bi-O, conductivities of polycrystalline rhombohedral samples are unaffected by Ba:Sr, whereas temperature ranges of the β_2 - β_1 polymorphic transition are. Recently, we proved that the conductivity of both polycrystalline and single-crystal rhombohedral samples is sensitive to spatial direction. For single crystals, the conductivity is highest perpendicular to the c-axis. Along the conduction plane, the conductivities are significantly higher than those of polycrystalline rhombohedral samples; perpendicular to that plane they are significantly lower. Uniaxial pressing of polycrystalline samples results in some preferential alignment of crystals with c-axis parallel to the compression axis. Therefore, measurements perpendicular to the pressing axis result in higher conductivities than ones parallel to that axis. The BaBiO_3 perovskite phase, a pure electronic conductor, has conductivities of 10 to 10^2 S/cm at 350-800°C in air. The conductivity of the biphasic rhombohedral-perovskite assemblage, a composite mixed ionic-electronic conductor, varies less with temperature and is between 10^{-1} and 1 S/cm in air. The conductivity profile of this composite with a volume ratio of 50%-50% is very similar to that of pure BaBiO_3 with no sharp changes in conductivity near the β_2 - β_1 transition. Electrical conductivities and structural properties of several composite samples with different rhombohedral- BaBiO_3 volume ratios are under investigation. Oxygen permeation properties of the biphasic rhombohedral-perovskite assemblages are also being examined. Structural characterization of Ba-Sr-Bi-O single rhombohedral crystals was done by scanning electron microscopy using secondary electron imaging and electron backscatter diffraction. Lattice parameters of five different Ba-Sr-Bi-O rhombohedral compositions with constant AE:Bi ratio but interchanging amounts of Ba:Sr were measured using X-ray powder diffraction method.

11:15 AM GG4.8

LITHIUM AND CESIUM DOPING OF PURE SILICA ZEOLITES: PREPARATION AND CHARACTERIZATION OF INORGANIC ELECTRIDES. Andrew S. Ichimura, James L. Dye, Department of Chemistry, Michigan State University, East Lansing, MI; Luis A. Villaescusa, Miguel Cambor, Instituto de Tecnología Química (CSIC-UPV), Universidad Politécnica de Valencia, Avda. Los Naranjos, Valencia, SPAIN.

When aluminosilicates are doped with alkali metals from the gas phase, metal cationic clusters are formed (eg. Na_4^{3+}) that can couple to produce different magnetic and electric properties. In our work, the pure silica zeolites ITQ-4 and ITQ-7 were doped with alkali metals from solution and gas phases. Both silicates absorb lithium from methylamine solutions to yield F-center like species. The 'excess' electrons couple antiferromagnetically in both silicates and lead to rich EPR spectra in the case of Li-doped ITQ-7. Interestingly, Li-doped ITQ-4 is EPR silent despite substantial paramagnetism determined by magnetic susceptibility measurements. The most likely locations for the excess electrons are within the extensive pore structure of each silicate, while the lithium cations may be trapped in small cavities between the major channels. Hence, these lithium doped silicates suggest the formation of a thermally stable 'inorganic electride'. ITQ-4 readily absorbs cesium from the vapor phase. The final product contains 35% by weight cesium. At this doping level, four cesium atoms occupy each unit cell and effectively fill the major channels of ITQ-4. The magnetic and electric properties of this solid that consists essentially of 1-D zig-zag cesium chains will be described. The metal concentration and effective reducing power of the doped materials were determined, and each system was further characterized by NMR and DRIFT spectroscopy. The properties of metal doped silicates are of fundamental interest and they may find applications as reducing agents in organic synthesis and anion exchange materials.

11:30 AM GG4.9

ELECTRONIC CONDUCTION MECHANISMS IN THE NANOTUBULAR CRYSTALS OF CETINEITES FROM AB-INITIO ELECTRONIC STRUCTURE CALCULATION. Frank Starrost, Evgueni E. Krasovskii, Oliver Tiedje, Sven Brodersen, Wolfgang Schattke, Institut für Theoretische Physik und Astrophysik, Christian-Albrechts-Universität, Kiel, GERMANY; Jörg Jockel, Ulrich Simon, Institut für Anorganische Chemie, Universität GH, Essen, GERMANY.

Recently, an investigation of basic properties of a new class of nanoporous chalcogenoantimonates (Phys. Rev. **61**, 15707 (2000)) revealed interesting features of the excited states' band structure which gave rise to exploring the type of electronic conduction. Especially, the crystalline arrangement of tubes with diameter slightly smaller than 1 nm which extend almost unperturbed throughout the whole crystal suggests ideal conductivity within the tubes at some excitation energies of this generally semiconducting material. This kind of conduction should be strongly related to the content of the otherwise hollow tubes, e.g. to water, which, to date, can be entirely extracted only in one of these compounds. Other conduction mechanisms as hopping along the tube walls, or along the molecules in between the tubes mediating their cohesion, compete and are clarified. Experimental data from gas adsorption of smaller molecules are available and show the necessity of electronic structure calculations also for tube filling with impurity molecules. In addition to the calculations for the ideal crystal with empty tubes, supercell calculations are self-consistently carried through with an extended LAPW code for general potential shapes. Excitation probabilities and mobilities are determined on this ab-initio basis. The configuration and the arrangement of the filling molecules have been assumed from crystal data and from heuristic binding arguments supported by single total energy determinations. The correspondence between the electronic structure and the conductivity are discussed for a variety of these compounds with special emphasis on the free electron-like ideally conducting excited state confined to the interior of the tubes.

11:45 AM GG4.10

ELECTRONIC STRUCTURE OF TIN SULFIDE AND TIN DISULFIDE. P.E. Lippens, M. Womes, J. Olivier-Fourcade, J.C. Jumas, Laboratoire des Agregats Moleculaires et Matériaux Inorganiques, CNRS UMR 5072, Universitè Montpellier II, Montpellier, FRANCE.

Tin sulfide-based materials have been widely studied both in solid state chemistry for the versatile coordinating characteristic of tin and sulfur and in solid state physics for their interesting optical and electrical properties. We present a comparison between the electronic structures of tin sulfide and tin disulfide based on different experimental methods: x-ray photoemission spectroscopy (XPS), x-ray emission spectroscopy (XES), x-ray absorption spectroscopy (XAS) and Mossbauer spectroscopy. The results are analysed from linear

augmented plane wave (LAPW) calculations of the XES and XAS spectra, the electronic band structures, the total and partial densities of states, the hyperfine Mossbauer parameters and the electronic charge densities. This provides a rather accurate picture of both the occupied and unoccupied electron states of the two materials and allows to correlate the data obtained from complementary experimental tools. For example, the variations of the tin Mossbauer isomer shift are correlated to changes in the XAS spectra at the Sn L3 edge. We also propose a discussion of the experimental data from the chemist's point of view based on the oxidation numbers, the activity of the lone pairs and the nature of the chemical bonds. This approach is related to the results of the LAPW calculations and could be useful for a qualitative interpretation of the properties of more complex tin sulfide-based compounds.

SESSION GG5: MAGNETISM AND MANGANATES

Chairs: John E. Greedan and Peter B. Battle
Tuesday Afternoon, November 28, 2000
Room 304 (Hynes)

1:30 PM GG5.1

SUBSTITUTIONAL CHEMISTRY AND EXOTIC MAGNETISM IN TERNARY RUTHENATES. R.J. Cava, T. He, and P. Khalifah, Princeton University, Department of Chemistry and Princeton Materials Institute, Princeton, NJ; Q. Huang, University of Maryland, Department of Materials and Nuclear Engineering, College Park, MD, and NIST Center for Neutron Research, Gaithersburg, MD.

The Ruddlesden-Popper phases based on alkaline metal ruthenates have been of considerable recent interest due to the evolution from high temperature ferromagnetism to superconductivity at low temperatures on decreasing structural dimensionality. Our research has been in exploring further this evolution in different chemical systems. Here the comparison of the magnetic properties of the $\text{Sr}_{1-x}\text{Ca}_x\text{RuO}_3$ and $\text{Sr}_{1-x}(\text{La}_5\text{Na}_{.5})_x\text{RuO}_3$ perovskites are reported. By comparison of the properties of these systems as a function of structural distortion, we demonstrate for the first time the suppression of ferromagnetism by off-site charge disorder. This effect is comparable in magnitude to the structural distortion effect. We further report the comparison of the transport and magnetic properties of $\text{La}_3\text{Ru}_3\text{O}_{11}$ and $\text{La}_4\text{Ru}_6\text{O}_{19}$, two materials with the same effective Ru valence and Ru-O structural network but dramatically different properties. The difference is attributed to the strong metal-metal bonding in the latter material.

1:45 PM GG5.2

METAL CYANIDE NETWORKS FORMED AT AN AIR-WATER INTERFACE: STRUCTURE AND MAGNETIC PROPERTIES. Jeffrey T. Culp, Daniel R. Talham, Univ of Florida, Dept of Chemistry, Gainesville, FL.

Numerous one-, two-, and three-dimensional metal cyanide networks are known that use various transition metal geometries as structure directors. In addition, the ability of the cyanide ligand to mediate magnetic exchange has led to interesting magnetic properties such as meta-magnetism in some low dimensional metal-cyanides and magnetic ordering at temperatures as high as room temperature in three-dimensional Prussian blue analogues. In order to investigate the structure directing ability of an interface on metal cyanide networks, amphiphilic hybrid inorganic/organic metal-cyanide complexes have been prepared. The amphiphilic nature of these complexes combined with the ambidentate nature of the cyanide ligands allows formation of extended two-dimensional bi-metallic networks at the air-water interface. The transfer of these films to solid supports by the Langmuir-Blodgett technique results in monolayer or multi-layer assemblies that can be characterized by grazing incidence x-ray diffraction (GIXD) and SQUID magnetometry. The structure and magnetic properties of these materials demonstrate the potential of the air-water interface to act as a structure directing element in the formation of low dimensional extended inorganic networks.

2:00 PM *GG5.3

SPIN DIMER ANALYSIS OF THE SPIN EXCHANGE INTERACTIONS IN EXTENDED MAGNETIC SOLIDS. M.-H. Whangbo, H.-J. Koo, D. Dai, North Carolina State Univ, Dept of Chemistry, Raleigh, NC.

The spin exchange interactions in various extended magnetic solids of V^{4+} , Cr^{3+} , Mn^{3+} , Ni^{2+} and Cu^{2+} cations were examined by calculating the electronic structures of their spin dimers, i.e., the structural units containing two adjacent spins. The qualitative trends in the spin exchange parameters J of these solids are well explained by the one-electron spin orbital interaction energies calculated for their spin dimers using the extended Huckel theory. On a quantitative level, the spin exchange parameter J for a spin dimer can be calculated as

the energy difference between the highest-spin and the broken-symmetry states of the spin dimer using the density functional theory, regardless of the number of unpaired spins per spin site. We examine how the anisotropy of spin exchange interactions is related to the crystal structure in oxides, fluorides and chlorides of Cu^{2+} , oxides of V^{4+} , fluorides of Ni^{2+} and Mn^{3+} , as well as oxides and sulfides of Cr^{3+} .

3:00 PM GG5.4

MAGNETISM AND STRUCTURE IN THE $\text{La}_{2-x}\text{Sr}_x\text{GaMnO}_6$ SERIES. E.J. Cussen, L.D. Noailles, M.J. Rosseinsky; Liverpool University, Department of Chemistry, Liverpool, UNITED KINGDOM; P.D. Battle, Inorganic Chemistry Laboratory, University of Oxford, Oxford, UNITED KINGDOM; S.J. Blundell, A.I. Coldea, I.M. Marshall, J. Singleton, Clarendon Laboratory, University of Oxford, Oxford, UNITED KINGDOM.

The influence of the substitution of diamagnetic cations at the Mn site in CMR manganates on the details of the magnetic ordering and crystal chemistry is little studied. Here we report on the structural and magnetic phase diagram of $\text{La}_{2-x}\text{Sr}_x\text{GaMnO}_6$. Upon strontium doping this perovskite crystallizes in the space group $I2/a$ adopting a different tilt scheme (a-b-b-) than the Pmna $\text{La}_2\text{GaMnO}_6$ parent structure (a-b-c-). The space group is confirmed by lab x-ray, high-resolution neutron and electron diffraction. All compounds in the series are insulators and there is a ferromagnetic to spin-glass transition around $x=0.4$. As x increases the magnetoresistance increases where ferromagnetism is retained. The activation energy decreases with increasing x . The structural evolution on cooling through the Curie temperature of $\text{La}_{1.7}\text{Sr}_{0.3}\text{GaMnO}_6$ has been monitored by neutron diffraction. Upon cooling, the monoclinic angle decreases and is accompanied by a lowering of symmetry for the ferromagnet but not the spin-glass $\text{La}_{1.5}\text{Sr}_{0.5}\text{GaMnO}_6$.

3:15 PM GG5.5

EFFECTS OF COPPER SUBSTITUTION ON MANGANITE PEROVSKITE LaMnO_3 : ELECTRICAL AND MAGNETO-RESISTIVE PROPERTIES. R. Cloots, B. Vertruyen, A. Rulmont, H. Bougrine, Ph. Vanderbemden, and M. Ausloos, SUPRAS, University of Liege, BELGIUM.

Substitution of copper on manganese sites in LaMnO_3 has been attempted for various concentrations of Cu. Materials have been characterized by chemical and physical means. An anomalous peak in the magnetoresistance is discussed. The presence of silicon at the grain boundaries coming from the preparation process causes a severe shift in the electrical resistance transition temperature. The electrical properties of these copper substituted materials have been compared to the ones of undoped LaMnO_3 systems.

3:30 PM GG5.6

MICROMAGNETIC AND MAGNETORESISTANCE STUDIES OF FERROMAGNETIC $\text{La}_{0.83}\text{Sr}_{0.13}\text{MnO}_{2.98}$ CRYSTALS. Guerman Popov^a, Sergei V. Kalinin^b, Rodolfo A. Alvarez^b, Martha Greenblatt^a and Dawn A. Bonnell^b. ^aDepartment of Chemistry, Rutgers the State University of New Jersey, Piscataway, NJ. ^bDepartment of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA.

Magnetic force microscopy (MFM) and atomic force microscopy (AFM) were used to investigate the surface topography and micromagnetic structure of an as-grown $\text{La}_{0.83}\text{Sr}_{0.13}\text{MnO}_{2.98}$ crystal with colossal magnetoresistance (CMR). The crystals were grown by fused salt electrolysis in a melt obtained from a mixture of Cs_2MoO_4 and MoO_3 to which SrMoO_4 , MnCO_3 and La_2O_3 were added. Chemical composition was analyzed by ICP, and the oxygen nonstoichiometry was analyzed by iodometric titration. The crystals are rhombohedral ($R\bar{3}c$) as determined by powder X-ray diffraction. Magnetic and transport measurements indicate that the ferromagnetic ordering at 310K is associated with an insulator-metal transition at the same temperature. A maximum negative magnetoresistance (~62%) is observed at 290K in an applied magnetic field of 5T. Magnetic hysteresis measurements indicate a coercive field of 21G; however, full magnetic saturation is not observed up to 5T. The magnetoresistance increases sharply (1.8%) with increasing magnetic field up to 20G, and then it increases slowly with increasing field. MFM and AFM were used to study the (110) surface as well as a number of unspecified surfaces. It was found that surface topography of as-grown crystals exhibits well-developed surface corrugations due to extensive twinning. The corrugation angle at twin boundaries was related to the unit cell parameters. Magnetic force microscopy images show that magnetic domain boundaries are pinned to the crystallographic twins; a small number of unpinned boundaries are observed. The statistical analysis of domain boundary angle distribution is consistent with cubic magnetocrystalline anisotropy for this material. Unusual magnetization behavior in the vicinity of topological defects on the surface is also reported. MFM contrast was

found to disappear above the ferromagnetic Curie temperature; after cooling at the same surface a new magnetic structure comprised of Bloch walls of opposite chiralities developed.

3:45 PM GG5.7

DETERMINATION OF Mn VALENCE STATES IN LANTHANUM STRONTIUM MANGANITES BY ELECTRON MICROPROBE. Karoline Müller, T. Kreschollek, J.K. Meen, D.K. Ross and D. Elthon, Dept of Chemistry and Texas Center for Superconductivity, Univ of Houston, Houston, TX.

We will present an analytical technique that uses the L x-ray emission spectrum ('soft' x-rays) to determine the valence state of Mn in manganites in which La, Sr, or both occupy the perovskite A site. A 2-10 μm diameter area is excited by a focused electron beam and characteristic x-rays are measured by wavelength dispersive spectrometry. Chemical analysis of cations and oxygen by electron probe microanalysis and the determination of Mn valence state are performed at the same time and on the same area. The method requires homogeneous, well characterized standard lanthanum strontium manganites that have been analyzed by bulk techniques. This ensures accurate and precise analyses as inter-element corrections may be definitively accounted for. Therefore this technique gives high-quality information pertaining to phase segregation and degree of homogeneity at the micron-scale. Manganites with a variety of La:Sr have been synthesized. At 1450°C and in pure oxygen, there appears to be complete mixing of La and Sr on the A site. Even Sr-rich manganites contain Mn^{3+} as well as Mn^{4+} so they are oxygen-deficient. The $\text{Mn}^{4+}:\text{Mn}^{3+}$ depends on temperature and oxygen pressure in the La-free system and has a complex dependence on those parameters and La:Sr for the mixed manganites. At temperatures below ~1400°C and in oxygen, SrMnO_{3-x} adopts a structure related to a hexagonal four-layer structure and there is a miscibility gap between Sr-saturated (La,Sr) manganites and hexagonal 4L SrMnO_{3-x} . This gives us the ability to investigate the effects of crystal structure, La:Sr, and Mn valence on the soft x-ray spectrum of Mn.

4:00 PM GG5.8

MAGNETOTRANSPORT PROPERTIES OF THE FERRO-MAGNETIC INSULATOR $\text{La}_{1.5}\text{Sr}_{0.5}\text{MnRhO}_6$. Amalia I. Coldea, Ishbel M. Marshall, Stephen J. Blundell, John Singleton, University of Oxford, Clarendon Laboratory, UNITED KINGDOM; Liam D. Noailles, Peter D. Battle and Matthew J. Rosseinsky, University of Oxford, Inorganic Chemistry Laboratory, UNITED KINGDOM.

We have investigated the magnetic and electrical properties of the ferromagnetic insulator $\text{La}_{1.5}\text{Sr}_{0.5}\text{RhMnO}_6$. Rh substitution sustains ferromagnetic ordering, in contrast with the behaviour of other dopants on the Mn-sites, but modifies the electrostatic potential leading to carrier localisation. A significant magnetoresistance is found in this system which is largest at the Curie temperature (T_C) and is attributed to the field-induced suppression of critical spin fluctuations. Impedance spectroscopy is also used in an attempt to identify the role of grain boundaries and their contribution to the observed magnetoresistance in our polycrystalline material.

4:15 PM GG5.9

RESISTIVE ANOMALY RELEVANT TO Nd MOMENTS IN THE ANTIFERROMAGNETIC PHASE OF THE BANDWIDTH-CONTROLLED MANGANITES. Hideki Kuwahara, Sophia Univ, Dept of Physics, Tokyo, JAPAN and PRESTO, JST, Tokyo, JAPAN; Kohei Noda, Ryuichi Kawasaki, Sophia Univ, Dept of Physics, Tokyo, JAPAN.

Recent our study on $\text{Nd}_{0.45}\text{Sr}_{0.55}\text{MnO}_3$ compound with the layered antiferromagnetic (AF) spin structure has revealed that it shows an extremely large anisotropy in resistivity. The observed large anisotropy is due to confinement of the spin-polarized carriers within the ferromagnetic sheets induced by the magnetic-ordering as well as $d_{x^2-y^2}$ type orbital-ordering. In the present work, we have investigated electronic and magnetic properties of $(\text{Nd}_{1-y}\text{Sm}_y)_{0.45}\text{Sr}_{0.55}\text{MnO}_3$ ($0 \leq y \leq 1$) crystals, in which one-electron bandwidth (W) is systematically decreased from the parent compound ($y=0$) with increase of y . We have found the metal-insulator phase boundary in the ground states of this system: The anisotropic metallic state with AF structure ($y=0$) has been transferred to the AF insulator ($0.3 \leq y$) in zero field. The critical composition y changes from 0.3 to 0.5 by application of a magnetic field of 12T. This implies that the magnetic field induced the broadening W and the resultant insulator-to-metal transition. We have found another remarkable transition concerning the ordering of Nd moments in low temperatures. The very subtle drop in resistivity superimposed upon the conventional CMR was observed for the isothermal MR measurements ($\rho(H)/\rho(0) \approx 5\%$ at 4T and 2K). The transition fields for these anomalies monotonically decrease with increase of temperature and disappear above ~25K. It turned out that the resistive drop is due to the field-induced ordering of Nd moments from DC magnetization measurements. The Nd

moments seem to order below 25K in zero field, which is consistent with the recent neutron scattering measurement for the similar Nd-based manganite with a different hole doping level ($x=0.30$).

4:30 PM GG5.10

X-RAY MAGNETIC COMPTON SCATTERING OF DYCO₅. Hayato Miyagawa, Yasuhiro Watanabe, Susumu Nanao, Univ of Tokyo, Institute of Industrial Science, Tokyo, JAPAN; Nozomu Hiraoka, Akihisa Koizumi, Nobuhiko Sakai, Himeji Institute of Tech, Material Science Division, Hyogo, JAPAN; Msaichiro Mizumaki, Yoshiharu Sakurai, Japan Synchrotron Radiation Research Institute(JASRI), Hyogo, JAPAN.

In the intermetallic compound, DyCo₅, a ferrimagnetic coupling exists between Dy and Co sites but the reliable value of these magnetic moments has not been reported because a neutron diffraction analysis is difficult for Dy which is the one of neutron absorption atoms. We have measured high resolution (~ 0.6 a.u.) magnetic Compton profiles using elliptically polarized synchrotron radiation at room temperature (at SPring-8 BL08W) for single crystalline sample of DyCo₅. The distribution of magnetic electrons in kinetic space was obtained directly and the ratio of spin magnetic moments at each atomic site and the spin polarization of conduction electrons are estimated.

SESSION GG6: POSTER SESSION NEW MATERIALS, MESO/NANOPOROUS MATERIALS

Chairs: John B. Wiley and Slavi C. Sevov
Tuesday Evening, November 28, 2000
8:00 PM

Exhibition Hall D (Hynes)

GG6.1

EFFECT OF POLYMERIZATION OF PRECURSOR SOLUTIONS ON CRYSTALLIZATION AND MORPHOLOGY OF Ce_{0.9}Gd_{0.1}O_{1.95} POWDERS. Shuqiang Wang, Masanobu Awano, Kunihiro Maeda, FCRA, Synergy Ceramics Laboratory, Nagoya, JAPAN.

Nano-scale solid electrolyte Ce_{0.9}Gd_{0.1}O_{1.95}(CGO) powders were synthesized from controlled polymerization processes of mixing nitrate and ethylene glycol at the temperatures below 130°C. It was found that crystallization and morphology of the derived powders change with the temperatures and time used in the polymerization of the precursor solutions. For the precursor solutions heated at 65°C for about 200 hrs and dried at 130°C, the organic formates of Ce³⁺ and Gd³⁺ ions with good crystallization were obtained as intermediate compounds, which were identified by FTIR and XRD. Moreover, it was observed by SEM that the Ce(Gd)-formate powders exhibited well crystallized needle-like anisotropic growth morphology which remained during subsequent calcination processes to form the CGO powders. However, when the stirring time of the precursor solutions exceeded 400 hrs, single cubic CGO crystallites were formed directly from the as-dried powders with an average diameter of less than 100nm. The interrelations between the polymerization process of the precursor solutions and the crystallization of the derived powders were further investigated by means of FTIR, TG-DTA, TG-MASS and TEM.

GG6.2

STUDY ON CHEMISTRY PURIFICATION OF TITANIUM DIBORIDE SYNTHESIZED BY COMBUSTION SYNTHESIS PROCESSES. Wang Weimin, Fu Zhengyi, Wang Hao, Wuhan University of Technology, State Key Lab of Advanced Technology for Materials Synthesis and Processing, Wuhan, PR CHINA.

TiB₂ Ceramic has excellent physico-chemical properties such as high melting point, high hardness, good corrosion resistance and high temperature mechanical properties. At the same time, TiB₂ ceramic has also an excellent electricity conductivity, which make TiB₂ materials have a great wide application areas as advanced engineering ceramics. In this paper, Self-Propagation Combustion Synthesis technique was used to synthesize the TiB₂ ceramics powder from various metal oxides by following basic chemistry reaction: TiO₂ + B₂O₃ + 5Mg = TiB₂ + 5MgO. In order to obtain the pure TiB₂ powder, the chemistry purification processes is necessary. The thermodynamics and kinetics of chemistry treatment processes were analysed. The influence of synthesis conditions on the microstructure of synthesized TiB₂ mixture and the relation between the chemistry treatment parameters and purity of TiB₂ powder were studied. The study results showed that the purity of TiB₂ powder is dependence on chemistry purification (acid -washing) conditions. The main processes parameters that influenced the purity of TiB₂ powder were the concentration of hydrochloric acid, amount of excessive acid, the particle size of TiB₂ powder mixture, and the chemistry treatment time and temperature. The fine TiB₂ powder with very high purity can be obtained by suitable chemistry processes.

GG6.3

SYNTHESIS OF NANO-SIZED BARIUM STRONTIUM TITANATE BY A GLASS RECRYSTALLIZATION METHOD. Y.K. Hong, M.H. Park, University of Idaho, Magnetic and Electronic Materials Research Laboratory, Department of Materials and Metallurgical Engineering, Moscow, ID; C.F. Lo, P.S. Gilman, Praxair-MRC, Orangeburg, NY.

Ultra-fine barium strontium titanate (Ba_{1-x}Sr_xTiO₃: x = 0.0 to 1.0) particles were produced by a glass re-crystallization method. A mixture of glass component containing boron (B) and fundamental component containing barium (Ba), strontium (Sr), and titanium (Ti) was melted, followed by quenching into iced water to prepare two separated Ti-rich and B-rich amorphous phases. During subsequent annealing of quenched flakes, strontium titanate (SrTiO₃) nucleated first, followed by the formation of barium strontium titanate crystallites. Non-agglomerated barium strontium titanate particles were obtained by leaching out glass components of the annealed flakes with a dilute hydrochloric acid. The barium strontium titanate particle size distributes from 40 to 70 nanometer with an average about 50 nanometer. These particles have serious implications for possible fabrication of future multilayer ceramic capacitors and sputtering targets. Nucleation mechanism will be presented in this paper.

GG6.4

DECORATION OF SILICON CARBIDE NANOTUBES CoFe₂O₄ SPINEL. C. Estournés, Groupe des Matériaux Inorganiques, Institut de Physique et Chimie des Matériaux de Strasbourg (UMR7504 CNRS-ULP-ECPM), Strasbourg, FRANCE; C. Phamm-Huu, M.J. Ledoux, Laboratoire de Chimie des Matériaux Catalytiques, ECPM-GMI-CNRS, Université Louis Pasteur, Strasbourg, FRANCE.

Nanoscale materials have attracted a great deal of attention in the recent years because their chemical and physical properties may differ significantly from the bulk properties as a result of surface or quantum size effects. However, these properties are highly dependent on the size of the particles and the presence or not of interactions between their surface and ligands, contaminants or a support. Recently, there has been great interest to tap the potential of carbon nanotubes in the area of catalysis. On one way, the tubes can function as supports for heterogeneous catalysis and be decorated either with transition or noble metals. On other way, transition metals or alloys nanoparticles are employed in order to grow carbon nanotubes. These particles, generally encapsulated in the tubes, can be used in catalysis field for magnetic separation whether they exhibit soft ferromagnetic behavior.

Some of the authors have recently succeeded in the synthesis of a medium surface area silicon carbide nanotubes with different diameters. The research described in the present article concern the use of these SiC nanotubes as precursors for preparing CoFe₂O₄ decorated nanotubes and the characterization of such nanocomposites. The nanocomposites was prepared by incipient wetness impregnation of the dried support with a stoichiometric aqueous solution of the cobalt and iron nitrates. After drying, subsequent annealing treatment were performed under air in the temperature range 600 to 900°C. X-ray Diffraction and High Resolution Transmission Electron Microscopy reveal the presence of spinel nanoparticles at the surface of the tubes. Magnetic properties of the nanocomposites show in the magnetic field explored (up to 5T) that saturation magnetization is not observed neither at room temperature nor at 5 Kelvin. The nanometric character of the spinel particles is also confirmed by the coercive field (2T) observed at low temperature.

GG6.5

STRUCTURAL AND THERMAL STABILITY PROPERTIES OF MONOMETALLIC Co-HIDROTALCITE. Beatriz Zapata, Gerencia de Catalisis, Instituto Mexicano del Petróleo and Dpto. Química, Universidad Autónoma Metropolitana-I, MEXICO; Pedro Bosch, Dpto. Química, Universidad Autónoma Metropolitana-I, MEXICO; Miguel A. Valenzuela and Geolar Fetter, Laboratorio de Catalisis y Materiales, IPN-ESIQUIE, MEXICO.

A monometallic Co₆²⁺Co₂³⁺(OH)₁₆⁻(NO₃)₂.nH₂O hydrotalcite-like compound (HT) has been prepared by a careful precipitation of an aqueous solution of cobalt nitrate (II) in air atmosphere, followed by microwave irradiation. The sample was dried in vacuum at room temperature and calcined in nitrogen atmosphere at 400°C. For comparison purposes, one sample was prepared by a conventional procedure employing aging in the crystallization step. Cobalt nitrate (II) was also thermally treated as a reference. The characterization was carried out by XRD, DTA/TGA and nitrogen physisorption. Only the irradiated sample showed the HT-structure. In the conventional preparation Co₃O₄ was detected. The lowest thermal stability of the irradiated sample was about 200°C and a phase transition providing Co₃O₄ was observed in the interval 300-400°C. The specific surface areas (SSA) were around 48 m²/g in both irradiated and conventional

fresh samples. After heating at 400°C, a significant decrease in SSA was observed with the irradiated sample. Cobalt nitrate had the same behaviour as the conventional sample. It seems that the microwave irradiation weakens the interlayer Co²⁺-OH bonds and the thermal stability is decreased. Nevertheless, Co₃O₄ (400°C) showed the higher SSA if the conventional precipitation route was used (≈38 m²/g).

GG6.6

FORMATION AND MICROSTRUCTURE VARIATION OF CERUM OXIDE PREPARED BY THE HYDROTHERMAL PROCESS SYNTHESIS. Hsien-Cheng Wang and Chung-Hsin Lu, Department of Chemical Engineering, National Taiwan University, Taipei, TAIWAN ROC.

The demand of slurries utilized in chemical mechanical polishing becomes more imperative in recent years. Fine cerium oxide particles have attracted a great deal of attention because of its good physical and chemical properties during polishing. Cerium oxide is regarded as one of the most important compounds used in CMP among the rare earth family. In this study, cerium oxide has been fabricated by a newly developed hydrothermal process. The pure and well-crystallized cerium carbonate oxide powders were synthesized at as low as 100°C under hydrothermal treatment for less than one hour. Prolonging the heating time increased the particle size of cerium carbonate oxide. After calcination at elevated temperatures, orthorhombic cerium carbonate oxide completely transformed into cubic cerium oxide, and pure cerium oxide with fine particle size was successfully obtained. The transformation process was further examined by electron microscopy and thermal analysis. In comparison with the traditional processes, the pure cerium oxide was obtained at a relatively low temperature. With an increase in calcination temperature, the crystallite size of cerium oxide powders increased and the microstructures of powders also changed. Besides, the crystallinity of cerium oxide was significantly influenced by the calcination atmosphere. By controlling the oxygen atmosphere during calcination, the crystallinity of cerium oxide became increased. It probed out the fact that oxygen played a determinant role in the development in the crystal structure of cerium oxide.

GG6.7

SYNTHESIS AND STRUCTURE OF A MIXED IRON-COBALT PHOSPHATE FLOURIDE. Dan Wang, Ranbo Yu, Takahiro Takei, Nobuhiro Kumada and Nobukazu Kinomura, Institute of Inorganic Synthesis, Faculty of Engineering, Yamaguchi University, Kofu, JAPAN.

A mixed-metal phosphate flouride containing iron and cobalt in 1:1 ratio, FeCo(PO₄)F has been hydrothermally synthesized from the strating mixture of FeCl₃, CoCl₂, H₃PO₄ (85%), H₂H(CH₂)₃NH₂, NH₄F, and H₂O with the molar ratio of 1: 1: 2: 3: 4: 120 at 180°C for 3-5 days. The crystalline product has been characterized by means of single-crystal X-ray diffraction, thermal analysis, infrared spectroscopy, and scanning electron microscopy. The compound crystallized in the monoclinic system, space group Cc (no. 9), with lattice parameters of a = 12.968(5) Å, b=6.444(2) Å, c=9.818(4) Å, β=118.27(2)°, V=722.6(5) Å³. M = 228.75, Z = 8 (R=0.032, R_w=0.033). Along the c axis of the structure, corner-sharing FeO₄F₂ octahedra and Co(2)O₄F trigonal pyramids connect each other to form chains via alternative corner-share and edge-share, and in the latter, flouride atom is involved. The chains of Fe and Co are connected through oxygen and flouride bridges, as well as phosphate groups to give a three-dimensional framework structure.

GG6.8

ANALYSIS OF TIME RESOLVED LIFETIME EMISSION DECAY DATA FOR AMORPHOUS VANADIUM XEROGEL AND CRYSTALLINE VANADIUM SILICALITE (VS-1). Donald F. Carter, Albert E. Stiegman, Dept of Chemistry, Florida State University, FL.

The time-resolved photoemission properties of vanadium(V) sites, distributed in amorphous silica xerogels and in crystalline silicate zeolitic matrices, are reported. The basic structure of the vanadium site in both of the matrices is of pseudotetrahedral geometry (C3v) with a short terminal V=O bond and three equivalent Si-O-V linkages. Due to this orbital parentage the photoemission processes of the vanadium are acutely sensitive to the coordination environment. In the amorphous xerogel materials a broad distribution of sites are occupied. This can be detected by the observation of non-mono-exponential emission decays that are best fit using a Gaussian distribution of the logarithm of the lifetimes. In the case of the vanadia-silicalite materials, discrete crystallographically defined sites are occupied. This is evidenced by the lifetime data which cannot be analyzed by a continuous distribution.

GG6.9

SYNTHESIS OF LAMELLAR MESOSTRUCTURED ZINC OXIDE BY HOMOGENEOUS PRECIPITATION METHOD. Atsushi

Hozumi, Masahiko Inagaki, Yoshiyuki Yokogawa, Tetsuya Kameyama, National Industrial Research Institute of Nagoya, Ceramics Technology Department, Bioceramics Laboratory, Nagoya, JAPAN.

The fabrication of mesostructured materials by using supramolecular assemblies of surfactant molecules as templates has attracted attention and been applied to the synthesis of mesoporous silica (MPS). Although extensive researches on MPS have been reported in the literature, studies on the other mesostructured materials, that is, metal oxides have not been published so much. In this study, we report a simple procedure for the synthesis of mesostructured zinc oxide. This process is based on the combination of the anionic surfactant molecules and the inorganic metal species during homogeneous precipitation reaction. Mesostructured zinc oxide was synthesized in a solution prepared as follows. 1-hexadecanesulfonic acid sodium salt (HDSASS) was added in H₂O adjusting its pH of 2 by adding HNO₃. The mixture was stirred for about 10 min at 338 K until the HDSASS powder completely dissolved. Zinc nitrate hexahydrate (ZNH) and hexamethylenetetramine (HMT) were then added to the solution and mixed with stirring for about 5 min at 338 K. The final reactant molar ratio of ZNH/HDSASS/HMTA/H₂O was 1 : 0.05~1 : 8 : 1000. The solution was then heated in an oven maintained at 368 K for 24 h. After complete reaction, the powdery precipitates were filtered and washed with Milli Q water. Finally, they were lyophilized for 24 h and placed in a glass container. In order to eliminate the organic molecules from the as-synthesized precipitates, the samples were treated thermally in a furnace maintained at 573 K for 1h in air. In typical XRD patterns of as-synthesized precipitates, several ordered (00l) reflection peaks, indicating that the samples formed well-ordered lamellar mesostructures, were detected. Furthermore, the high-angle reflection peaks corresponding to the crystal zinc oxide phase were simultaneously observed. However, these (00l) reflection peaks disappeared when the samples were calcined. The mesostructured zinc oxide was found to be thermally unstable.

GG6.10

NANOSTRUCTURED TiN OXIDE AND Pt-DOPED TiN OXIDE STUDIED AS THIN FILMS BY ELECTRON PARAMAGNETIC RESONANCE (EPR) AND X-RAY PHOTOELECTRON (XPS) SPECTROSCOPIES. Franca Morazzoni, Carmen Canevali, Norberto Chiodini, Claudio Maria Mari, Riccardo Ruffo, Roberto Scotti, Alessia Zago, Univ. Milano-Bicocca, Dept. of Materials Science, Milano, ITALY; Lidia Armelao, Eugenio Tondello, CNR-CSSRCC, Univ. Padova, Dept. of Inorganic Chemistry, Padova, ITALY; Elza Bontempi, Laura Eleonora Depero, Univ. Brescia, Dept. of Mechanical Engineering, Brescia, ITALY.

The surface reactivity of SnO₂ towards reducing and oxidizing gases is responsible for the gas sensing properties of this semiconductor oxide. According to the currently accepted mechanism of gas sensing, strong increases in sensitivity are expected in the case of oxide materials with very small grain size (< 6 nm). Thus the use of nanosized materials seemed a powerful tool to obtain highly sensitive gas sensor devices. We were able to obtain nanostructured (particle size 3-6 nm) SnO₂ thin films by gelation of an alkoxide tin precursor. The addition of small amounts of a noble metal was commonly used to increase sensor response. Our recent studies on transition metal-doped SnO₂ demonstrated that the more intimate the semiconductor-metal contact the easier the electronic exchange at the semiconductor-gas interphase and the higher the electrical sensitivity of the material. Nanostructured (particle size 3-6 nm) platinum-doped SnO₂, with the noble metal substituting Sn should give the best intimate metal-semiconductor contact. We were able to obtain thin films of platinum-doped SnO₂ where the noble metal substituted tin in SnO₂ lattice by simultaneous gelation of an alkoxide tin precursor, tetra(tert-butoxy)tin(IV), and a noble metal precursor, bis(acetylacetonato) platinum(II). The investigation of SnO₂ defects, of the metal electronic state and of the surface chemisorbed species plays a fundamental role in understanding the gas sensing mechanism. SnO₂ and platinum-doped SnO₂ thin films here described displayed a great amount of defects and of chemisorbed species; moreover all the noble metal centers are involved in redox processes. This allowed an in situ EPR (first time on thin films as prepared, to the best of our knowledge) and XPS investigation of the interaction with reducing (CO) and oxidizing (air) atmospheres, and the results were compared with the electric measurements performed on the same films.

GG6.11

THIN SUPPORTED DENSE PEROVSKITE MEMBRANES BY PULSED LASER DEPOSITION. L.M. van der Haar, H.J.M. Bouwmeester, H. Verweij, Univ of Twente, Dept of Chemical Technology, E.A.F. Span, D.H.A. Blank, H. Rogalla, Univ of Twente, Dept of Applied Physics, Enschede, NETHERLANDS.

Cobalt based perovskite-type oxides are of interest as potential oxygen separation membranes. Under operating conditions, usually above 700°C, oxygen ions are transported through the membrane by a

vacancy mechanism. Charge compensation occurs by a simultaneous flow of electronic charge carriers. The driving force for transport is a difference in the oxygen partial pressure applied across the membrane. For $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ perovskites high oxygen fluxes have been reported, increasing with Sr content, which A-site substituent serves the creation of oxygen vacancies in the ABO_3 perovskite lattice. A promising approach to maximise the oxygen fluxes through these membranes is the reduction of the membrane thickness to the μm -range. These membranes need to be supported to provide sufficient mechanical strength. An attractive method for depositing thin films is Pulsed Laser Deposition (PLD). Advantages of this technique include stoichiometric material transfer in conjunction with high deposition rates. In this study, dense $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ layers were deposited by PLD on 30% porous $\alpha\text{-Al}_2\text{O}_3$ and $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ substrates. Their properties were investigated with SEM, XRD and oxygen permeation measurements. On $\alpha\text{-Al}_2\text{O}_3$ supports, dense amorphous layers were obtained at room temperature. Due to different thermal expansion behaviour, the layers fractured during heating to 650°C . This problem was not encountered when $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ supports were used. Dense, $5\mu\text{m}$ thick crystalline layers were deposited on these supports at 690°C . At 1000°C these membranes exhibit a oxygen flux of 1.4×10^{-6} mole $\text{cm}^{-2} \text{ s}^{-1}$, which is substantially higher than the flux measured under identical conditions for a non-supported 0.5 mm thick membrane of the same composition. Oxygen permeation data is presented and discussed in terms of the three possible rate-limiting processes: bulk diffusion, oxygen surface exchange and mass transfer limitation due to the support.

GG6.12

A NEW THREE-DIMENSIONAL LANTHANIDE FRAMEWORK CONSTRUCTED BY OXALATE ACID AND 3,5-PYRIDINEDICARBOXYLIC ACID. Michael A. Lawandy, Long Pan, Xiaoying Huang, Jing Li, Department of Chemistry, Rutgers University, Camden, NJ.

Hydrothermal reactions of rare-earth metal nitrates with oxalic acid and 3,5-pyridinedicarboxylic acid (H_2pddc) in triethylamine/water solutions have yielded isostructural polymers with the general formula: $[\text{Ln}(\text{pddc})(\text{C}_2\text{O}_4)_{1/2}(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$. [$\text{Ln} = \text{La}(\mathbf{1})$, $\text{Pr}(\mathbf{2})$, $\text{Nd}(\mathbf{3})$, $\text{Eu}(\mathbf{4})$ and $\text{Er}(\mathbf{5})$]. These compounds crystallize in monoclinic system, space group $P2_1/n$, $Z = 4$, with only slight variations in their unit cell parameters: $\mathbf{1}$ $a = 7.747(2)$, $b = 9.954(2)$, $c = 15.134(3) \text{ \AA}$, $\beta = 98.64(3)^\circ$, $V = 1153.8(4) \text{ \AA}^3$; $\mathbf{2}$ $a = 7.688(2)$, $b = 9.897(2)$, $c = 14.955(3) \text{ \AA}$, $\beta = 98.43(3)^\circ$, $V = 1125.6(4) \text{ \AA}^3$; $\mathbf{3}$ $a = 7.707(2)$, $b = 9.895(2)$, $c = 15.006(3) \text{ \AA}$, $\beta = 98.54(3)^\circ$, $V = 1131.7(4) \text{ \AA}^3$; $\mathbf{4}$ $a = 7.638(2)$, $b = 9.842(2)$, $c = 14.809(3) \text{ \AA}$, $\beta = 98.42(3)^\circ$, $V = 1101.2(4) \text{ \AA}^3$; $\mathbf{5}$ $a = 7.573(2)$, $b = 9.761(2)$, $c = 14.630(3) \text{ \AA}$, $\beta = 98.10(3)^\circ$, $V = 1070.7(4) \text{ \AA}^3$. The structure of these compounds composes of 2D $\text{Ln}(\text{pddc})$ layers that are interconnected by chelating oxalate. Within the layer, each rare-earth metal forms a monodentate bond with each of the four pddc groups. The metal centers in the neighboring layers are bridged through μ_4 -oxalate, resulting in a three-dimensional framework. The remaining two sites around the eight-coordinate Ln are occupied by water molecules. All five compounds exhibit paramagnetic behavior.

GG6.13

NEW BIMETALLIC COORDINATION POLYMER NETWORKS SYNTHESIZED USING METAL CONTAINING BUILDING BLOCKS. Yu-Bin Dong, Mark D. Smith, Hans-Conrad zur Loye, University of South Carolina, Department of Chemistry and Biochemistry, Columbia, SC.

In an effort to create extended bimetallic coordination polymer networks, we have utilized a class of metal-containing ligands obtained by the reaction of 2-pyrazinecarboxylate or 2-methylpyrazine-5-carboxylate with a series of metal salts ($\text{M} = \text{Cu}(\text{II})$, $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Fe}(\text{II})$, $\text{Sr}(\text{II})$, $\text{Mn}(\text{II})$, $\text{La}(\text{III})$, $\text{Cr}(\text{III})$). In these ligands, the metal lies in a chelating coordination environment which effectively prevents metal ion exchange when they are used to coordinate to other metal centers. More importantly, these ligands contain not only a transition metal center but also retain free coordination sites, which have been used to prepare several new mixed-metal (Ag-Cu , Cu-Hg , Ni-Hg , Co-Hg , Zn-Hg) coordination polymer networks. The synthesis and structures of several mixed metal systems, including a novel, open, non-interpenetrating $\text{Cu}(\text{II})\text{-Hg}(\text{II})$ mixed-metal cuboid framework encapsulating nearly linear HgI_2 guest molecules, will be described.

GG6.14

PREPARATION OF MESOPHASE CERIUM(IV) OXIDES VIA SURFACTANT TEMPLATING ROUTE. Masahiko Inagaki, Atsushi Hozumi, Yoshiyuki Yokogawa, Tetsuya Kameyama, National Industrial Research Institute of Nagoya, Kita-ku, Nagoya, JAPAN.

Mesoporous materials based on transition metal oxides are promising as highly functional materials, such as, electrically, magnetically or optically functional host materials, as well as catalysts and molecular sieves. Cerium(IV) oxide (ceria) and trivalent or divalent cation doped ceria have capabilities of redox reaction and oxygen ion conducting. If such ceria can be synthesized as mesoporous solids, these materials might find applications in gas sensor, fuel cells and high-surface area redox catalysts. Here, we report on the first synthesis of a mesophase ceria via hexamethylenetetramine (HMT) homogeneous precipitation method. Cerium(III) nitrate (CeN), templating agent, HMT and water were mixed in a molar ratio of 1: 0.1-2: 1-15: 100-1000. 1-Hexadecanesulfonic acid sodium salt (HDSASS) was used as templating agent. HDSASS was dissolved in H_2O at 65°C , and then, CeN and HMT added to the HDSASS solution and then stirred for about 30 min at 65°C . The mixed solution was placed in a TeflonTM vessel which sealed with a cap and was heated in an oven maintained at a temperature $65\text{-}95^\circ\text{C}$ and kept at that temperature for 10-40 h. The resulting dispersion were filtered through a $1 \mu\text{m}$ filter. The precipitates were washed with water a few times then lyophilized. In order to remove template agent, as-prepared powders were calcined at 350°C . The low-angle XRD patterns of the as-prepared powders showed the peaks at $d=4.1$, 2.1 and 1.4 nm which attributable to the (001), (002) and (003) of a lamella phase. The wide-range ($2\theta=10\text{-}70^\circ$) XRD patterns also exhibited the reflection peaks of CeO_2 with a fluorite structure. However, low-angle reflection peaks disappeared in the calcined specimens. This indicates that the mesostructured CeO_2 which prepared at present study is thermally unstable.

GG6.15

ELECTRONIC AND OPTICAL STUDIES OF COEXISTING 5 AND 6 ATOM RINGS IN TETRAHEDRAL a-C. R.M. Valladares, A.G. Calles, UNAM-Facultad de Ciencias, Depto. de Física, México-DF, MEXICO; M.A. Mc Nelis, México-DF, MEXICO; Ariel A. Valladares, UNAM-Instituto de Investigaciones en Materiales, México-DF, MEXICO.

Finding clathrate structures in crystalline carbon has been an unsuccessful endeavour and the rigidity of the carbon-carbon bonds have been invoked as the responsible factor in these infructuous attempts. However, in the amorphous counterpart it may be possible to create clathrate-like structures since the non-crystallinity could allow the formation of less energetic structures that contain 5 and 6 atom rings. In this work we further the study of the amorphous and crystalline clusters used elsewhere¹. The amorphous clusters have a total of 57 carbon atoms plus 52 hydrogens to saturate the outermost dangling bonds and have planar 5-atom rings and boat-like 6-atom rings as found in the amorphous bulk. The crystalline clusters contain 59 carbon atoms plus 60 hydrogen saturators with *only* chair-like 6-atom rings, like in the tetrahedral crystal (diamond structure). We report *ab initio* calculations, using the *DMol* code, of the total energy, the electronic (density of states) structure and the optical properties of the two types of clusters, with and without relaxation of the structures, in order to see the effect of the type of atom rings found in the amorphous structures compared to those found in the crystal.¹ Ariel A. Valladares, Alexander Valladares, Renela M. Valladares and Mary A. Mc Nelis, *J. Non-Cryst. Solids*, **92** (1998) 209-221.

GG6.16

MODIFIED SOL-GEL SYNTHESIS OF VANADIUM OXIDE NANOCOMPOSITES CONTAINING SURFACTANT IONS, AND THE PARTIAL REMOVAL OF THESE SURFACTANTS. Arthur Doble, Peter Zavalij and M. Stanley Whittingham, Institute for Materials Research and Department of Chemistry, State University of New York at Binghamton, Binghamton, NY.

Recently, there has been much interest in creating new layered transition metal oxides. Vanadium oxides may be used as sorbents, catalysts, and cathodes. The modified sol-gel technique allows for some control towards the final structure of the compound. Using this technique, a new layered product has been synthesized. $\text{VO}_2\text{PO}_4\text{C}_{12}\text{H}_{25}\text{H}_2\text{O}_n$ is the general formula of the layered product with a layer spacing of 40 \AA . After removal of the organic, the compound converts to a hexagonal phase. The compounds were analyzed using FTIR, TGA, SEM, and NMR. Extensive ^{51}V NMR studies were done on the compounds. The synthesis, composition, and structure of these compounds will be discussed. This work was supported the the National Science Foundation.

GG6.17

A NOVEL 3D MIXED-METAL COORDINATION POLYMER CONSISTING OF INCLINED INTERPENETRATING NETWORKS. Long Pan, Nancy Ching, Xiaoying Huang and Jing Li, Department of Chemistry, Rutgers University, Camden, NJ.

The hydrothermal reactions of $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{K}_2\text{Cr}_2\text{O}_7$ with 4,4'-bpy (4,4'-bipyridine) have resulted in a new coordination polymer with the formula $[\text{Cu}(4,4'\text{-bpy})(\text{Cr}_2\text{O}_7)] \cdot \text{H}_2\text{O}$. Crystal data for the

structure are as follows: monoclinic crystal system, $P2_1/c$, $a = 8.176(2)$ Å, $b = 14.718(3)$ Å, $c = 15.952(3)$ Å, $\beta = 101.60(3)^\circ$, $V = 1880.4(7)$ Å³, $Z = 4$. The title compound contains a three-dimensional structure formed by interpenetrating networks, each having a "brick wall" pattern with a cross-section of ca 11.1×22.0 Å. Every hexagon ring in a net has two inclined (6,3) nets passing through it. The shortest Cr-Cu distance is 3.545 Å. We will discuss the synthesis, crystal structure characterization and selected properties of this complex.

GG6.18

A STRUCTURAL ANALYSIS METHOD FOR GRAPHITE INTERCALATION COMPOUNDS. Tatsuo Nakazawa, Kyoichi Oshida, Nagano Nat'l Coll of Tech, Dept of Electronics and Computer Sci, Nagano, JAPAN; Takashi Miyazaki, Nagano Nat'l Coll of Tech, Dept of Electrical Engineering, Nagano, JAPAN; Morinobu Endo, Shinshu Univ, Faculty of Engineering, Nagano, JAPAN; Mildred S. Dresselhaus, Massachusetts Inst of Tech, Dept of Physics, Cambridge, MA.

Well-staged acceptor graphite intercalation compounds (GICs) exhibit many useful electrical properties, such as a large magnitude conductivity with a metallic temperature-dependence, and expect to apply for the electrical material. The electrical and mechanical properties of GICs is thought to strongly depend on its staging structure. In order to analyzing the micro-structure of materials, the transmission electron microscope (TEM) observation is one of the most useful techniques because it gives very detailed information about the nature of the lattice structure and the anomalies found in a very small sample. In this study, a method of high-resolution TEM observation combined with digitized image analysis is used to get more quantitative evaluation of the stage structure in GICs. Analysis of the microstructure of GICs is largely enhanced by using this technique. GICs can be synthesized in the fiber matrix of vapor grown carbon fibers (VGCFs) which consist of a honeycomb network of concentrically stacked layers of graphene planes around the fiber axis. While TEM observations of well-staged acceptor GICs with CuCl_2 intercalants have revealed the stage structure of GICs, these observations have not yielded much quantitative information. Digitized image analysis is applied to promote the quantitative interpretation of the TEM images and to clarify the structure of GICs. TEM images of precursor VGCFs, heat-treated VGCFs, and CuCl_2 GICs are evaluated by means of the image analysis by a 2-dimensional (2D) fast Fourier transform (FFT). It has been found in this study that the lattice images of CuCl_2 GICs consist of different frequency images corresponding to specific frequencies. The stage structure of CuCl_2 GICs is investigated by analyzing the reconstruction of the TEM image.

GG6.19

A NOVEL ROUTE FOR THE SYNTHESIS OF $\text{LiAl}_x\text{Co}_{1-x}\text{O}_2$ AND THEIR STRUCTURAL PROPERTIES. M.S. Tomar, A. Hidalgo, Physics Department, University of Puerto Rico, Mayaguez, PR; S. Filippov, R.S. Katiyar, University of Puerto Rico, San Juan, PR; K.A. Kuenhold, University of Tulsa, Tulsa, OK.

LiCoO_2 is an important cathode material for rechargeable batteries. $\text{LiAl}_x\text{Co}_{1-x}\text{O}_2$ is known to enhance the intercalation voltage of cathode. We have developed a reliable and less expensive method to prepare $\text{LiAl}_x\text{Co}_{1-x}\text{O}_2$, where simple salts of the constituent elements with organic solvents are used for the synthesis. Thin films were deposited by spin coating. X-ray diffraction, impedance spectroscopy, and Raman spectroscopy were used for structural characterization of thin film and bulk material for various compositions. Thin films can be deposited on stainless steel substrate at annealing temperature below 650° . Work supported by DOE-EPSCoR grant.

GG6.20

FIRST OBSERVATION OF POLYTYPES IN RARE-EARTH BORON-RICH BORO-CARBO-NITRIDES. Fuxian Zhang, Andreas Leithe-Jasper, Takaho Tanaka, National Institute for Research in Inorganic Materials, Tsukuba, Ibaraki, JAPAN.

We firstly found polytypes in quarternary rare-earth boron-rich boro-carbo-nitrides with nominal compositions of $\text{REB}_{15.5}\text{CN}$, $\text{REB}_{22}\text{C}_2\text{N}$, $\text{REB}_{28.5}\text{C}_4$ (RE=Sc, Y, and heavy rare-earth elements) whose crystal structures are composed of a three dimensional network based on interconnected boron icosahedra and octahedra and have rhombohedral symmetries of 9R, 12R and 15R, respectively. Crystal structure of the first one was analysed using single crystal data and for the latter two structure models were given based on both powder X-ray diffraction and electron diffraction data and crystal chemical consideration referring the first one's crystal structure. Those crystal structures have a similarity with the B_4C crystal structure which is based on a rhombohedral packing of B_{12} icosahedra and three atom C-B-C chains lie along the three-fold axis. The B_4C crystal structure

can be understood as a stacking of icosahedra net layers along c-axis. In the $\text{REB}_{15.5}\text{CN}$, $\text{REB}_{22}\text{C}_2\text{N}$ and $\text{REB}_{28.5}\text{C}_4$ structures every third, fourth or fifth icosahedra layer of the B_4C structure is replaced by a B_6 octahedra net layer, respectively, which is the origin of the polytype. Because of size difference of the icosahedra and the octahedra the replacement creates interstitial sites where rare-earth element atoms are allocated. The C-B-C chains still lie along three fold axis and N atoms play a role to bridge B_{12} icosahedra.

GG6.21

A NOVEL BORON-RICH SCANDIUM BORO-CARBO-SILICIDE; $\text{ScB}_{15}\text{C}_{0.8}\text{Si}_{0.2}$; FLOATING ZONE CRYSTAL GROWTH AND STRUCTURE ANALYSIS. Takaho Tanaka, Akira Sato, National Institute for Research in Inorganic Materials, Tsukuba, Ibaraki, JAPAN.

In our previous paper [1] we have reported the existence of a new scandium boron-rich boro-carbide, $\text{ScB}_{15}\text{C}_{0.8}$ which decomposes at high temperatures without melting, although we could not index the powder diffraction result. We found that small amount of Si addition could allow $\text{ScB}_{15}\text{C}_{0.8}$ to coexist with a liquidus phase, which makes the floating zone crystal growth possible as a novel compound of an isostructural $\text{ScB}_{15}\text{C}_{0.8}\text{Si}_{0.2}$. $\text{ScB}_{15}\text{C}_{0.8}\text{Si}_{0.2}$ has a face-centered cubic structure with lattice constant $a=2.0321$ nm and space group of $P4_3m$. It was found that the crystal structure solved using single crystal data is a new structure type of boron-rich borides, where there are three Sc sites, two Si sites and twenty-two B sites in which carbon was tentatively assigned to locate at bridging sites by replacing boron atoms. Boron framework is constructed by three B_{12} icosahedra and one B_{10} polyhedron which is a new type of boron polyhedron. Sc and Si are allocated into interstitial sites of the boron framework. [1] Y. Shi, A. Leithe-Jasper and T. Tanaka, J. Solid State Chem., 148 (1999) 250.

GG6.22

REDUCIBILITY STUDY OF THE OF $\text{LaM}_x\text{Fe}_{1-x}\text{O}_3$ (M : Ni, Co) PEROVSKITE. C. Estournés, Groupe des Matériaux Inorganiques, Institut de Physique et Chimie des Matériaux de Strasbourg (UMR7504 CNRS-ULP-ECPM) Strasbourg, FRANCE; H. Provendier, L. Bedel, C. Petit, A.C. Roger, A. Kienemann, Laboratoire de la Réactivité Catalytique, des Surfaces et Interfaces (UMR7515 CNRS-ULP-ECPM) Strasbourg, FRANCE.

Solid solutions of $\text{LaM}_x\text{Fe}_{1-x}\text{O}_3$ (with M= Ni and Co) have been used in Fischer-Tropsch reaction and partial oxidation of methane. In both catalytic reactions, the active part is reported to be reduced metal particles; the size and nature of which give large difference in the distribution of products. Oxide structures have been made to control the final catalysts by its reduction under the used gases. An understanding of this important step has been made by additional studies. Therefore, reducibility of both solid solutions have been studied by x-ray diffraction (XRD), iron Mössbauer spectrometry, in situ magnetic measurements and temperature programmed reduction (TPR), in order to point out the mechanisms occurring during the catalytic reactions.

In nickel system, TPR measurements show two reduction peaks. After total reduction, all catalysts exhibit ferromagnetic behavior at room temperature. In situ magnetization in 1 Tesla on heating the sample under reducing atmosphere shows no significant change for temperatures up to 1100K. On cooling only one magnetic transition is observed for each sample indicating that only one Curie temperature is observed. These Curie temperatures are in between those known for bulk nickel and iron and decreases with the initial nickel content of the perovskite. This indicates that nickel is reduced first and induces the reduction of iron, leading to the formation of an alloy.

In cobalt system, TPR measurements reveal again two reduction areas. However, in-situ magnetization on heating the sample shows a sharp increase of the magnetization only for $x=0.25$, 0.40 and 1 corresponding to the formation of metallic cobalt nanoparticles. All other materials present only one increase of the magnetization for temperatures similar to those observed for the second reduction in TPR corresponding to the formation of CoFe alloys. All catalytic reactions studies are in accordance with the reduction process of the materials.

GG6.23

EXTRACTION OF NANO SIZE PORE BOUNDARIES OF ACTIVATED CARBON BY IMAGE ANALYSIS OF TEM PICTURES. Takashi Miyazaki, Nagano National College of Technology, Dept of Electrical Engineering, Nagano-shi, JAPAN; Kyoichi Oshida, Tatsuo Nakazawa, Nagano National College of Technology, Dept of Electronics Information Engineering, Nagano-shi, JAPAN; Morinobu Endo, Shinshu University, Dept of Electrical Engineering, Nagano-shi, JAPAN.

Activated carbons are used widely as absorbent materials and are expected to be useful as new electrical materials, for their very large

specific surface areas. In order to examine detailed information, such as an adsorption property, the detail configuration of pore in the material needs to be analyzed. It is impossible to observe the pore directly, of course, the analization is usually carried out for the pictures based on the image of a transmission electron microscope(TEM). However, the quantitative validation of pore boundaries is difficult, since TEM image photographs of the activated carbon has the ambiguous shade gradient in the boundary part of pores. In this report, we will show the application of the idea of fuzzy template to the parsing of TEM images, and the extraction of the boundaries. The picture which include ambiguous light and shade image is considered to be a fuzzy set, and the boundary extraction is performed from the idea of the 'interior' and the 'exterior' obtained on the basis of the fuzzy template drawn from the finite fuzzy topology. This method is applied to the TEM images of activated carbon. The activated carbon materials are thought to have the complicated architecture with various sizes of pores, from the analyzed results. Since it should be supposed that it is hard to detect small pores by means of well known gas-adsorption method, the method proposed in this report is more suitable to analyze the pore architecture of the active carbon in detail.

GG6.24

NOBEL CONVERSION OF AN AURIVILLIUS PHASE $\text{Bi}_2\text{O}_2[\text{SrNaNb}_3\text{O}_{10}]$ INTO THE PROTONATED FORM OF THE LAYERED PEROVSKITE BY THE ACID LEACHING OF THE BISMUTH OXIDE SHEET. Yoshiyuki Sugahara and Masashi Shirata, Waseda Univ, Dept of Applied Chemistry, School of Science & Engineering, JAPAN; Wataru Sugimoto, Shinshu Univ, Dept of Fine Materials Engineering, Faculty of Textile Science & Technology, Nagano JAPAN.

It is well known that some layered perovskites ($\text{M}[\text{A}_{n-1}\text{B}_n\text{O}_{3n1}]$ and $\text{M}_2[\text{A}_{n-1}\text{B}_n\text{O}_{3n1}]$; $\text{M}=\text{Rb, K, etc.}$) undergo ion-exchange reactions, and protonated forms ($\text{H}[\text{A}_{n-1}\text{B}_n\text{O}_{3n1}]$ and $\text{H}_2[\text{A}_{n-1}\text{B}_n\text{O}_{3n1}]$) can be obtained by acid treatment. Aurivillius phases ($\text{Bi}_2\text{O}_2[\text{A}_{n-1}\text{B}_n\text{O}_{3n1}]$) are known to be another type of layered perovskites, and the bismuth oxide sheets and perovskite-like slabs are interstratified in their structures. In this paper, the bismuth oxide sheet in an Aurivillius phase ($\text{Bi}_2\text{O}_2[\text{SrNaNb}_3\text{O}_{10}]$) was selectively leached by acid treatment to give a corresponding protonated form. X-ray diffraction (XRD) and transmission electron microscopy (TEM) revealed that the basal spacing decreases after the acid treatment. On the contrary, the a axis was unchanged after the acid-treatment, which indicates the retention of the perovskite-like slab structure during the acid treatment. Inductively-coupled plasma (ICP) emission spectroscopy and thermogravimetry (TG) showed that the composition of the acid-treated product was $\text{H}_{1.8}[\text{Bi}_{0.21}\text{Sr}_{0.80}\text{Na}_{0.95}\text{Nb}_3\text{O}_{10}]$. The acid-treated product can accommodate n -alkylamines, which supports the layered structure of the acid-treated product.

GG6.25

CATION EXCHANGE MECHANISM AND SELECTIVITY ON MNO_2S WITH THE 2×2 TYPE TUNNEL STRUCTURE. Masamichi Tsuji, Tokyo Institute of Technology, Research Center for Carbon Recycling and Utilization, Tokyo, JAPAN; Hirofumi Kanoh, Kenta Ooi, Shikoku National Industrial Research Institute, Takamatsu, JAPAN.

Hydrous manganese dioxides synthesized usually contain cationic impurities coming from their starting materials in their crystal structure. These can be removed by acid-treatment to form the acid or H form. It can be referred to as manganic acids and its cation-exchanged form may be called manganic acid salts. They show different cation exchange selectivity, depending on the mode of preparation and the crystal structure. A manganic acid with the 2×2 type tunnel structure is one of the synthetic inorganic ion exchange materials that show interesting alkali cation exchange selectivities. However, for better and deeper understanding the cation exchange properties of these manganic acids, further study is needed on their cation exchange mechanism and selectivity. This paper will present cation exchange mechanism and selectivity of several manganic acids with the 2×2 type tunnel structure synthesized through different modes of preparation: starting materials, synthesis temperatures, subsequent chemical treatment, etc.

GG6.26

DIAMETER SELECTIVE SYNTHESIS OF SEMICONDUCTOR NANOWIRES. Mark S. Gudiksen and Charles M. Lieber, Harvard University, Department of Chemistry and Chemical Biology, Cambridge, MA.

Recent interest in low-dimensional semiconductor materials has been motivated by the push for miniaturization of electronic and optoelectronic devices and a need to understand the fundamentals of nanoscale chemistry and physics. In particular, one-dimensional (1D)

systems are exciting from both fundamental and applied viewpoints. Fascinating physical phenomena, such as Luttinger liquid behavior, and numerous applications from interconnects to scanning probe microscopy tips, require high-quality, well-defined 1D nanostructures. Experimental progress in the field of 1D nanostructures has often been limited by our ability to create new materials in this size regime with controlled size, structure, and composition. In pursuit of this end, nearly monodisperse samples of single crystalline GaP nanowires have been synthesized with diameters of 10, 20, and 30 nm and lengths greater than $10\ \mu\text{m}$ by exploiting well-defined gold colloids as catalysts in our laser catalytic growth (LCG) process. In this method, Ga and P reactants are generated by laser ablation of solid GaP, and subsequently are directed into a nanowire structure by the gold nanocluster catalyst. Transmission electron microscopy (TEM) analysis of the nanowires prepared in this way demonstrates that the distribution of wire diameters is defined by the colloid catalysts. High-resolution TEM shows that the wires are single crystal zinc blende with a $[111]$ growth direction, and energy dispersive X-ray analysis (EDAX) confirms that the nanowire composition is stoichiometric GaP. The use of monodisperse nanocluster catalysts combined with the LCG method will enable the growth of virtually any semiconductor nanowire with well-defined, controlled diameter, and thus opens up many opportunities for assembly of functional devices. Recent results in applying this synthesis technique to the fabrication of single nanowire heterostructures will also be discussed.

GG6.27

ELECTRONIC STRUCTURE AND PHOTOCHEMICAL PROCESSES OF HIGH-VALENT EARLY TRANSITION METAL SITES IN SILICA XEROGEL MATRICES. A.E. Stiegman, Department of Chemistry, Florida State University, Tallahassee, FL.

Metal-silica xerogels containing early, high-valent transition metals (groups 4, 5 and 6), dispersed the microporous matrix are all highly luminescent, with very long-lived excited states. Since all of the metals are in their highest oxidation state the excited state necessarily arises from an oxo-to-metal charge-transfer transition. The nature of this excited-state has been probed for several of these materials by electronic (absorption and emission) and vibrational spectroscopy. This has led to a detailed assignment of the spectroscopic transitions and a general understanding of the nature of the long-lived emissive state. In addition, these materials all undergo novel photochemical reactions including atom abstraction on substrates such as saturated hydrocarbons the initiation of vinyl polymerization. This latter reaction has led to the fabrication of organic-inorganic nanophase materials. The observed photochemistry can be rationalized based on the electronic structure of the metal sites.

GG6.28

A NEW MICROPOROUS SILICATE WITH 12-RING CHANNELS. Jacques Plévert, The University of Tokyo, Dept of Chemical System Engineering, Tokyo, JAPAN; Yoshihiro Kubota, Takahisa Honda, Yoshihiro Sugi, Gifu University, Dept of Chemistry, Gifu, JAPAN.

A new crystalline microporous silicate was synthesized under hydrothermal conditions in the presence of a newly designed organic compound acting as structure-directing agent. The solid tends to come along with another microporous phase ZSM-12. The structure of the novel molecular sieve was determined from synchrotron powder diffraction data of a calcined sample containing both phases. The new solid is characterized by a system of one-dimensional 12-membered ring channels running parallel. The framework of the new structure is particularly interesting as it is closely related to the framework of both zeolites mordenite and ZSM-12. The new solid exhibits the same channel net as ZSM-12 and shows the same projection of the framework along the pores as mordenite. The pore opening is 0.6-0.7 nm in free diameter, making the new material potentially interesting for catalysis as it is classified as a large pore molecular sieve and shows thermal and hydrothermal stabilities.

GG6.29

DEPOSITION AND CHARACTERIZATION OF YAG FILMS AND POWDERS BY PLASMA SPRAY SYNTHESIS. P. Sujatha Devi, J. Margolis, S. Sampath, H. Herman, SUNY at Stony Brook, Center for Thermal Spray Research, Dept. of Materials Science and Engineering; H. Liu, C.P. Grey, SUNY at Stony Brook, Dept. of Chemistry; J.B. Parise, SUNY at Stony Brook, Dept. of Geosciences and Center for High Pressure Research, Stony Brook, NY.

Plasma /thermal spraying of metals, ceramics and composites is a well-established technology for the deposition of coatings on various substrates. However, thermal spraying of liquid feed-stocks is a relatively new and emerging method to produce ceramic coatings and powders. Yttrium Aluminum Garnet ($\text{Y}_3\text{Al}_5\text{O}_{12}$ -YAG) materials have been widely studied for the application in fluorescent lighting and solid-state lasers. To explore the possibility of thermal spraying of liquid feed stocks, to develop ceramic powders and coatings, attempts

were made to develop YAG from sols and suspensions considering it as a representative model compound. YAG powders and coatings were developed for the first time by a novel solution plasma spraying technique using an RF plasma of around 40 kW power and a helium/argon plasma radial gas mixture. Precursor sol of YAG is prepared by careful control of the composition and pH of a mixture of boehmite sol and yttrium nitrate in aqueous media. Grit blasted steel substrates were used for making coatings of desired thickness. The thickness of the coatings depended on the concentration of the sol as well as the number of cycles of liquid injection. The synthesized coatings were characterized by powder XRD, SEM and ^{27}Al MAS NMR techniques. X-ray diffraction of the as sprayed coating confirms the presence of YAG as the major phase, with a very small amount of YAlO_3 (YAP) as the second phase. ^{27}Al MAS NMR indicates some disorder in the developed YAG phase. The phase development and microstructure will be presented in detail. Future work will focus on the synthesis of a variety of inorganic materials by this process.

GG6.30

INVESTIGATION AND CHARACTERIZATION OF THE PHASE DEVELOPMENT AND REACTION KINETICS DURING THE FORMATION OF REACTIVE INFILTRATED ALUMINA ALUMINID COMPOSITES. U. Wassmuth, R. Guenther, A. Bartels, R. Bormann, Materials Science and Technology, Technical University of Hamburg Harburg, Hamburg, GERMANY.

Novel alumina aluminide alloys (3A) based on $\text{TiO}_2/\text{Al}_2\text{O}_3/\text{Al}$ -alloy and $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{Al}$ -alloy have been synthesized by an in situ reaction during reactive infiltration of a liquid aluminum alloy into reactive oxide precursors at temperatures up to 800°C and applied pressures about 40 MPa. The reactive infiltration process performed by squeeze casting enables the production of ceramic-intermetallic composites with outstanding properties as thermal stability and high wear resistance and represents a low cost manufacturing. Reactive infiltration initiates the reaction between the liquid aluminum alloy and the reactive oxide due to thermal activation and the exothermicity of the materials systems. The aluminide phase formation and reaction mode were characterized by x-ray analysis, calorimetric studies and SEM studies. It was carried out that during the aluminide formation, intermediate phases occurred with influence on the reaction kinetics as a retardation of the reaction mechanism. Furthermore, the influence of infiltration condition as short processing times, low processing temperatures and fast solidification of the liquid aluminum were taken into account for characterizing the alumina aluminide phase formation.

GG6.31

THE SYNTHESIS AND CHARACTERIZATION OF NOVEL ALUMINUM AND GALLIUM DIPHOSPHONATES. Howard G. Harvey, Royal Institution of Great Britain, London, UNITED KINGDOM; Simon J. Teat, CLRC Daresbury Laboratory, Warrington, UNITED KINGDOM; Martin P. Attfield, School of Crystallography, Birkbeck College, London, UNITED KINGDOM.

The synthesis and structure determination of the novel aluminum diphosphonate $\text{Al}_2[\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3](\text{H}_2\text{O})_2\cdot\text{H}_2\text{O}$ and its gallium analogue are described. Both materials are synthesized hydrothermally from an HF/ pyridine solvent system. The aluminum form was synthesized as microcrystals from which a single crystal data set was collected using high-flux synchrotron radiation. The structure was solved by direct methods, and the final refined structure used as the starting model for the Rietveld refinement of the gallium containing material. The structures consist of chains of corner sharing MO_4F_2 octahedra (where M = Al or Ga) with bridging F atoms linking the octahedra. The chains contain two types of MO_4F_2 octahedra which differ in their coordination by the F atoms, one having a *trans* arrangement of the two F atoms and the other having a *cis* arrangement. The other apices of the octahedra consist of O atoms from the ethylenediphosphonate groups or coordinated water molecules. The chains of octahedra are linked together in the two directions perpendicular to the chain direction by the ethylenediphosphonate groups. The resulting structure contains a one-dimensional channel system. The channels are relatively small, but do contain extra-framework water molecules. The validity of the crystal structure determination is confirmed by the use of ^{27}Al and ^{19}F MAS solid state NMR. The thermal gravimetric analysis of the materials show weight losses associated with the removal of the extra-framework water, the coordinated water molecules and degradation of the organic components of the ethylenediphosphonate groups. The removal of the extra-framework water is accompanied by a structural transition of the materials.

GG6.32

SYNTHESIS OF CoFe_2O_4 NANOPARTICLES VIA THE FERRIHYDRITE ROUTE. A. Manivannan and M. S. Seehra, Physics Department, West Virginia University, Morgantown, WV.

Magnetic properties of technologically important fine particles of CoFe_2O_4 depend not only on the size of the particles but also on their method of preparation [1]. Here, we report a new method for synthesizing CoFe_2O_4 nanoparticles for size ≥ 5 nm and the method has the advantage of upward scaling for synthesizing larger amounts. This method involves first producing the two line Co-ferrihydrate [2] as evidenced in x-ray diffraction (XRD) by reacting appropriate amount of NaOH and $\text{FeCl}_3/\text{CoCl}_2$ solutions at pH = 7. Heating the Co-ferrihydrate to 325°C converts it to CoFe_2O_4 particles with size ≈ 5 nm as confirmed by XRD. Annealing the powder at higher temperatures increases the particle size so that for annealing at 700°C for 5hrs yields 36 nm CoFe_2O_4 particles. In magnetic measurements, the Co-ferrihydrate is a superparamagnet with $T_B = 40$ K, with particle size ≈ 2 nm as determined by transmission electron microscopy (TEM). For CoFe_2O_4 the variations of the hysteresis loop parameters and their TEM morphologies with particle size will be presented.

GG6.33

Abstract Withdrawn.

GG6.34

LITHOSILICATES: A NEW CLASS OF MICRO-POROUS MATERIALS. So-Hyun Park, Haiming Liu, Clare P. Gery, John B. Parise, Dept of Chemistry SUNY at Stony Brook, NY.

Recently, several novel open lithosilicate structures have been synthesized and characterized using a combination of NMR spectroscopy, synchrotron single crystal X-ray diffraction and powder neutron diffraction. They possess interesting new topologies, which feature Li and Si partitioned into distinct structural elements within the framework. The structure and ion-conductive properties of a particularly Li-rich member of this family, RUB-29, will be discussed.

GG6.35

Abstract Withdrawn.

GG6.36

SYNTHESIS OF STRONTIUM DOPED LANTHANUM COBALT OXIDE POWDER USING A CHEMICAL PRECIPITATION TECHNIQUE. Kirk Card, Michael Wemple, Suvankar Sengupta, Superconductive Components, Inc., Columbus, OH.

Sub-micron strontium-doped lanthanum cobalt oxide powder has been prepared by precipitating an acidic aqueous solution of metal salts, in the desired stoichiometric ratio, with a quaternary ammonium hydroxide solution. Addition of quaternary ammonium carbonate to the quaternary ammonium hydroxide solution has enabled for complete precipitation of all metal cations as hydroxide and/or carbonate salts. The effect of the pH of the final solution on the degree of precipitation and particle size of the resultant powder was studied. Also investigated was effect of varying the carbonate concentration in the quaternary ammonium hydroxide solution. Precursor powders were obtained that could be calcinated and sintered at temperatures significantly lower than the traditional solid-state method. Final samples were characterized using standard techniques (XRD, ICP, TEM, etc.); these data will be presented.

GG6.37

A NANOSCALE CATALYST PREPARATION: SIX-ATOM GOLD CLUSTER DEPOSITION ON TITANIA. Charles C. Chusuei, Xiaofeng Lai, Kent A. Davis, Eric K. Bowers, D. Wayne Goodman, Manal A. Rawashdeh-Omary, Mohammad A. Omary, John P. Fackler, Paul S. Bagus, Dept of Chemistry, Texas A&M Univ, College Station, TX.

Nanosized Au cluster agglomeration has been a long standing problem in the preparation of planar model catalyst systems. A novel Au/ TiO_2 catalyst preparation method was investigated. Six-atom gold clusters (in the form of a $\text{Au}_6(\text{PPh}_3)_6$ colloidal suspension) was deposited onto a $\text{TiO}_2(110)$ single crystal via CH_2Cl_2 solution. Scanning tunneling microscopy (STM) and spectroscopy (STS) revealed structures consistent with unagglomerated, single unit entities. Electron stimulated desorption (0.12 Coulombs/cm 2) was then performed. X-ray photoelectron spectroscopy, high resolution electron energy loss spectroscopy (HREELS) and STM showed evidence for removal of the triphenyl phosphine ligands. Band gap measurements from HREELS, STS and optical spectroscopy suggest that metal/metal oxide support interactions affect the Au electronic structure.

GG6.38

NOVEL SYNTHESSES OF DENSE, NEAR NET-SHAPED CERAMIC-RICH COMPOSITES AT MODEST TEMPERATURES WITH THE USE OF VOLUME-INCREASING INCONGRUENT REDUCTION REACTIONS. Ken Sandhage, Dept of Materials Science & Engineering, Ohio State University, Columbus, OH.

A novel approach for synthesizing dense, near net-shaped, ceramic-rich composites via the use of volume-increasing incongruent reduction reactions will be presented. Although not usually recognized as such, oxidation-reduction reactions between solid ceramic and liquid metals can be considered to be incongruent reduction (IR) reactions (by analogy to incongruent dissolution or incongruent vaporization). In some cases, such IR reactions generate more ceramic volume than is consumed. Examples of such volume-increasing IR reactions include: $3\text{Mg Al}_2\text{O}_3 = 3\text{MgO} + 2\text{Al}$ [1] $\text{Zr WC} = \text{ZrC} + \text{W}$ [2] where {} refers to a species present in a metallic liquid. The volume of 3 moles of MgO is about one-third larger than the molar volume of Al_2O_3 , whereas the molar volume of ZrC is about one-fourth larger than the molar volume of WC (note: the combined volume of ZrC and W is about twice the volume of WC). In the present work, low-melting metallic liquids (e.g., Mg or Mg alloys, Zr-Cu alloys) are infiltrated (at ambient pressure) into, and allowed to undergo an IR reaction with, porous, shaped, rigid (partially-sintered) ceramic preforms (e.g., porous Al_2O_3 or WC). As the IR reactions proceed, the prior pore volume is filled with the solid reaction products, and the metallic liquid is squeezed back out of the preform. Hence, dense, ceramic-rich composites are produced that retain the shape and dimensions of the porous, rigid preform. The syntheses of: i) lightweight, electrically-insulating, MgO-rich composites at 900-1000°C, ii) tough, co-continuous composites of MgAl_2O_4 and Fe-Ni-Al alloys at 900-1000°C, and iii) very high melting, carbide-rich ZrC/WC/W-based composites at 1200-1300°C will be discussed.

SESSION GG7: MICRO/MESO/NANOPOROUS MATERIALS; INORGANIC-ORGANIC HYBRIDS
Chairs: Gerard Ferey and Mark T. Weller
Wednesday Morning, November 29, 2000
Room 304 (Hynes)

8:30 AM GG7.1

INTERCONVERSION, ROBUSTNESS AND CHIRALITY IN MOLECULAR FRAMEWORK STRUCTURES. E.C. Cussen, T.J. Prior, M.J. Rosseinsky, University of Liverpool, Department of Chemistry, Liverpool, UNITED KINGDOM; C.J. Kepert, Department of Chemistry, University of Sydney, NSW, AUSTRALIA.

There has been considerable interest in the synthesis of zeolite analogues by the formation of co-ordination polymer frameworks. This presentation addresses two areas where the molecular frameworks show different chemistry from the zeolites. The first is the control of chirality in chiral co-ordination polymers based on benzene-1,3,5-tricarboxylate, where molecules bound to helical coordination polymer frameworks can control the helix handedness. The second is the difference between thermal and chemical stability in metal-4,4'-bipyridyl frameworks. Frameworks which are thermally stable are still susceptible to interconversion to other frameworks upon exposure to structure-directing guest species.

8:45 AM GG7.2

TRANSITION METAL OXIDE BASED ZEOTYPES - INORGANIC MATERIALS AT THE COMPLEX OXIDE- ZEOLITE BORDER. Mark T. Weller, Paul F. Henry and Robert W. Hughes, Dept of Chemistry, University of Southampton, UNITED KINGDOM.

A structural feature that can relate two of the most important classes of inorganic materials, complex oxides and zeolites, is linked MO_4 tetrahedra, where M is a late first row transition element such as Fe, Co, Ni or Cu. Structures containing species such as FeO_4 and CuO_4 linked together by the more common tetrahedral units such as silicate and phosphate therefore offer the potential benefits of combining the properties of complex oxides, e.g. electronic and magnetic, with those zeolites, e.g. porosity. New examples of compounds recently synthesised and containing $(\text{Fe,Co,Ni,Cu})\text{O}_4$ units will be taken from a number of zeotype systems. For the ABW zeolite structure type new materials based on NiO_4 and CuO_4 , tetrahedral, and NiO_5 , CuO_5 , pentagonal bipyramidal, co-ordination of the composition AMPO_4 will be described. Details of the structures and phase behaviour in the $\text{RbNi}_{1-x}\text{Cu}_x\text{O}_4$ ($1 < x < 0$) system will be given. Phase behaviour as function of temperature, and related to the ferroelectric properties of this family of compounds, will also be described. A second set of examples will be taken from the zeotype JBW structure type where porous, hydrated aluminosilicate blocks alternate with condensed units of the composition sodium aluminosilicate. The synthesis and structure of $\text{CsNa}_2[\text{Al}_3\text{Si}_3\text{O}_6]\cdot n\text{H}_2\text{O}$ will be described as well as other materials from this family with framework and non-framework substitutions. Finally examples taken from the rarer zeotype systems CAS and BIK will be described involving replacement of the part of the framework with transition metal based units.

9:00 AM *GG7.3

FACTS AND FICTION IN THE DESIGN OF MODULAR POROUS

CRYSTALS. O.M. Yaghi, M. Eddaoudi, T. Rieneke, BangLin Chen, University of Michigan, Department of Chemistry, Ann Arbor, MI; M. O'Keeffe, Hailian Li, J. Plevert, Arizona State University, Department of Chemistry, Tempe, AZ.

Preparation of porous networks from molecular modules (coordination complexes and clusters) has been the subject of intense interest due to the potential for design of structures with highly specific function. This presentation will provide the answer to the following questions: (a) Is it possible to have high free volume in a maximally interpenetrating structure? (b) Is molecular weaving better than interpenetrating for achieving porosity and framework stability? (c) Can the outcome of modular assembly be predicted? The relevance of these considerations to the successful synthesis of porous networks with pore sizes and volumes beyond those commonly observed for the most porous zeolites will be presented as well.

10:00 AM GG7.4

A COMPUTATIONAL STUDY OF THE TRANSLATIONAL MOTION OF PROTONS IN ZEOLITE H-ZSM-5. Marion E. Franke, Ulrich Simon, RWTH Aachen, Institute of Inorganic Chemistry, Aachen, GERMANY; Marek Sierka, Joachim Sauer, Humboldt University of Berlin, Institute of Chemistry/Quantum Chemistry, Berlin, GERMANY.

The mobility of the protons in H-form of zeolites is of fundamental interest, since it may be related to their catalytic activity. Due to the strong, partially covalent interactions with the anionic zeolite lattice, the motion of protons is assumed to be restricted to jumps between the four oxygen atoms surrounding one aluminum center (Brønsted-acid site). In this paper we report for the first time the calculation of stationary points on the potential energy surface relevant for the translational motion of protons in zeolite H-ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio = 190) by a combined quantum mechanics - interatomic potential function approach (QM-Pot). The calculated energies of the six equilibrium proton positions, T-OH-Si (T=Al,Si), connecting two neighboring Al-sites, show a symmetrical course reaching its maximum for a proton position in the middle between these sites. The energies of the transition structures show a similar trend, whereas their absolute value depends on the local structure of the respective Si-O-Si unit. Therefore, the decrease of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, defining the spatial distance of the Al-sites in zeolites, leads to a decrease of the distance dependent activation energy (E_A) for proton jumps between the Al-sites, as soon as their Coulomb potential starts to overlap. Taking the highest energy of the transition structure as E_A , the translational motion of the proton may appear with a barrier of about 200 kJ/mol. This is much lower than the full deprotonation energy of ~13 eV necessary to create a "quasi-free" mobile proton. The deprotonation energy of an Al-OH-Si bridge is obviously compensated by the energy gained by binding the proton to the bridging Si-O-Si-groups. These results are in excellent agreement with the model of proton transport in H-ZSM-5 deduced from impedance measurements.

10:15 AM GG7.5

DISORDERED MESOPOROUS SILICATES FORMED BY TEMPLATING OF A LIQUID CRYSTAL (L_3). Abds-Sami Malik, Daniel M. Dabbs, Ilhan A. Aksay, Princeton University, Dept. of Chemical Engineering and Princeton Materials Institute, Princeton, NJ; Hang-Shing Ma, George W. Scherer, Princeton University, Dept. of Civil and Environmental Engineering and Princeton Materials Institute, Princeton, NJ; Howard E. Katz, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

For a wide range of technological applications, the need for optically transparent, monolithic, mesoporous silicates is readily apparent. These include filtration, catalysis, and optoelectronics. We have previously reported on the synthesis of such materials,^{1,2} which are formed by the addition of tetramethoxy silane to a liquid crystal solution (L_3) of hexanol, cetylpyridinium chloride, and 0.2 M hydrochloric acid, and we are continuing our investigation to examine their properties. We are now able to obtain defect, fracture-free and transparent material (0.5 cm X 3 cm disks) via drying of the silicate in supercritical isopropanol, ethanol, or CO_2 . The dried materials possess pore volumes of ca. 1.0 cm^3/g , with BET surface areas > 1000 m^2/g . The bulk modulus, measured from beam bending, is ca. 200 MPa. IR spectroscopy shows that we are then able to successfully re-infiltrate the dried material with hydroxyethylacrylate, a photo-polymerizable monomer, and complete the polymerization. The material did not fracture during the re-infiltration and polymerization process. These findings suggest many possible applications for these unique materials.

- 1) K.M. McGrath, *Langmuir* **1997** *13* 1987-995.
- 2) K.M. McGrath, D.M. Dabbs; N. Yao; I.A. Aksay, S.M. Gruner, *Science* **1997** *277* 552-56.

10:30 AM GG7.6

NON-OXIDIC ANALOGS OF MCM-41 AND MCM-48. NANOSTRUCTURED NON-OXIDIC SOLIDS WITH LARGE MESOPORES BASED ON THE ZINTL ANIONS $[\text{GeQ}_4]^{4-}$, $[\text{SnQ}_4]^{4-}$ (Q=Se, Te) and $[\text{Ge}_4\text{Q}_{10}]^{4-}$, (Q=Se, Te). Pantelis Trikalitis and Mercouri G. Kanatzidis, Department of Chemistry, Michigan State University, East Lansing, MI.

The supramolecular assembly of the simple tetrahedral Zintl anion $[\text{SnSe}_4]^{4-}$ with transition metals in the presence of cetylpyridinium surfactant molecules led to the formation of a new family of mesostructured metal tin selenide materials. The products have well defined stoichiometric compounds with general formulae $(\text{Cpy})_{4-2x}\text{M}_x\text{SnSe}_4$ ($0.75 < x < 1$; M=Mn, Fe, Zn, Cd, Hg). XRD powder patterns and transmission electron microscopy (TEM) images show that the mesophases has a local hexagonal symmetry with pore size ranging between $35 \approx$ and $40 \approx$ depending on the transition metal used. All compounds are medium band gap semiconductors with $1.5 < E_g < 2.5$ eV. The distance between the inorganic pores and their width depend linearly upon the surfactant chain length and therefore can be easily tuned. The conditions that lead to hexagonal, cubic and worm-hole pore topologies will be discussed. In addition to X-ray diffraction and TEM these hybrid phases were characterized with thermal analysis, Raman, Far-IR and solid-state electronic spectroscopy. This work establishes that it is possible to construct organically templated structures with heavy SiO_4 -analogs to produce semiconducting solids with well-defined mesopores.

10:45 AM *GG7.7

ELECTRONICALLY CONDUCTING INORGANIC/ORGANIC HYBRID MATERIALS. Winny Dong, Kevin Johnston, Bruce Dunn, UCLA, Dept. of Materials Science and Engineering, Los Angeles, CA.

The transition metal oxide materials which are used in electrodes for lithium secondary batteries are characterized by relatively low electronic conductivity. To overcome this behavior, composite electrodes are prepared in which an appropriate conductor is added to obtain the necessary level of electronic conductivity. Inorganic/organic synthesis approaches offer the promise of achieving the desired electrical and electrochemical properties within a single material. The inorganic/organic material can be designed to combine the lithium intercalation properties of the transition metal oxide with the high electrical conductivity of a conducting polymer. This paper reviews our work on the synthesis and properties of inorganic/organic hybrid materials composed of molybdenum oxide and various conducting polymers including polypyrrole and polyaniline. The sol-gel methods used in the synthesis provide molecular level mixing of the constituents leading to xerogels as well as high surface area hybrid aerogels. The most significant results have been achieved using polypyrrole. By controlling synthesis conditions, it is possible to form a continuous network of polypyrrole throughout the hybrid material and achieve a 100 fold increase in electrical conductivity as compared to the pristine molybdenum oxide aerogel. Electrochemical measurements indicate that these hybrid materials also exhibit enhanced lithium ion intercalation. Recent results for hybrid materials containing chromium oxide will also be presented.

11:15 AM GG7.8

FRAMEWORKS OF TRANSITION METALS LINKED BY ORGANIC LINKERS WITH TWO OR MORE DIFFERENT FUNCTIONAL GROUPS. Slavi C. Sevov, Dept of Chemistry and Biochemistry, Univ of Notre Dame, Notre Dame, IN.

Hybrid inorganic/organic materials with open-framework or layered structures are known for many transition metals linked by functionalized organic molecules such as organic diphosphonates, polycarboxylates, polynitriles, etc., species with a more than one equivalent functional groups. We have studied the effect of pH on such a system of cobalt-methylenediphosphonate-sodium hydroxide and report three new compounds, $\text{Na}_3\text{Co}[(\text{O}_3\text{PCH}_2\text{PO}_3)(\text{OH})]$, $\text{Na}_2\text{Co}(\text{O}_3\text{PCH}_2\text{PO}_3)_2\text{H}_2\text{O}$, and $\text{Co}_2[(\text{O}_3\text{PCH}_2\text{PO}_3)(\text{H}_2\text{O})]$, that form at very basic, moderately basic, and acidic conditions, respectively. More interesting structural chemistry should be expected from linkers with two or more different functionalities. Both the carboxylic and phosphonic groups in carboxyethylphosphonic acid are used to coordinate to cobalt atoms in the new compound $\text{Co}_3(\text{OOCCH}_2\text{CH}_2\text{PO}_3)_2\text{H}_2\text{O}$. Taking one more step further in complexity we have studied linkers with three different functional groups, phosphonated amino acids. The structures of two new compounds, $\text{Zn}(\text{O}_3\text{PCH}_2\text{CH}(\text{NH}_3)\text{COO})$ and $\text{Zn}(\text{O}_3\text{PCH}_2\text{CH}_2\text{CH}(\text{NH}_3)\text{COO})$, are three-dimensional frameworks made of zinc coordinated by both the carboxylic and phosphonic ends of the organic molecules. The amino groups are protonated and terminal in the voids of the frameworks.

11:30 AM GG7.9

THE FIRST COVALENT INORGANIC-ORGANIC NETWORK OF HYBRID CHALCOGENIDES: STRUCTURES THAT MAY LEAD

TO A NEW TYPE OF QUANTUM WELLS. Xiaoying Huang, Jing Li, Dept. of Chemistry, Rutgers Univ., Camden, NJ; Huaxiang Fu, Dept. of Physics, Rutgers Univ., Camden, NJ.

Solvothermal reactions in superheated amines have resulted in hybrid chalcogenides containing unprecedented covalent architecture of inorganic-organic networks with unusual metal-amine coordination. The crystal structures of $[\alpha\text{-ZnTe}(\text{en})_{1/2}]$ (I) (en = ethylenediamine), $[\beta\text{-ZnTe}(\text{en})_{1/2}]$ (II), $[\text{ZnTe}(\text{pda})_{1/2}]$ (III) (pda = 1,3-propanediamine) have been analyzed by single crystal X-ray diffraction. All three compounds are composed of two-dimensional $[\text{ZnTe}]$ semiconductor layers and organic molecule L (L=en, pda) interconnected via unique covalently Zn-N bridging bonds. Both the experiment measurements and DFT calculations show that the compounds exhibit a large blue shift in their optical absorption spectra compared to the parent chalcogenide semiconductors. We attribute this large shift to the quantum confinement effect.

11:45 AM GG7.10

Abstract Withdrawn.

SESSION GG8: SYNTHESIS, NEW METHODS, NEW MATERIALS

Chairs: Jacques Livage and Joseph W. Kolis
Wednesday Afternoon, November 29, 2000
Room 304 (Hynes)

1:30 PM GG8.1

SYNTHESIS OF LARGE ZSM-5 CRYSTALS UNDER HIGH PRESSURE. Xiqu Wang, Allan J. Jacobson, University of Houston, Department of Chemistry and Materials Research Science and Engineering Center, Houston, TX.

ZSM-5 type microporous materials are usually synthesized at mild temperatures below 500 K because higher temperatures lead to formation of dense phases. In this presentation, we show that the synthesis temperature can be raised up to 573 K by applying a high pressure to stabilize the structure-directing organic templates. The elevated temperature and pressure favor the formation of crystals of improved quality. Silicalite-I crystals with an uniform size of ca. $0.7 \times 0.2 \times 0.2$ mm have been obtained by heating a gel prepared from TMA-silicate solution, TPABr and sodium hexafluorosilicate at 523 K under a pressure of 80 MPa. Influences of synthesis conditions on the crystal sizes have been studied by systematically changing temperature, pressure and gel compositions. At the specific conditions of 523 K and 80 MPa, a linear correlation was found between the crystal size and the F/Si mole ratio of the starting gel, which enables preparation of uniform crystals of silicalite-I with preset dimensions.

1:45 PM GG8.2

SOMS, A NEW CLASS OF Na/Nb/X/O MICROPOROUS AND PEROVSKITE PHASES. T.M. Nenoff, M. Nyman, Sandia National Laboratories, Albuquerque, NM; A. Tripathi, J. Parise, Dept. of Earth Sciences, SUNY, Stony Brook, NY.

Exploratory hydrothermal synthesis methods have produced novel microporous Sandia Octahedral Molecular Sieves (SOMS) that are highly selective for divalent cations. After ion exchange and then either wash or thermal treatment, these new Nb-based phases collapse into thermally stable novel (Na,M)/Nb/X/O perovskite phases (M = divalent cation). The method of synthesis for all the molecular sieve phases and also the perovskite phases are fully described. The framework structure of one of these materials (SOMS-1), consists of stacked layers of Na octahedra alternating with double chains of edge-shared Nb/Ti-centered octahedra. Within the framework resides exchangeable Na-cations. Both framework and extra-framework Na sites are ion exchanged with Sr, without structural collapse. This structure suggest possible mechanisms for the unique type of ion exchange. Characterization of all phases includes powder and single crystal X-ray diffraction, elemental analyses, surface area, thermal analyses, ion exchange studies, and chemical and radiation stability studies.

This work was supported by the U.S. DOE under contract DE-AC04-94AL85000.

2:00 PM GG8.3

HYDROTHERMAL SYNTHESSES OF VANADIUM OXIDES FROM AQUEOUS SOLUTIONS. Nathalie Steunou, Christian Bonhomme, Jocelyne Maquet, Jacques Livage, Chimie de la Matière Condensée, Université Pierre et Marie Curie, Paris, FRANCE.

Vanadium oxide based materials have been extensively studied as reversible cathodes in lithium batteries. They are often synthesized via wet chemistry methods such as precipitation, sol-gel or hydrothermal syntheses. Depending on the experimental conditions

such as pH, temperature and pressure, condensation reactions can lead to a large variety of polyoxovanadate phases. A chemical control of these condensation reactions would be required in order to synthesize tailor-made materials that exhibit improved electrochemical properties. The nature of the molecular precursors mainly depends on pH but the way they self-assemble to give a solid phase depends on foreign ions in the solution. Chain metavanadates made of four fold coordinated vanadium centers are precipitated in basic aqueous solutions. Decavanadates are precipitated at room temperature around pH 7 whereas layered vanadium oxides are formed via hydrothermal syntheses in the same pH range. Some reduction occurs when organic cations such as tetramethyl ammonium cations are used leading to mixed valence polyoxovanadates. Anions such as chloride or iodide behave as templates leading to the formation of large polyoxovanadate clusters. This communication discusses the chemical processes involved in the formation of polyoxovanadates from aqueous solutions and the structural relations between molecular precursors and solid phases.

2:15 PM GG8.4

SYNTHESIS, MAGNETISM AND OPTICAL PROPERTIES OF NEW METAL GERMANATES AND SILICATES IN SUPER-CRITICAL WATER. Mehtap Eanes, Edward E. Abbott, Joseph W. Kolis, Clemson Univ., Dept of Chemistry, Clemson, SC.

Germanates and silicates are excellent building blocks for new solid materials because they often have interesting microporous and optoelectronic properties. We have been exploring the hydrothermal route to these materials using strong aqueous base as the mineralizer. This has proven to be an effective method to synthesize new compounds, as well as for the growth of large crystals. In basic conditions, GeO_2 and transition metal oxides react to form new compounds. Also, alkali metals can become incorporated, forming novel low dimensional solids. Both f-block and d-block metals form metal germanates and silicates. In addition to interesting optical properties, many of the compounds have unusual magnetic behavior. For example, the vanadium germanates and silicates are spin-Peierls compounds. The synthesis, structure and physical properties of these compounds will be presented.

2:30 PM GG8.5

ASSEMBLY OF METAL-ANION ARRAYS WITHIN PEROVSKITE HOSTS - TRANSITION-METAL ION EXCHANGE BEHAVIOR OF DION-JACOBSON TYPE LAYERED PEROVSKITES. T.A. Kodenkandath, M.L. Viciu, X. Zhang, J.A. Sims, E.W. Gilbert, F.-X. Augrain, J.-N. Chotard, G.A. Caruntu, L. Spinu, W.L. Zhou, J.B. Wiley, Dept. of Chemistry and the Advanced Materials Research Institute, Univ. of New Orleans, New Orleans, LA.

Currently our group is working to develop low-temperature synthetic strategies for controlling the structure and valence of mixed-metal oxides. Topotactic methods based on ion exchange and intercalation are being utilized to access new compounds. Most recently we have focused our efforts on studying the transition-metal ion-exchange behavior of Dion-Jacobson type layered perovskites. In some systems (e.g., copper chloride), the co-exchange of both the metal cation (M) and halide anion (X) occurs to produce an ordered metal-halide array within the host. This behavior, however, is only observed with a few of the first row transition metals. Details on the synthesis and characterization of a series of exchange products will be presented and product variation as a function of the host, the metal halide, and the reaction conditions will be discussed.

3:15 PM GG8.6

COMBINATORIAL SYNTHESIS OF $(\text{Ba}_{1-x}\text{Sr}_x)\text{TiO}_3$ PEROVSKITE FILMS: TEM STUDY OF MICROSTRUCTURAL EVOLUTION. Leonid A. Bendersky, MSEL, NIST, Gaithersburg, MD; Ichiro Takeuchi, Dept. of Materials and Nuclear Eng., Univ. of Maryland, College Park, MD.

In combinatorial synthesis of thin film oxides, in order to generate large compositional variations, several methods of forming compounds are employed. In particular, the precursor technique can truly enhance the combinatorial nature of the experiment because this enables the creation of different compositions by permutations and thickness variations of precursors. Compounds are formed through controlled thermal treatments of multilayers of amorphous precursors deposited at room temperature. It was previously shown that this technique can be used to obtain predominantly single-phase epitaxial $(\text{Ba}_{1-x}\text{Sr}_x)\text{TiO}_3$ (BST) films as determined by x-ray diffraction and Rutherford backscattering [1]. The BST films were made from TiO_2 , $\text{BaF}_2/\text{BaCO}_3$, and $\text{SrF}_2/\text{SrCO}_3$ layers on single crystal LaAlO_3 substrates. In this paper we discuss high-resolution transmission electron microscopy studies of these films. The goal was to understand the fundamental growth mechanisms of the precursor technique as well as to investigate the limitation of the approach. Microstructure, defects, crystallography of phases, and structure of a film/substrate

interface of films with various compositions in final stages of annealing, as well as in transient stages, will be discussed.

[1] H. Chang, C. Gao, I. Takeuchi, Y. Yoo, J. Wang, P.G. Schultz and X.-D. Xiang, "Combinatorial Synthesis and High Throughput Evaluation of Ferroelectric/Dielectric Thin-Film Libraries for Microwave Applications", Applied Physics Letters, 72, 2185 (1998).

3:30 PM GG8.7

PREPARATION OF NEW BISMUTH OXIDES BY HYDROTHERMAL REACTION. N. Kumada, T. Takei, N. Kinomura, Faculty of Engineering, Yamanashi University, Kofu, JAPAN; A.W. Sleight, Dept of Chemistry, Oregon State University, Corvallis, OR.

We have reported various new bismuth oxides prepared by hydrothermal reaction using $\text{NaBiO}_3 \cdot n\text{H}_2\text{O}$ as a starting material. Some of new compounds had pentavalent bismuth, for example, Bi_2O_4 , LiBiO_3 and ABi_2O_6 (A=Mg,Zn) etc. were obtained by hydrothermal reaction below 150°C . When used transition metal or rare-earth metal solutions, new bismuth oxides with trivalent bismuth were obtained. In the case of $\text{Cr}(\text{NO}_3)_3$ solution chromium bismuth oxyhydroxides, $\text{HBI}_3(\text{CrO}_4)_2\text{O}_3$ was prepared, while in K_2CrO_4 solution a new bismuth chromium oxide, $\text{Bi}_8(\text{CrO}_4)\text{O}_{11}$ was prepared. We will review preparation and crystal structure of these new bismuth oxides.

3:45 PM GG8.8

BIOMIMETIC SYNTHESIS OF SINGLE CRYSTALS OF LITHIUM NIOBATE AT ROOM TEMPERATURE AND PRESSURE. Michael W. Pittercher, Yanan He, Patricia A. Bianconi, University of Massachusetts at Amherst, Amherst, MA.

Lithium niobate (LiNbO_3) crystals have a number of unique properties. Lithium niobate is at the same time ferroelectric, piezoelectric, pyroelectric, and has high nonlinearly optical and electro-optical coefficients and photorefractive sensitivity. These properties enable these crystals to be used widely in optical and acoustic devices, and also in lasers, waveguides and holography etc. Standard methods of synthesis of LiNbO_3 require high-temperatures to form single crystals (e.g. Czochralski method $>1000^\circ\text{C}$). There has been recent interest in metal alkoxides as precursors to lithium niobate, but temperatures in the range of $250\text{-}500^\circ\text{C}$ are still needed for crystallinity. We have developed a biomimetic method, which enables the crystallization of inorganic species to be controlled within a polymer matrix. The method has produced single, oriented crystals of cadmium and lead sulfides. We now report that this method can be used to produce single, oriented crystals of lithium niobate at room temperature and pressure.

4:00 PM GG8.9

SYNTHESIS OF NEW PEROVSKITE PHASES BY THE TOPOCHEMICAL REDUCTION OF LAYERED PRECURSORS. Raymond E. Schaak and Thomas E. Mallouk, The Pennsylvania State University, Department of Chemistry, University Park, PA.

Solid-state inorganic chemistry is dominated by high-temperature ($>1000^\circ\text{C}$) reactions, which usually limit product phases to those that are thermodynamically stable. As chemists seek to synthesize and fine-tune new materials with superior properties, subtle structural features become increasingly difficult to control thermodynamically. Low-temperature ($<600^\circ\text{C}$) topochemical reactions allow one to access kinetic phases that have interesting structures. Recently we reported the transformation of layered perovskites into non-defective three-dimensional phases using a new topochemical reduction reaction. For example, the layered parent phase, $\text{K}_2\text{Eu}_2\text{Ti}_3\text{O}_{10}$, is converted to $\text{CaEu}_2\text{Ti}_3\text{O}_{10}$ by room-temperature intercalation, then reduced in hydrogen to form the A-site ordered three-dimensional phase $\text{CaEu}_2\text{Ti}_3\text{O}_9$. Since the layered phases can be exfoliated and re-stacked in any sequence on a surface, the possibility of synthesizing interesting three-dimensional phases as thin films appears promising. We are currently working on extending the topochemical reduction of perovskites to easily reducible B-site cations, as well as other novel structural transformations using the A-site Eu^{3+} cation.

4:15 PM GG8.10

Abstract Withdrawn.

4:30 PM GG8.11

SYNTHESIS AND CHARACTERIZATION OF NOVEL TRANSITION METAL OXYNITRIDES. Simon J. Clarke, Patricia Blanco Garcia, University of Oxford, Inorganic Chemistry Laboratory, Department of Chemistry, Oxford, UNITED KINGDOM; Charles W. Michie, Matthew J. Rosseinsky, University of Liverpool, Department of Chemistry, Liverpool, UNITED KINGDOM.

We have been investigating oxynitrides containing early first row transition metals which are predicted to lie close to the metal-to-insulator boundary and should show a range of electronic

behaviors as diverse as those of first row transition metal oxides. Following the well-established synthesis of the insulating perovskite NdTaO_2 by reacting NaTaO_4 with flowing ammonia gas at 900°C [R. Marchand *et al.*, *Ann. Chim. Fr.*, **16**, (1991), 553], we have explored the reaction of the oxides $\text{NdTa}_{1-x}\text{V}_x\text{O}_4$ ($0.1 < x < 0.28$) with flowing ammonia. At 900°C we observe phase separation to NdTaO_2 , VN and Nd_2O_3 . However, using reaction temperatures between 650 and 750°C , a continuous structural transformation is observed from the oxide with the monoclinic NdTaO_4 structure type via a range of isostructural oxynitride phases to an oxynitride product with the face centered cubic pyrochlore structure type. Such a transformation involves replacement of oxide by nitride with concomitant generation of vacancies, and also a redistribution of the neodymium and transition metal cations. This unusual continuous structural transformation has been followed by X-ray and neutron powder diffraction measurements. The results of Rietveld analysis of these data will be presented. The oxynitrides obtained have a range of compositions with the limiting N/O ratio occurring in the anion-defective pyrochlore $\text{NdTa}_{0.72}\text{V}_{0.28}\text{O}_{2.00(5)}\text{N}_{1.25(5)}$ ($a = 10.684(1)$ Å); attempts to increase the N/O ratio invariably lead to phase separation. In all these compounds vanadium is reduced to an oxidation state close to 4 and the materials are black in color. Preliminary magnetic susceptibility measurements on these materials will be presented.

4:45 PM GG8.12

CHEMICAL SYNTHESIS AND PROPERTIES OF LAYERED $\text{Co}_{1-y}\text{Ni}_y\text{O}_{2-d}$ OXIDES. A. Manthiram, R.V. Chebiam, Texas Materials Institute, The University of Texas at Austin, Austin, TX.

Transition metal oxides in which the metal:3d and oxygen:2p bands overlap have drawn much attention in recent years due to their interesting electronic properties. However, such systems with highly oxidized couples such as $\text{Co}^{3/4}$ and $\text{Ni}^{3/4}$ are generally difficult to access by conventional high temperature procedures. We present here the chemical synthesis, characterization and properties of layered $\text{Co}_{1-y}\text{Ni}_y\text{O}_{2-d}$ for the entire range of y. The samples are synthesized by chemically extracting lithium from the layered $\text{LiCo}_{1-y}\text{Ni}_y\text{O}_2$ having the O3 structure with the oxidant NO_2PF_6 in acetonitrile medium at ambient temperature. While the initial O3 structure is maintained for $(1-x) > 0.38$ in $\text{Li}_{1-x}\text{CoO}_{2-d}$, the end member CoO_{2-d} consists of a mixture of an O1 phase (CdI₂ structure) and P3 phase. On the other hand, the end member NiO_{2-d} has the O3 structure (CdCl₂ structure) with a reduced c/a ratio of 4.8. More importantly, the cobalt system loses more oxygen than the nickel system on deep lithium extraction and the end members CoO_{2-d} and NiO_{2-d} have oxygen contents of 1.65 and 1.90 respectively. The differences in crystal chemistry and oxygen content between the two systems will be explained based on the relative positions of the redox energies and the electrostatic interactions. Additionally, the electrical and magnetic properties of these $\text{Co}_{1-y}\text{Ni}_y\text{O}_{2-d}$ oxides having direct metal-metal and 90 metal-oxygen-metal interactions will be presented and compared with those of perovskite oxides having 180 metal-oxygen-metal interactions.

SESSION GG9: POSTER SESSION
SOLID-STATE IONICS, BATTERY MATERIALS,
THERMO POWER, OPTICAL MATERIALS
Chairs: Harry L. Tuller and John S. O. Evans
Wednesday Evening, November 29, 2000
8:00 PM
Exhibition Hall D (Hynes)

GG9.1

Al, Bi, AND Y DOPED ANTIMONIC ACIDS: PREPARATION, ELECTRICAL PROPERTIES, AND WATER ADSORPTION BEHAVIOR. Kiyoshi Ozawa, Yoshio Sakka, Muneyuki Amano, National Research Institute for Metals, Tsukuba-shi, Ibaraki, JAPAN.

Several kinds of metal oxides doped antimonic acid $(1-x)\text{Sb}_2\text{O}_5 \cdot x\text{M}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Al}, \text{Bi}, \text{Y}, 0 \leq x \leq 1$), were prepared by a reaction of an aqueous H_2O_2 solution with metal alkoxides. The electrical properties of the materials were investigated through dc and ac conductivity measurements using polycrystalline compact discs. It has been clarified that the ionic transference numbers of $(1-x)\text{Sb}_2\text{O}_5 \cdot x\text{M}_2\text{O}_3 \cdot n\text{H}_2\text{O}$, ($0 \leq x \leq \sim 0.2$) exhibit all over 0.98 and the electrical conductivity depends on the number of the water molecules absorbed in the channel structure. In addition, water adsorption isotherms measurements have revealed that the number of the water molecules is affected not only by the relative humidity but also by a kind of M and its content x in $(1-x)\text{Sb}_2\text{O}_5 \cdot x\text{M}_2\text{O}_3 \cdot n\text{H}_2\text{O}$. In the presentation, for the first time, it is demonstrated how the $(1-x)\text{Sb}_2\text{O}_5 \cdot x\text{M}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ materials has been prepared. Next the electrical properties are discussed in connection with the water adsorption behavior.

GG9.2

OXYGEN-ION DIFFUSION IN $\text{Ba}_2\text{In}_2\text{O}_5$. Akihiko Yamaji, Kenji Tojyu and Tadaharu Adachi, Department of Mechanical Engineering, Tokyo Institute of Technology, Tokyo, JAPAN.

Brownmillerite ($\text{Ca}_2\text{Al}_2\text{O}_5$ - $\text{Ca}_2\text{Fe}_2\text{O}_5$ solid solution) structure can be regarded as an oxygen-ion deficient perovskite structure. Because of high proportion of the oxygen vacancies in the structure, this material could be a candidate of fast oxide-ion conductor. Goodenough *et al.* indeed observed a first-order transition to a fast oxide-ion conductor at 930°C for $\text{Ba}_2\text{In}_2\text{O}_5$ which adapts brownmillerite structure at ambient temperature. In the present study, we investigated the ion conductivity and the oxygen ion diffusion in $\text{Ba}_2\text{In}_2\text{O}_5$ system. The oxygen diffusion coefficients for $\text{Ba}_2\text{In}_2\text{O}_5$ ceramics were determined from the isotope-gas exchange measurement using the stable isotope ^{18}O as a tracer between 570°C and 1000°C . The abrupt changes in the diffusion coefficients are observed at 920°C . This change is caused by the phase transition from orthorhombic to the cubic phase at high temperature. The diffusion coefficients at a high temperature region above 920°C is given by $D = 9.86 \times 10^{-5} \exp(-66.91\text{kJ}/\text{RT}) \text{cm}^2/\text{sec}$ and below 920°C the those are given by $D = 3.90 \times 10^{-5} \exp(-83.06\text{kJ}/\text{RT}) \text{cm}^2/\text{sec}$. We can compare measured diffusion coefficients with those obtained from the ion conductivity measures values. The activation energy is almost same, but the diffusion coefficients from Nernst-Einstein equation are slightly larger than those obtained from the diffusion experiments. This difference will be discussed considering the transport number and the oxygen-ion carrier density.

GG9.3

CHARACTERIZATION OF SITE III SODIUM CATIONS IN LiNa_x INVESTIGATED USING ^{23}Na MAS NMR AND ^{23}Na MQMAS NMR SPECTROSCOPY. Robyn J. Accardi, Raul F. Lobo, University of Delaware, Dept of Chemical Engineering, Newark, DE; Hubert Koller, University of Münster, GERMANY.

The characterization of sodium cations in site III of LiNa_x was investigated using variable temperature ^{23}Na MAS NMR and ^{23}Na MQMAS NMR. Samples were investigated in vacuum and in the presence of oxygen. The paramagnetic shift effect of oxygen was used to determine the accessibility of these sodium cations. Variable temperature ^{23}Na MAS and MQMAS NMR was used to further enhance the shifts as the paramagnetic shift is inversely proportional to temperature. The room temperature ^{23}Na MAS NMR spectrum of the oxygen-containing sample shows a significant downfield paramagnetic shift of the site III cation resonance indicating the accessibility of these sodium cations to the oxygen molecules. However, this observed paramagnetic shift decreases substantially at lower temperatures. To better understand the various contributions to these observed shifts, ^{23}Na MQMAS NMR was used to calculate the isotropic chemical shifts, the quadrupolar shifts, and the quadrupolar coupling constants. It is known that the quadrupolar interactions will shift the resonance upfield in the opposite direction of the paramagnetic shift. The MQMAS spectra show that the quadrupolar coupling constant and quadrupolar shift of sodium remains the same irrespective of the presence or absence of oxygen. Therefore, a significant paramagnetic shift will be observed in the NMR spectra for the oxygen-containing sample. However, the upfield quadrupolar shift increases at lower temperatures such that a smaller downfield will be observed for the site III resonance in the low temperature NMR spectra.

GG9.4

AC CONDUCTIVITY STUDIES ON $\text{Ag}_{1-x}\text{Cu}_x\text{I}$ $x < 0.50$ SYSTEM. J.F. Jurado, Departamento de Física, Universidad Autónoma de Occ., Cali, COLOMBIA; R.A. Vargas, Departamento de Física, Universidad del Valle, Cali, COLOMBIA; B.-E. Mellander, Dept of Physics, Chalmers University of Technology, Gothenburg, SWEDEN.

We investigated the electrical properties of the $\text{Ag}_{1-x}\text{Cu}_x\text{I}$ system over a wide concentration range which were prepared from the melt. dc polarisation measurements indicated that samples with concentrations $x < 0.50$ are mainly Ag-conductor. ac response of the samples were analysed in admittance, permittivity and modulus formalisms in the frequency range 5 Hz to 13 MHz and the temperature range 20-200°C. The frequency variation of the ionic conductivity, $\sigma(\omega)$, obeys Jonscher's universal law at higher frequencies, $A\omega^n$, where A and n were found to be weakly temperature-dependent. The hopping rate, $\omega_p(T)$, has been evaluated showing that the temperature variation of dc conductivity arises mainly due to $\omega_p(T)$. The dielectric permittivity, ϵ^* , show frequency dependence that may be related to dielectric relaxation of the material. Also, the modulus spectra have been analysed in terms of non-exponential decay function, giving values of the Kohlrausch parameter, β , that indicate a non-Debye like behaviour of the ac conductivity.

GG9.5

HIGH OXIDATION STATE ALKALI-METAL LATE-TRANSITION-METAL OXIDES. Andrew L. Hector, John Owen, Emmanuelle Raekelboom, Mark T Weller, University of Southampton, Highfield, Southampton, UNITED KINGDOM.

One of the primary commercial benefits of many new electronic devices is portability. From this arises the need for compact, high power, lightweight primary and secondary (rechargeable) battery systems. The most exciting technology at present is the lithium batteries based on a lithium (or intercalation host) anode and a cathode which is usually an oxide of manganese or cobalt. The work to be presented will give examples of the synthesis and structures of novel materials with the potential to be effective lithium battery cathode materials. High oxidation states at the transition metal are necessary to maximise the cell potential. The synthetic methodology involves high pressure (with flowing oxygen or sealed systems) or highly active oxide reagents (e.g. Na_2O_2) to achieve high oxidation state products. The structure of Na_4FeO_4 has been determined. This is the first determination of the structure of tetrahedral ferrate(IV) and shows a strong Jahn-Teller distortion from ideal tetrahedral symmetry, similar to that observed in MnO_4^{3-} . A series of these molecular oxides are under investigation as potential primary battery materials. The mixed valence $\text{M}^{2/3}$ materials $\text{Li}_2\text{ACu}_2\text{O}_4$ (A=Li,Na) and $\text{KA}_2\text{Ni}_2\text{O}_4$ (A=Li,K) have edge-linked chains of MO_4 square planes running through the structures, giving a similar degree of structural stability, with respect to alkali metal deintercalation, to that observed in layered compounds. These materials have been investigated structurally and the electrochemistry is under investigation.

GG9.6

IN SITU XAFS STUDY ON LiNiO_2 CATHODE MATERIAL FOR LITHIUM-ION BATTERIES: THE INFLUENCE OF ELECTROCHEMICAL CYCLING AND THERMAL STABILITY. Takamasa Nonaka, Chikaaki Okuda, Yoshio Ukyo, Tokuhiko Okamoto, TOYOTA Central R&D Labs., Inc., Aichi, JAPAN.

LiNiO_2 is a promising cathode material for rechargeable lithium-ion batteries with high capacity. However, capacity fade is recognized not only during discharge/recharge cycling, but also during keeping at high temperatures. Ni-K edge X-ray absorption spectra of LiNiO_2 have been collected using in situ coin cells which are constructed for XAFS experiments. To investigate the electronic and structural changes during electrochemical cycling and during keeping at high temperatures, the cells of different cycling states and different keeping conditions (temperature, a period of keeping) were prepared. The experiments were performed by using beamline BL16B2 in SPring-8 (Super Photon ring-8 GeV, Hyogo, Japan). Upon charging the cell, the Ni-K absorption edge shifted towards higher energy, which indicate an increase in the oxidation state of Ni. The good correlation between the value of chemical shifts upon charging and the electric capacity of the cell was observed. From quantitative analysis of EXAFS data, it was revealed that the Jahn-Teller distortion of the NiO_6 octahedron is related to the capacity fade.

GG9.7

CHEMICAL DELITHIATION, THERMAL TRANSFORMATIONS AND ELECTROCHEMICAL BEHAVIOUR OF IRON-SUBSTITUTED LITHIUM NICKELATE. Pedro Lavela, Carlos Perez-Vicente, Jose L. Tirado, Universidad de Cordoba, Laboratorio de Quimica Inorganica, Campus de Rabanales, Cordoba, SPAIN.

The solid state chemistry of layered lithium nickelate has deserved the interest of many researchers, favored by its aptitude towards relevant applications in advanced battery technology. Recent works are devoted to improve its synthesis, characterization and electrochemical performance. Also, nickel substitution has allowed the formation of new materials containing Co, Al or Fe. Besides, the possible oxidation of the transition metal together with lithium extraction by chemical procedures was early revealed. The aim of this communication is to extend the study of the chemical deintercalation reactions to Fe-substituted lithium nickelate, and to evaluate the effects of this substitution on the thermal stability and electrochemical behavior of the resulting solids. Having in mind the solubility limits for iron substitution in lithium nickelate found in the literature, a sample with Fe to Ni ratio of 1 to 9 was used as starting material. Chemical lithium deintercalation of the ceramic products was achieved by acid treatment with aqueous hydrochloric acid solutions room temperature. The chemical composition of the samples showed that the Fe to Ni ratio remained unaffected through acid treatment. In contrast, the atomic Li to Ni ratio decreased significantly down to ca. 0.5 after acid treatment, which may be taken as indicative of a chemical desintercalation process. Moreover, the infrared spectra did not agree with the presence of hydrogen in the acid treated solids. An electrochemical proof that the nickel ions were oxidized by the chemical deintercalation process, was obtained by measuring cell

potentials of non-aqueous electrolyte lithium cells. The initial OCV value after relaxation was ca. 3.6 V, while 3.0 V were obtained with the fully intercalated oxide. Heat treating the deintercalated solids leads to the formation of rock-salt structure solids. The transformation temperature increases with iron content, giving special stability which is an interesting factor for batteries working under abusive conditions.

GG9.8

ELECTROCHEMICAL SYNTHESIS UNDER HYDROTHERMAL CONDITIONS OF α -, β -, AND γ - MnO_2 AND Li INSERTION BEHAVIOUR OF SELECTED COMPOUNDS. Laurie I. Hill, Romain Portal, Annie Le Gal La Salle, Alain Verbaere, Yves Piffard, and Dominique Guyomard, Institut des Materiaux Jean Rouxel, Laboratoire de Chimie des Solides, CNRS - University of Nantes, Nantes, FRANCE.

γ -Manganese dioxides are of technological interest due to their applications in primary and secondary lithium batteries as well as primary Zn alkaline batteries. α - MnO_2 is also of interest for use in secondary lithium batteries. An advantage of these Mn-based materials is their low cost and low toxicity. The structure of γ - MnO_2 consists of an intergrowth of pyrolusite, or β - MnO_2 , (rutile structure, 1x1 channels) and ramsdellite MnO_2 (1x2 channels). Therefore, samples of γ - MnO_2 can be characterized by the structural parameters P_r and M_t , where P_r corresponds to the amount of pyrolusite intergrowth contained in the material and M_t corresponds to the amount of microtwinning defects. These parameters can be determined by analysis of the X-ray diffraction pattern of a γ - MnO_2 material. Lower values of P_r and M_t generally lead to higher Li insertion capacities. [S. Sarciaux, A. Le Gal la Salle, A. Verbaere, Y. Piffard, and D. Guyomard, Mat. Res. Soc. Symp. Proc., **548**, 251(1999).] Using a hydrothermal-electrochemical synthesis route, we have synthesized a number of MnO_2 materials with α -, β -, or γ -structures. The γ - MnO_2 materials obtained are characterized by low P_r and M_t values compared to those found in γ - MnO_2 compounds prepared by traditional methods. The effect of variations in the synthesis conditions on the type of structures obtained and also on the structural parameters of the γ - MnO_2 materials obtained, as well as the lithium insertion properties of these materials, will be presented.

GG9.9

LITHIUM DEINTERCALATION IN $\text{LiNi}_{0.30}\text{Co}_{0.70}\text{O}_2$: REDOX PROCESSES, ELECTRONIC AND IONIC MOBILITY AS CHARACTERIZED BY ^7Li MAS NMR AND ELECTRICAL PROPERTIES. Dany Carlier, Michel Ménétrier, Claude Delmas, Institut de Chimie de la Matière Condensée de Bordeaux-CNRS and Ecole Nationale Supérieure de Chimie et Physique de Bordeaux, Pessac, FRANCE.

$\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ materials exhibit a layered structure built from alternate sheets of $(\text{Ni},\text{Co})\text{O}_6$ and of LiO_6 octahedra sharing edges. They are particularly interesting as positive electrode in lithium-ion batteries. The ^7Li MAS NMR spectra are sensitive to the presence of paramagnetic cations as nearest and next-nearest neighbours as low-spin Ni^{3+} in $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$. These contact shift (or Fermi contact) interactions are used to yield information on the lithium environment [1]. Electrochemically deintercalated $\text{Li}_x\text{Ni}_{0.30}\text{Co}_{0.70}\text{O}_2$ phases are characterized by XRD, ^7Li MAS NMR, electronic conductivity and thermoelectronic power. Ni^{3+} oxidation to Ni^{4+} occurs at the beginning of deintercalation, leading to a $\text{Ni}^{3+}/\text{Ni}^{4+}$ hopping which causes an exchange of the ^7Li NMR signals. The presence or not of lithium which do not interact with nickel ions (but with only diamagnetic Co^{3+} as 1^{st} and 2^{nd} neighbors) allows to discriminate between an electronic and an ionic exchange phenomenon, depending on composition and temperature. For x close to 0.70, an increase of the shift with temperature is observed, which is assigned to a hopping between Ni^{4+} and Co^{3+} . Therefore, the question as to which ion is actually oxidized during deintercalation is somewhat irrelevant around this composition. Finally, for $x < 0.70$, the presence of Ni hinders a true long-range electronic delocalisation between $\text{Co}^{4+}/\text{Co}^{3+}$ (LS) as it happens in Li_xCoO_2 ($x < 0.70$) [2]. However, electrons are clearly not localized, as seen from NMR and thermoelectronic power coefficient. [1] C. Marichal, J. Hirschinger, P. Granger, M. Ménétrier, A. Rougier and C. Delmas, Inorg. Chem., **34**, 1773 (1995). [2] M. Ménétrier, I. Saadoune, S. Levasseur, C. Delmas, J. Mater. Chem., **9**, 1135 (1999).

GG9.10

SOL-GEL SYNTHESIS AND PERFORMANCE OF AMORPHOUS DOPED LITHIUM MANGANESE OXIDES AS CATHODES FOR RECHARGEABLE LITHIUM BATTERIES. Fan Zhang, Marco Giorgetti and William H. Smyrl, Corrosion Research Center, Dept of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN.

Transition metal oxides have been widely studied for cathode

materials in Li secondary batteries. Lithium manganese oxides are of current interest as lithium insertion electrodes. The materials are being widely investigated because of attractive properties, such as high insertion potential and capacity, low cost and minimal environmental impact. Sol-gel processes are well known in the electrochemistry field because of their intrinsic ease of use at low temperature and low cost combined with the ease of manipulation. Recently, we developed a new approach for the preparation of amorphous doped lithium manganese oxides as cathode materials. The synthesis was based on the reaction of lithium permanganate with lithium fumarate in aqueous media. Lithium fumarate was prepared by reacting at 60 degree an aqueous solution of LiOH with fumaric acid. Lithium permanganate was prepared by ion exchange of the corresponding potassium salt. Solutions of the two salts were mixed and added to the hydroxide of the doping metal, then cured overnight at room temperature to obtain a hydrogel. Briefly, water in the hydrogel was first exchanged with acetone and then with hexane to form a suspension of the oxides. Aerogel powder was obtained by drying the hexanogel at moderate temperature under vacuum (60 degree). Ti, V, Fe, Co, Ni, Cu, Zn, Mg and Al doped in amorphous lithium manganese oxide compounds were discovered. These compounds were characterized by X-ray powder diffraction, electron microprobe, ICP, TGA and EDS. They reacted readily with lithium with capacity exceeding 220mAh/g and their electrochemical behavior in lithium cells was determined.

Acknowledgment: This work was supported by DOE under grant DE-FG02-93ER14384.

GG9.11

⁷Li-MAS NMR STUDIES OF LITHIATED MANGANESE DIOXIDE TUNNEL STRUCTURES: PYROLUSITE AND RAMSDELLITE. Younkee Paik, Young Joo Lee, Clare P. Grey, SUNY Stony Brook, Dept of Chemistry, NY.

Manganese dioxides are used worldwide as cathodes in lithium and zinc primary batteries. These cathodes contain the highly disordered manganese dioxide EMD (electrolytic manganese dioxide), which consists of an intergrowth of the pyrolusite and ramsdellite structures. In order to understand the mechanism of intercalation in this complex material, our work has focussed on understanding the intercalation processes that occur in the model systems pyrolusite (β -MnO₂) and ramsdellite (R-MnO₂). ⁷Li MAS NMR spectroscopy has been used to study these systems since it represents an ideal method for probing the local atomic and electronic environments of the lithium ions. The one-dimensional 1x1 and 1x2 tunnel structures, β -MnO₂ and R-MnO₂, respectively, were chemically intercalated with LiI. Two ⁷Li resonances were observed in lithiated pyrolusite at -9 and 110 ppm, which were assigned to Li ions in two different sites of the 1x1 tunnel surrounded by Mn(III) ions. Three ⁷Li resonances were observed in lithiated ramsdellite at very different frequencies (600, 110 and -1 ppm). The resonance at 600 ppm, which is observed at low lithium intercalation levels, is assigned to Li ions coordinated to both Mn(III) and Mn(IV) ions in the tetrahedral site of the 1x2 tunnel, while the resonance at 110 ppm is due to Li near Mn(III) ions and appears at higher Li levels. The resonance at 1 ppm is associated with a long spin-lattice relaxation time (T₁ = 100 ms) and is assigned to Li ions in diamagnetic local environments, either on the surface of the R-MnO₂ particles or in the form of impurities such as Li₂O or Li₂CO₃. Extensions of this work to study EMD following discharging lithium primary cells are now underway.

GG9.12

ALUMINUM BASED ANODE MATERIALS FOR LITHIUM BATTERIES. Shoufeng Yang, Peter Zavalij, M. Stanley Whittingham, State University of New York at Binghamton, Institute for Materials Research, Binghamton, NY.

Aluminum based binary compounds have large capacity as future anode materials compared with the industry standard graphite. Compounds such as Al_{0.43}C_{0.57}, AlB₂ and AlN will be tested with lithium as the counter electrode. We tested Al_{0.43}Si_{0.57} and found about 2.2 moles of lithium could be intercalated, a corresponding capacity about 2100A-h/kg, almost six times of the capacity for graphite, but it faded quickly due to the structural deterioration. The further work will be done to improve the reversible capacity with several approaches.

GG9.13

LITHIUM CONDUCTIVITY OF A PEROVSKITE-TYPE Li-Sr-Ta-Zr-O SOLID ELECTROLYTE. C.H. Chen, K. Amine, E. Sperling and G. Henriksen, Electrochemical Technology Program, Chemical Technology Division, Argonne National Laboratory, Argonne, IL.

High lithium-ion conductivity, especially at room temperature, and chemical stability against metallic lithium and lithiated graphite negative electrodes are two main requirements for a solid electrolyte

in an all solid-state lithium battery. Perovskite-type materials ABO₃ in which A=La, Li and B=Ti exhibit high lithium ion conductivities, with a bulk conductivity at 30°C of 1.2 mS/cm and a grain-boundary conductivity of 0.03 mS/cm [1]; this solid electrolyte is only stable above 1.6 V (vs. Li⁰) because Ti(IV) can be reduced to Ti(III) below this voltage. Argonne National Laboratory has developed a new, highly conducting perovskite-type Li-Sr-Ta-Zr-O structure, in which the A and B cations of SrZrO₃ are partially substituted by Li and Ta, respectively. Four compositions were selected and synthesized to find an optimal composition. Sintering temperatures between 1200 and 1400°C were used to determine the optimum synthesis conditions. X-ray diffraction was used to identify the crystalline phases within the sintered products. The lithium-ion conductivity of these materials was measured by AC impedance spectroscopy. The sample with optimized composition, Li_{3/8}Sr_{7/16}Ta_{3/4}Zr_{1/4}O₃, exhibited a bulk lithium-ion conductivity at 30°C of 0.2 mS/cm and a grain-boundary conductivity of 0.13 mS/cm. This solid electrolyte was found to be stable between 0 and 2.5 V against metallic lithium.

Reference:

1. C.H. Chen and K. Amine, submitted to Solid State Ionics.

GG9.14

A COMPOSITE IONIC-ELECTRONIC CONDUCTOR OF (Ca,Sr,Ba)-Bi OXIDES. James K. Meen, Oya A. Gökçen, D. Ivester, I-C. Lin, Karoline Müller, Binh Nguyen, and Jochen Saar, Dept of Chemistry and Texas Center for Superconductivity, Univ of Houston, Houston, TX.

The rhombohedral alkaline earth-bismuth oxide phase, an oxygen ion conductor, does not coexist stably with an electronic conductor in any of the three binary systems, Ca-Bi oxide, Sr-Bi oxide, Ba-Bi oxide. A rhombohedral phase containing Ba and Sr or Ca or both is in thermodynamic equilibrium with the electronic conductor BaBiO₃ and a stable composite ionic-electronic conductor may be synthesized. The range of composition of the rhombohedral phase that coexists with BaBiO₃ at 725°C in the Sr-Ba-Bi ternary system is Ba/(Ba Sr) approximately 0.25-0.90 (cat.%) with Bi cation content ranging from 0.72% (Sr-rich) to 0.80% (Ba-rich). In the Ca-Sr-Ba-Bi quaternary system at the same temperature, a rhombohedral phase with Ca:Sr:Ba from 0.05:0.05:0.90 to 0.40:0.35:0.25 coexists with BaBiO₃. Although the conductivity of the rhombohedral phase (at constant Bi:[Ca Sr Ba]) is fairly insensitive to the mixture of alkaline earth elements, the polymorphic transformation temperature and the upper thermal stability limit of the rhombohedral phase are both strong functions of Ca:Sr:Ba. The Ba-Bi rhombohedral phase transforms to the high-temperature form that has much greater ionic conductivity) at the lowest temperature the lowest temperature we measured is 510°C. The Ca-Bi phase transforms at the highest temperature we have measured temperatures as high as 732°C. (To a first approximation the transformation temperature changes with cation composition in a linear manner.) The thermal stabilities of the rhombohedral phase and of the biphasic assemblage tend to be higher for the Ca-rich than for the Ba-rich variants. The temperature range over which a useful composite conductor can operate is, therefore, strongly dependent upon the bulk composition of the system.

GG9.15

VAPOR PHASE SYNTHESIS OF NANOSTRUCTURED ENERGY STORAGE MATERIALS. Amit Singhal, Ganesh Skandan, Nanopowder Enterprises Inc., Piscataway, NJ; Glenn Amatucci, Telcordia Technologies, Red Bank, NJ.

Small rechargeable (or secondary) batteries are being used in increasing number to power portable equipment such as, power tools, computers, camcorders, toys, and wireless communication devices. There is a tremendous demand for rechargeable batteries with high energy density, good cycling life, light-weight, and low cost with reliability and safety. Nanostructured materials with specific characteristics are finding use in energy storage applications. We have developed a new vapor phase process, called Combustion Flame Chemical Vapor Condensation (CF-CVC), where discrete nanoparticles with a metastable structure have been produced to enhance electrochemical properties of electrode materials in rechargeable Li-ion batteries. Nanopowders of V₂O₅, CoO_x and Sn/SnO_x were developed using our vapor phase process for producing both positive and negative electrodes. Preliminary results on electrodes made from this powders are most promising. For example, positive electrodes made of nano V₂O₅ have shown a specific energy of 900 Wh/kg in a Li-metal cell. In addition, the discharge-charge curve of nano - V₂O₅ is continuous. In contrast, commercial V₂O₅ has a stepwise curve, which is unsuitable for practical rechargeable Li-ion batteries. In this presentation, the nanopowder production process and the electrochemical characteristics of these nanopowders in a rechargeable Li cell, will be discussed.

GG9.16

SYNTHESIS AND CHARACTERIZATION OF MANGANESE

VANADIUM OXIDES. Katana Ngala, Peter Zavalij and Stanley Whittingham, Inst for Matls Research & Dept of Chemistry, State Univ of New York at Binghamton, Binghamton, NY.

Hydrothermal synthesis of a novel compound, $Mn_9V_2O_5 \cdot nH_2O$, using NH_3 as the structure directing template has been accomplished. It has been indexed using the triclinic unit cell parameters; $a=10.989(1)$, $b=15.413(2)$, $c=3.786(0)$, $\alpha=91.432(9)$, $\beta=90.000(7)$ and $\gamma=98.899(4)$. The δ -phase compound, $[(CH_3)_4N]_x Mn_9V_2O_5 \cdot nH_2O$, synthesized by our group by using tetramethylammonium hydroxide as the organic template, demonstrated a high electrochemical capacity of about 220mAh/g. By controlling the pH of the reaction and the Mn:V ratio, a more pure δ -phase has been synthesized. The syntheses and electrochemical performances of these compounds will be discussed. This work was supported by Department of Energy.

GG9.17

MICROPOROUS RUTHENIUM OXIDE FILMS FOR ENERGY STORAGE APPLICATIONS. J.P. Zheng, Q.L. Fang, Department of Electrical and Computer Engineering, Florida A&M University and Florida State University, Tallahassee, FL.

The ruthenium oxide is one of most promising materials for electrochemical capacitors with high power and high energy density due to its high specific capacitance, high conductivity, and good electrochemical reversibility and stability. In this paper, high porous ruthenium oxide films were prepared using ruthenium ethoxide solution at low temperatures. The specific capacitance of the ruthenium oxide film electrode made with ruthenium ethoxide solution is much higher than that made using the traditional ruthenium chloride solution. It was found that amorphous form ruthenium oxide films with high porosity could be formed at temperatures of 100-200°C. At temperatures above 250°C, crystalline form ruthenium oxide films were formed. Electrochemical capacitors were made with ruthenium oxide film electrodes and were tested under constant current charging and discharging. The maximum specific capacitance of 560 F/g was obtained from the electrode prepared at 200°C. The interfacial capacitance increased linearly with increasing the film thickness. A value of interfacial capacitance as high as 4 F/cm² was obtained from the electrode prepared at 200°C.

GG9.18

EXPERIMENTAL STUDY OF IONIC CONDUCTIVITY AND DEFECTS OF CaO-DOPED CeO₂ ELECTROLYTE MATERIALS. Yuanzhong Zhou*, Xi Chen, Dept. of Physics, Huazhong University of Science and Technology, Wuhan, CHINA. *Currently with Fairchild Semiconductor, South Portland, ME.

The defects and ionic transmission characteristics of CaO-doped ceria have been investigated by electrical measurement, structure characterization and positron annihilation experiment. The study demonstrated CaO-doped CeO₂ could be a good oxygen ion conductor with high conductivity and low activation energy. The materials $(CeO_2)_{1-x}(CaO)_x$ with $0.05 < x < 0.3$ was prepared from CeO₂ and CaCO₃ by solid state reaction. Electrical conductivity was measured by impedance spectrum method. It indicated that the materials has high conductivity. The Arrhenius plots showed that the conductivity has a higher activation energy, which depends on concentration of CaO, for low temperature ($< \sim 600C$) and a lower activation energy of around 0.58eV for high temperature ($> \sim 600C$). The ionic transference number was measured by concentration cell of oxygen at temperature 400C-960C. It demonstrated that dopant CaO effectively suppressed electronic conductivity in ceria and the material is a pure ionic conductor. The analysis of X-ray diffraction and EDX indicated that the materials consists of single phase of fluorite-type solid solution at $x < 0.15$. When $x > 0.15$, the materials is a mixture of fluorite-type solid solution and rock-salt CaO. The concentration of free oxygen vacancies reached maximum at $x \sim 0.12$, as indicated by positron lifetime and electrical conductivity.

GG9.19

TWO DIFFERENT INTERACTIONS BETWEEN OXYGEN VACANCIES AND DOPANT CATIONS FOR IONIC CONDUCTIVITY IN CaO-DOPED CeO₂ ELECTROLYTE MATERIALS. Yuanzhong Zhou*, Xi Chen, Dept. of Physics, Huazhong University of Science and Technology, Wuhan, CHINA. *Currently with Fairchild Semiconductor, South Portland, ME.

The electrical measurement have indicated that the conductivity of CaO-doped CeO₂ has a higher activation energy for low temperature ($< \sim 600C$) and a lower activation energy for high temperature ($> \sim 600C$). The activation energy for low temperature is also a function of CaO concentration. Two different models of interaction between oxygen vacancy and doped cation have been used to interpret the different activation energies in the plots of conductivity vs. reciprocal temperature. Diffusion based on hopping of oxygen ions was assumed as the mechanism of electrical conduction. Oxygen

vacancies were assumed to present as either individual vacancies or defect association with dopant calcium ions. Theoretical analysis indicated that in high temperature region electrical conductivity is dominated by individual oxygen vacancies and activation energy is for oxygen ion hopping. In low temperature region, however, conductivity is dominated by oxygen vacancies associated with doped calcium ions and activation energy is the energy for hopping of one oxygen ion plus half of the association energy between one oxygen vacancy and one calcium ion.

GG9.20

DEFECTS AND TRANSPORT IN CERIA-PRASEODYMIA SOLID SOLUTIONS. Todd Stefanik, Harry Tuller, Massachusetts Institute of Technology, Cambridge, MA.

While semiconductor gas sensors find widespread use, they often suffer from limited gas selectivity. Unlike conventional semiconducting materials such as tin oxide, cerium oxide and related fluorite solid solutions provide flexibility in properties via control of both electronic and ionic conductivity. As part of a program to examine ceria-praseodymia solid solutions as gas sensing materials, the bulk defect chemistry in the system has been studied.

GG9.21

PREPARATION AND CHARACTERIZATION OF NANO-CRYSTALLINE Ca_{1-x}Sn_xF₂ WITH FLUORIDE-ION CONDUCTING PROPERTIES. Georges Dénès, Kun Guo, Philippe Hébert, Jérôme Le Nouvel, and Zhimeng Zhu, Concordia University, Dept. of Chemistry and Biochemistry, Laboratory of Solid State Chemistry and Mössbauer Spectroscopy, and Laboratories for Inorganic Materials, Montréal, Québec, CANADA.

The highest fluoride ion conductivity is found in tin(II)-metal(II) fluorides, where the metal(II) is a large alkaline earth (Sr or Ba) or lead. In addition, their conductivity is purely ionic, i.e. the transport number for electron is very small ($\tau_e < 0.01$). PbSnF₄ is the highest performance fluoride-ion conductor and it has found applications in chemical sensors. However, the combination of tin(II) and lead(II), two weak metals in suboxidation states, in the same material, results in instability under oxidizing conditions. Tin(II) cannot be eliminated, since we established earlier that it is necessary for enhancing the fluoride ion conduction. It is therefore tempting, in order to minimize the chance of sample oxidation, to replace lead(II) by alkaline earth metals, which are very stable in the divalent state, and have no suboxidation state. The systems containing strontium and barium are presently under investigation in our laboratory. The system containing calcium was examined by another group in an earlier study, and was reported to give poorly crystalline materials, and the reactions were not reproducible. We have re-examined it and found that the lack of reproducibility reported earlier was due to some conditions of preparation that were not known to be important and were not controlled properly. We have identified these conditions, and with adequate control, two hitherto unknown materials have been identified, crystalline CaSn₂F₆ and the microcrystalline Ca_{1-x}Sn_xF₂ solid solution. Their preparation and characterization will be presented.

GG9.22

Abstract Withdrawn.

GG9.23

ESR SPECTRAL OBSERVATION OF LITHIUM INSERTION BEHAVIOUR OF VANADIUM MOLYBDENUM OXIDE.

Mika Eguchi, Fumihiko Maki, Satomi Iwabe, Yoshihiro Momose, Ibaraki Univ, Dept of Material Science, Fac of Engineering, Ibaraki, JAPAN.

The effects of structural modification caused by substitution of Mo for a part of V in V₂O₅ on structural changes upon lithium insertion were investigated. For this purpose $(V_{1-y}Mo_y)_2O_5$ ($y=0.25$) was synthesized, and its insertion behaviour and structural changes upon lithium insertion were analysed by ESR method. In $(V_{0.75}Mo_{0.25})_2O_5$, the phases except for the starting material were not observed upon lithium insertion, and no phase transformation characteristics of V₂O₅ occurred. From ESR measurement, a broad singlet signal of V(IV) was found, but those of Mo(V) were not detected. The line width of the signal V(IV) increased steeply at $0.7 < x < 1$. The open circuit potentials became less noble with increasing x, and dropped steeply at $0.7 < x < 1$. These dependencies closely correlate with structural changes estimated from results of ESR and XRD analyses. At $2.7 < x$ ω -phase oxide was formed.

GG9.24

THERMAL ANALYSIS OF TYPE-I GERMANIUM CLATHRATES. Sandra B. Schujman, Dept. of Physics, Applied Physics and Astronomy, Rensselaer Polytechnic Institute, Troy, NY, George S. Nolas, Marlow Industries, Inc., Dallas, TX; Glen A. Slack, Dept. of

Physics, Applied Physics and Astronomy, Rensselaer Polytechnic Institute, Troy, NY.

The compounds $\text{Eu}_8\text{Ga}_{16}\text{Ge}_{30}$ and $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ crystallize with the Type-I hydrate clathrate structure with either Eu or Sr filling up the clathrate cages. We made simultaneous Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) on these two compounds that show that they melt congruently, the one filled with Eu at a lower temperature than the one filled with Sr. This result implies that the vibrations of the guest atom affect the overall properties of the lattice, instead of the melting point being just a property of the framework. We will present results measured on these compounds and also on materials with intermediate compositions.

GG9.25

INTERSTITIAL ATOMS IN Mn_5Si_3 TYPE STRUCTURES.

Robert Schneidmiller, S. Kuriakose, Joseph W. Kolis, Terry M. Tritt, Clemson Univ, Clemson, SC.

Mn_5Si_3 type structures possess the ability to accommodate a wide range of interstitial atoms. These atoms can form two chains in the unit cell, $\text{A}_5\text{B}_3\text{Z}$, where A = transition metal, B = main group and Z = various interstitial atoms. Changes in lattice parameters of $\text{A}_5\text{B}_3\text{Z}$ have been correlated to specific Z atoms in many of these compounds. Electronic effects of Z on A_5B_3 compounds have been studied much less. We report the synthesis of several Mn_5Si_3 type structure compounds with interstitial atoms and measurement of their thermoelectric properties.

GG9.26

DEVELOPMENT OF A POROUS FeSi_2 THERMOELECTRIC CONVERSION ELEMENT FOR A RECIPROCATING FLOW COMBUSTION SYSTEM. Futoshi Katsuki, Toshiro Tomida, Sumitomo Metal Industries Ltd, Corporate Research and Development Laboratories, Amagasaki, JAPAN; Akihiro Takata, Sanyo Special Steel Co., Ltd, Technological Research Laboratory, Himeji, JAPAN; Masahiro Katoh, Tokyo Tungsten Co., Ltd, Research and Development Division, Toyama, JAPAN.

Thermoelectric elements and power generation systems, which convert heat into electricity, have been extensively studied. Recently, Echigo et al., have proposed a novel thermoelectric power generation system¹, using a porous thermoelectric device. In the proposed reciprocating flow combustion system, a flammable gas flows through the porous element and combustion occurs at an end of the element, leading to a large temperature difference between the inlet and the outlet of the element. This steep temperature difference in the element is favorable for the thermoelectric conversion with high performance. Such porous elements should be oxidation-resistant at high temperatures and perform in the wide temperature range. Although a compound semiconductor FeSi_2 can be an appropriate material with respect to these requirements, there have been few reports on porous FeSi_2 elements. In the present study, heavily porous FeSi_2 bulky materials for thermoelectric conversion elements have been developed via a spark plasma sintering process². The element with a porosity ratio of about 45% was molded into a U-type thermoelectric device, in which the p-type and n-type FeSi_2 were separated by a insulating glass fiber sheet. Ni sheet electrodes were firmly attached, simultaneously by the sintering process, to the surface of the element. Thermoelectric properties were evaluated to examine its potential for the power generation as a gas-combustion type thermoelectric device. Measured thermoelectric power and apparent internal resistivity of the porous element are 0.5 - 0.7mV/K at 300 - 500K and $1 \times 10^{-2} \Omega\text{m}$ at RT respectively. In the reciprocating flow combustion system, the large temperature difference of about 250K/cm was formed in the porous element with length of 17mm, and thermoelectromotive force reached at 230mV. 1) R. Echigo et al., Proc. 10th Int. Heat Transf. Conf., Brighton, 3(1994), 173. 2) F. Katsuki et al., Mater. Trans., JIM, 41(2000), 624.

GG9.27

IMPROVEMENT OF THERMOELECTRIC PROPERTIES OF OXIDE CERAMICS BY CHEMICAL DOPING AND NANOSTRUCTURAL CONTROL. Masanobu Awano, Yoshinobu Fujishiro, Hiroyoshi Takagi, Natl. Industr. Res Inst. of Nagoya, JAPAN; Motoyuki Miyata, Kunihiro Maeda, Synergy Ceramics Laboratory, Nagoya, JAPAN.

Oxide ceramics were examined for their possible application as thermoelectric materials on the view point of precisely controlled carrier doping by chemical processing and high electrical conductivity with effective phonon scattering by three dimensional nanostructure control technique. Uniform doping of small amount of Nb, Ta and Sb in titania ceramics to increase the carrier concentration was successfully proceeded by chemical doping. Enhancement of electrical conductivity over two order higher than the sintered body fabricated

conventionally at optimum doping amount was revealed. Additional Zr doping improved thermal stability of dopants through the cyclic heating and cooling condition by the role of Zr as an effective diffusion suppressor in titania crystalline lattice. In-situ analysis of microstructure development and the dependence of electrical properties on structural factors by TEM and SEM were attempted. Segregation of dopants at grain boundaries were observed through heating of polycrystalline sample upto 1000 degree C when without suppressor. Segregation of nanoparticles in matrix effective for phonon scattering was observed in controlled heating schedule. Micro four-probe electrical analysis in selected region for intra- and inter-grain clarified the relation between microstructure and conductivities.

GG9.28

ELECTRODEPOSITION OF THERMOELECTRIC NANOWIRE COMPOSITES.

Amy L. Prieto¹, Marisol Martín-González¹, Joseph F. Behnke², Melissa S. Sander¹, Angelica M. Stacy¹, Ronald Gronsky², Timothy Sands². ¹Department of Chemistry, University of California, Berkeley, CA. ²Department of Materials Science, University of California, Berkeley, CA.

Dimensionally restricted materials present a wide range of potential applications, ranging from thermoelectric power generation to information storage and processing. We have focused on the synthesis of nanowire composites of thermoelectric materials¹. Nanowires are promising materials for thermoelectric applications because quantum confinement has been shown to increase thermoelectric efficiency²⁻⁴. We have used electrochemical methods to synthesize and fill porous anodic alumina. We have electrodeposited nanowires of varying diameters of Bi_2Te_3 , CoSb_3 , and Bi-Sb. Characterization of the nanowire/porous Al_2O_3 composite materials using X-Ray diffraction (XRD) to determine the phase, degree of crystallinity, and orientation of the nanowires will be presented. We have also used scanning electron microscopy (SEM) in conjunction with energy dispersive spectroscopy (EDS) to determine the extent of pore-filling, the morphology, and the composition of the resulting composite materials. ¹G. Mahan, B. Sales, J. Sharp, Physics Today 1997, 50, 42. ²T.C. Harman, P.J. Taylor, D.L. Spears, M.P. Walsh, J. Electron Mater 2000, 29, L1. ³R. Venkatasubramanian, T. Colpitts, E. Watko, J. Hutchby, IEEE 15th International Conference on Thermoelectrics 1996, 454. ⁴S. Cho, A. DiVenere, G.K. Wong, J.B. Ketterson, J.R. Meyer, Phys.Rev. B-Condensed Matter 1999, 59, 10691.

GG9.29

NICKEL DETERMINATION BY COMPLEXATION UTILIZING A FUNCTIONALIZED OPTICAL WAVEGUIDE SENSOR.

Erin S. Carter, Klaus-Hermann Dahmen, Florida State University, Dept of Chemistry, Tallahassee, FL.

This research focuses on the design of chemically functionalized optical waveguide sensors. The waveguide is an optically transparent solgel coated onto a glass substrate chip. By having a higher refractive index than the substrate, the waveguide internally reflects a laser beam to photodetectors at both ends of the chip. The adsorption of any species onto the waveguide surface changes the light propagation, and therefore its effective refractive index, N. The change in N is dependent upon the amount of analyte present. By covalently bonding specific chemical receptors onto its surface, it can be designed to target a particular analyte. This research involves functionalizing the surface of the waveguide with ED3A, EDTA, and with a nitrilotriacetic acid (NTA) moiety in order to complex out of solution Ni^{2+} and/or Ca^{2+} . The change in N and the thickness of the adlayer will allow the concentration to be determined.

GG9.30

Abstract Withdrawn.

GG9.31

CONTINUOUS WAVE LASER ACTION FROM LANTHANIDE DOPED NANOALUMINA POWDERS, SYNTHESIS AND PROPERTIES. R.M. Laine, T. Hinklin, S. Rand and G. Williams, Depts. of MS&E, Chemistry and the Applied Physics Division, University of Michigan, Ann Arbor, MI.

Nanosized delta-alumina powders doped with lanthanides can be produced by flame spray pyrolysis (FSP) of very simple, low cost aluminum precursors doped with ceria. This scaleable synthesis route produces single crystal nanopowders at $\dot{\sim}$ 100 g/h with surface areas of 50-120 m²/g. Typical powders consist of homogeneously doped unaggregated single crystals, with particle sizes ranging from 10-30 nm average diameter. Similar micron sized powders are exploited for their cathodoluminescence behavior. By reducing the size of the particles and thus the interparticle cavity, the scattering regime is changed from diffusive to strong scattering causing photon localization. Lasing occurs due to the localization within the gain medium. Details

concerning the alkoxide chemistry, flame spray pyrolysis, and the lasing behavior of nanosized doped powders will be discussed.

GG9.32

SYNTHESIS AND CHARACTERIZATION OF $Sb_{0.75}(III)Sb_{0.75}(V)TiO_5$: A NEW NON-CENTROSYMMETRIC MIXED VALENT ANTIMONY TITANIUM OXIDE. N.S.P. Bhuvanesh, I. Rusakova, P. Shiv Halasyamani, Department of Chemistry, University of Houston, Houston, TX.

The synthesis and characterization of a new mixed valent antimony titanium oxide, $Sb_{0.75}(III)Sb_{0.75}(V)TiO_5$, is reported. Powder X-ray and electron diffraction measurements are consistent with a C-centered monoclinic cell with $a = 16.532(1)\text{\AA}$, $b = 4.7862(4)\text{\AA}$, $c = 5.4375(4)\text{\AA}$, and $\beta = 91.097(2)$. A structural model based on a layered intergrowth of Sb_2O_3 and rutile-type sheets is presented. Powder non-linear optical measurements, using 1064nm light, indicate $Sb_{0.75}(III)Sb_{0.75}(V)TiO_5$ is SHG active.

GG9.33

FIRST PRINCIPLES SIMULATIONS OF ELEMENTARY RE-OXIDATIVE REACTIONS ON THE $SnO_2(110)$ SURFACE. Ben Slater, Richard Catlow, The Royal Institution of Great Britain, London, UNITED KINGDOM; David Williams, Dept of Chemistry, London, UNITED KINGDOM; Marshall Stoneham, Dept of Physics and Astronomy, London, UNITED KINGDOM.

We have recently carried out a concerted study of elementary re-oxidation reactions occurring at the $SnO_2(110)$ surface. Stannic oxide is a widely used, tuneable gas-sensor and combustion catalyst, where the surface chemistry plays a crucial part in determining surface conductivity and gas sensing action. Despite the widespread application of SnO_2 as a gas sensor, there is no generally accepted model which can account for observations such as increased conductivity of a partially reduced SnO_2 surface in the presence of oxygen, a phenomenon which is fundamental in the sensing process. In this work we describe how first principles methods (embodied in the VASP program) and employed on massively parallel resources, have been used to elucidate mechanistic, dissociative reaction pathways at the surface, of strategic importance within the general Mars and van Krevelen reaction. Specifically we describe the relative energetics of dissociating O_2 , O_2^- and O_2^{2-} at perfect and reduced surfaces and the subsequent effect on surface conductivity. Furthermore, we relate our predictive results to recent experimental work on the iso-structural $TiO_2(110)$ surface.

GG9.34

OPTICAL PROPERTIES AND UPCONVERSION FLUORESCENCE IN Er^{3+} -DOPED ZnA GLASS. X. Zhang, S. Buddhudu, K. Pita, Y.L. Lam, C.H. Kam, Photonics Research Group, Division of Microelectronics, School of Electrical and Electronic Engineering, Nanyang Technological University, SINGAPORE; E. Daran, LAAS-CNRS, Toulouse Cedex, FRANCE.

Rare earth doped fluoride glasses are suitable host materials for short wavelength lasers, optical amplifiers and optical waveguide devices in the infrared region. The well-studied ZrF_4 -based system, ZBLAN, suffers from several problems like low chemical durability, low mechanical strength and low glass transition temperature in the respect of practical applications.

In this work, we report the optical properties and upconversion emission of Er^{3+} doped in a new ZrF_4 -based glass system namely $ZrF_4-ZnF_2-AlF_3$ and labeled as ZZnA. The ZZnA glass was prepared in a similar way to the ZBLAN glass, and the typical glass composition was $20ZrF_4-30ZnF_2-25AlF_3-10BaF_2-14YF_3-1ErF_3$. Compared to ZBLAN glass, ZZnA shows several important advantages including high chemical stability, high mechanical strength and excellent glass forming characteristics.

Room temperature absorption spectra for 1% Er^{3+} doped ZZnA glass have been recorded in the range of 200 to 1100 nm. Judd-Ofelt intensity parameters (Ω_t with $t=2, 4, 6$) have been calculated by fitting the absorption bands observed in the spectra. The Ω_2 value ($2.29 \times 10^{-20} \text{ cm}^2$) is smaller than that obtained in ZBLAN glass ($2.91 \times 10^{-20} \text{ cm}^2$), which indicates a higher covalence of ZZnA glass than ZBLAN glass. With the obtained Ω_t values, the radiative transition probabilities and the branching ratio have been calculated. Upon 800 nm laser excitation, Er^{3+} doped ZZnA glass shows intense upconversion emission at both 25 K and 300 K. The most intense emission was observed in green from $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition. Other two emission bands are in red to $^4F_{5/2} \rightarrow ^4I_{15/2}$ transition and in blue to $^2H_{9/2} \rightarrow ^4I_{15/2}$ transition. At room temperature, a weak band due to $^2H_{11/2} \rightarrow ^4I_{15/2}$ transition has been also detected between 515 and 535 nm. According to the energy level of Er^{3+} , all the upconversion emissions result from a two-step process except the blue one, which is owing to a three-step process. The upconversion mechanisms will be discussed in the paper.

GG9.35

SOFT-CHEMISTRY SYNTHESIS OF LITHIUM NICKEL DIOXIDE BASED MATERIALS FOR RECHARGEABLE BATTERIES. V. Manivannan, C.-K. Park, W.B. Ebner, Chul Chai, SKC America, NJ; D.-J. Ihm and Y.-J. Shim, SKC Co., Ltd, Chonan City, KOREA.

Soft-chemistry methods of synthesis, which have good control over the particle engineering, are increasingly used to overcome the difficulties associated with the processing of doped Lithium Nickel Dioxide materials. Problems associated with the synthesis and performance such as stoichiometry, specific capacity and poor cycle life, force researchers to look for possible manipulations in the Nickel system. Presence of dopants like Co would preserve structural integrity, enhance compositional controllability and suppress irreversible capacity. Wet processing technique like sol-gel provide a convenient way of synthesizing materials of high quality because of their inherent advantage in controlling powder microstructure (grain size, morphology etc.) which in turn affect the agglomeration of the particles and overall stoichiometry of the materials. Thus, tailor-making materials with the desired structure-property relationship are achievable by these low-temperature synthetic routes. In this presentation, we show the application of such methods for the synthesis of doped Lithium Nickel Dioxide materials. As an example, several members of the series Lithium Nickel Cobalt Dioxide are prepared, their electrochemical performance studied with respect to the choice of precursor materials and their results are compared.

GG9.36

NO DECOMPOSITION PROPERTY OF LANTHANUM MANGANITE POROUS ELECTRODES. Kazuyuki Matsuda, Takao Kanai, Fine Ceramics Research Association, Synergy Ceramics Laboratory, Nagoya, JAPAN; Masanobu Awano, National Industrial Research Institute of Nagoya, Nagoya, JAPAN; Kunihiro Maeda, Fine Ceramics Research Association, Synergy Ceramics Laboratory, Nagoya, JAPAN.

NOx decomposition property of electrochemical cells composed of YSZ solid electrolyte and $La_{1-x}(Ca,Sr)_xMnO_3$ porous electrodes were examined. $La_{1-x}(Ca,Sr)_xMnO_3$ powders were prepared by solid-state reaction using corresponding metal oxides and carbonates. The powders were dispersed in polyethylene glycol and screen-printed on both sides of the electrolyte pellet. The electrochemical decomposition of NO was carried out in the temperature range from 873 to 1173K by passing a mixed gas of 1000ppm NO and 2% O_2 in He. The concentration of NO and N_2 in the outlet gas from the reactor was monitored by a NOx gas analyzer and gas chromatography, respectively. NO was reduced to N_2 and O_2 , when the DC voltage was applied to the cell. The applied voltage dependence of NO decomposition was investigated. It was shown that the NO decomposition ratio increased with the increase of the applied voltage. The effects of temperature and dopants on the NO decomposition property were also investigated.

Research supported by AIST, MITI, Japan, under the Synergy Ceramics Project, part of the work supported by NEDO.

SESSION GG10: SOLID-STATE IONICS, BATTERY MATERIALS, ENERGY STORAGE

Chairs: Miguel A. Alario-Franco and Clare P. Grey
Thursday Morning, November 30, 2000
Room 304 (Hynes)

8:30 AM GG10.1

BISMUTH ENHANCED ELECTROCHEMICAL STABILITY OF COBALT HYDROXIDE USED AS ADDITIVE IN Ni/CD AND Ni/MH BATTERIES. Valerie Pralong, Agnes Delahaye-Vidal, Bernard Beaudoin, Jean-Marie Tarascon, University of Picardie Jules Verne, Laboratory of Reactivity and Chemistry of Solids, Amiens, FRANCE.

For performance purposes, the electrochemically active positive electrode in Ni-based rechargeable alkaline batteries consists of $Ni(OH)_2$ particles coated with $CoOOH$. The positive attributes of the $CoOOH$ coating, however, vanish upon cycling because it transforms into Co_3O_4 or even $Co(OH)_2$ through dissolution-crystallization processes. The benefit of adding Bi-based salts or bismuth oxide to prevent these phase transformations will be presented by detailing the reaction mechanisms. From chemical and electrochemical studies, coupled with potentiometric titration and UV-visible spectroscopy, we will demonstrate that the positive effect of Bi additives is twofold. Firstly, Bi adsorption onto the Co-surface modifies the $CoOOH$ chemical reactivity and thereby its dissolution. Secondly, since bismuth forms Bi-Co-oxohydroxo complexes in solution, as experimentally proved, it delays the precipitation of the Co_3O_4 and $Co(OH)_2$ phases during cycling. Finally, an implementation of these

findings towards the most efficient use of nickel positive electrodes containing Co-based additives will be shown.

8:45 AM **GG10.2**

METAL - MESOPOROUS SILICA - COMPOSITES AS POTENTIAL HYDROGEN STORAGE SYSTEMS. Michael Froeba, Univ of Erlangen-Nuernberg, Inst of Inorg Chem, Erlangen, GERMANY; Ralf Koehn, Univ of Hamburg, IAACH, Hamburg, GERMANY; Jan Hanss, Yu-Hong Zhang, Armin Reller, Univ of Augsburg, Solid State Chemistry, Augsburg, GERMANY.

The storage of hydrogen in metals, i.e. as metal hydrides is one of the most relevant features of the fast growing hydrogen technology, which plays a key role in the emerging regenerative energy systems. The extensive use of metal hydrides as hydrogen storage systems is limited by either thermodynamic reasons, or by the diffusion of hydrogen through bulk material, or by the non-reversibility of the hydriding / dehydriding i.e. charging / discharging cycles (usually leading to textural changes of the metals or alloys) or by the price of the best suited metals or alloys. Nevertheless, in practical devices metal hydrides are used successfully, e.g. La-Ni-hydrides in advanced high performance batteries. Recent studies have confirmed that in the cavities of mesoporous silica of the MCM family metals or metal compounds can be immobilized. Moreover, XAS and thermogravimetric studies gave evidence for the reversible reduction and re-oxidation of metal oxides within the pores of the silica matrix. Here we report on the synthesis and the characterisation of metal - mesoporous silica - composites. The formation and the degradation of the metal hydrides within the matrix has been investigated by XAS spectroscopy as well as by combined thermogravimetry / mass spectrometry. The reactivity of the metal hydride - silica - composite in air and oxygen - a most important feature in terms of safety for practical applications - has been tested by combined thermogravimetry, differential scanning calorimetry and mass spectrometry. On the basis of all experimental findings the relevant potentials such as storage capacity, charging/discharging cycle stability, etc. are discussed.

9:00 AM ***GG10.3**

RECENT DEVELOPMENTS IN ANODE AND CATHODE MATERIALS FOR LITHIUM-ION ELECTROCHEMICAL CELLS. Michael M. Thackeray, John T. Vaughan and Christopher S. Johnson, Chemical Technology Division, Argonne National Laboratory, Argonne, IL.

State-of-the-art lithium-ion electrochemical cells use a lithiated-graphite negative electrode (LiC_6) coupled to a lithium-cobalt-oxide positive electrode (LiCoO_2) via an organic electrolyte. Because lithiated graphite electrodes operate at a potential only a few tens of millivolts above that of metallic lithium, there remain concerns about the inherent safety of lithium-ion cells, particularly when they reach the top of charge at approximately 4 V. Furthermore, LiCoO_2 is a relatively expensive material compared to other metal oxides, for example, those based on nickel or manganese. There is, therefore, a requirement to find alternative negative and positive electrodes to combat these safety and cost issues. In this presentation, recent advances that have been made to develop intermetallic insertion (negative) electrodes that operate at a few hundred millivolts above Li^0 , particularly those with nickel-arsenide- and zinc-blende-type structures, will be discussed. Lithium-manganese-oxide electrodes that are resistant to the transformation to a spinel-type structure and that offer the possibility of challenging LiCoO_2 as the positive electrode material of choice will be highlighted.

10:00 AM **GG10.4**

LI-INSERTION BEHAVIOR IN NANOCRYSTALLINE TiO_2 - $(\text{MoO}_3)_z$ CORE-SHELL MATERIALS. Gregory J. Moore, Annie Le Gal La Salle, Dominique Guyomard, Institut des Matériaux Jean Rouxel, CNRS-University of Nantes, FRANCE; Scott H. Elder, Pacific Northwest National Laboratory, Richland, WA.

Materials have been synthesized consisting of a TiO_2 core having MoO_3 on the surface as a shell, noted TiO_2 - $(\text{MoO}_3)_z$. The core-shell design ranges in a variety of sizes from 40-100 Å with a varying extent z of coverage, from a partial to a double layer, depending on the quantity of Mo in the reactants. The full study of the Li insertion behavior of a series of these core-shell materials, having a range of different coverage, has been carried out in order to determine the influence of the MoO_3 shell. Calculations have been done on the theoretical lithium capacity of these materials, using a maximum capacity of $\text{Li}_{0.5}\text{TiO}_2$ for the core, and $\text{Li}_{1.5}\text{MoO}_3$ at the $\text{TiO}_2/\text{MoO}_3$ interface, and they have been compared to that found experimentally. The reversible Li-insertion capacity was shown to increase from 0.2 to 0.9 Li per transition metal when the MoO_3 coverage increased to one monolayer. No Li insertion plateau related to the $\text{TiO}_2/\text{MoO}_3$ interface was observed. The redox voltage of the $\text{TiO}_2/\text{Li}_{0.5}\text{TiO}_2$ biphasic transformation increased with the MoO_3 coverage, up to 60

mV for one monolayer. This surprising effect was interpreted as due to a change in TiO_2 surface charge coming from the surface inductive effect of Ti-O-Mo bonds. On a more applied point of view, the cycling properties will be reported for these materials upon successive Li-insertion/deinsertion cycles. An introduction will be provided of the synthesis and general characterization of these materials but the emphasis will be given to the electrochemical study along with the interest of such compounds as negative electrodes of Li-ion batteries.

10:15 AM **GG10.5**

TRANSPORT PROPERTIES OF $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$. A.C. Palaniduz and H.L. Tuller, MIT, Dept of MS&E, Cambridge, MA.

$\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ (LSF) is considered as a model system in the quest for an oxygen permeation membrane material with satisfactory long-term properties. Four-probe equilibrium conductivity, heat-pulse thermopower, and coulometric titration measurements have been made on bulk LSF. Electron blocking thin films of yttria-stabilized zirconia are formed on bulk LSF samples by pulsed laser deposition, in order to measure the ionic conductivity of LSF as a function of partial pressure and temperature with two probe impedance spectroscopy. A tentative defect model is discussed with an emphasis on membrane requirements.

10:30 AM **GG10.6**

PARTIAL DISORDER INDUCED IN $(\text{Sc}_z\text{Yb}_{1-z})_2\text{Ti}_2\text{O}_7$ PYROCHLORE BY VARYING CHEMISTRY AND TEMPERATURE: AN IN SITU NEUTRON DIFFRACTION STUDY OF A POTENTIALLY FAST-OXYGEN CONDUCTING SYSTEM. Kevin W. Eberman, 3M Company, St. Paul, MN; Bernhardt J. Wuensch, M.I.T., Department of Materials Science and Engineering, Cambridge, MA.

Pyrochlores of the type $\text{A}_2\text{B}_2\text{O}_7$ crystallize in a superstructure of a defect fluorite $(\text{A,B})\text{O}_{1.75}$ array, with the cations ordered in alternating rows along $\langle 110 \rangle$. The anions fill two of the three types of available tetrahedral sites, leaving the third normally vacant. We find it fascinating that compounds with this structure generally prove to grossly violate Paulings Rules for the structure of an ionic crystal. We have recently reported a detailed structural study of a ternary B-site system consisting of three solid solutions $(\text{Y}_z(\text{B}'_y\text{B}''_{1-y}))_2\text{O}_7$ with Zr, Sn, and Ti, filling the B-site) by means of Rietveld refinement of neutron diffraction data. Compounds exist within these systems that have oxygen conduction sufficient to make them contenders as oxide fuel-cell materials. For these B-site substitution systems it was found that both tin and titanium rich compounds were fully ordered, but the substitution of zirconium for either tended to produce disorder. The Zr end-member is completely disordered, having the defect fluorite structure type. Partial disorder induced by substitution of Zr for either Ti or Sn produced the potentially interesting fast-ion conductors. Since the Sn(IV) cation in the 8-fold coordination of this structure is 97% the size of the Zr(IV) cation, it is clear that the preferred bonding and not the size of the cation determines the structure in this system. Both Sn(IV) and Ti(IV) in simple oxides are in 8-fold, but Zr(IV) is in 7-fold, coordination. In the present paper we describe the results of well over 500 Rietveld refinements of neutron diffraction data collected as a function of temperature and oxygen partial-pressure for the A-site substitution system, $(\text{Sc}_z\text{Yb}_{1-z})_2\text{Ti}_2\text{O}_7$. Partial disorder was observed for these systems as the average size of the A-cations decreased towards that of Ti(IV). Once present, disorder in these compounds was found to increase gradually above 1000C. We relate the observation of partially disordered states for $0.2 < z < 0.4$ to Zr substitution in the yttrium-based systems previously examined. Finally, we apply a more sophisticated model extending Pauling's Rules (proposed by I.D. Brown) to this system in an attempt to rationalize the crystal structures observed.

10:45 AM **GG10.7**

VANADIUM OXIDE FRAMEWORKS MODIFIED WITH TRANSITION METALS. Peter Y. Zavalij, M. Stanley Whittingham, Chemistry Department and Materials Research Center, State University of New York at Binghamton, Binghamton, NY.

The great interest in vanadium compounds is due to their potential use both as cathode materials for advanced lithium batteries and as catalysts. The special characteristics of vanadium that distinguishes it from other transition metals consists in wide range of oxidation states (from 5 to 3 and even 2), the often present vanadyl group, its red-ox properties and whole spectra of coordination polyhedra (tetrahedra, trigonal bipyramids, distorted and regular octahedra). Naturally, such great variety of oxidation states and coordination polyhedra results in even greater variety of vanadium oxide frameworks: from chains and tunnel structures through single and double sheets layers to 3D nets. Some of our earlier work of the pure vanadium oxide frameworks has been published as a review [1]. Often the vanadium oxide frameworks are modified with such transition metals as Mn, Fe, Co, Ni, Cu, Zn and others, which have usually octahedral coordination. Introduced

into vanadium oxide these metals produce additional variables for structural chemistry as well as for applications. Thus, the transition metals relatively to the vanadium oxide framework can play different roles. They can be simply a part of framework (ordered or disordered), they can form pillars or links between vanadium oxide chains, layers or clusters, or they can occupy cavities, tunnels or interlayer space without much interaction with main framework. Interacting with vanadium oxide framework transition metals modify the electronic configuration and therefore compound stability and properties that provides additional variable in the search for new materials. This work presents the structural analysis of modified vanadium oxide framework as well as reports on interesting new structures, such as $tma_4[Zn_4V_2O_8] \cdot 4H_2O$.

1. P.Y. Zavalij and M.S. Whittingham, Acta Cryst. B55, 627-663 (1999).

11:00 AM **GG10.8**

ATOMISTIC SIMULATION OF THE STRUCTURE AND PROPERTIES OF $Sr_4Fe_6O_{13}$. Craig A.J. Fisher, Japan Fine Ceramics Center, Nagoya, JAPAN; M. Saiful Islam, Dept of Chemistry, Univ of Surrey, UNITED KINGDOM.

An atomistic simulation model has been used to study the structure and defect energetics of the mixed ionic/electronic conductor $Sr_4Fe_6O_{13}$. Parameters were fitted to a Born-Mayer two-body potential function (incorporating the Shell Model to take into account electronic polarization) and the orthorhombic crystal structure, which consists of alternate layers of perovskite-type and rock salt-type units, successfully reproduced. Results of calculations of intrinsic (vacancies and interstitials) and extrinsic (dopant) structural and electronic defects will be reported. The most likely oxide ion migration pathway, based on calculations of stationary points between jump sites, will also be discussed.

11:15 AM **GG10.9**

STUDY OF THE STRUCTURAL CHANGES AND IONIC MOTION IN $MSnF_4$ ($M = Pb, Ba, Sr$) AND α - AlF_3 , WITH ^{19}F MAS NMR AND MOLECULAR DYNAMICS SIMULATIONS. Santanu Chaudhuri, F. Wang, Clare P. Grey, SUNY Stony Brook, Department of Chemistry, NY; Michael Castiglione, Mark Wilson, Paul A. Madden, Physical and Theoretical Chemistry Laboratory, University of Oxford, Oxford, UNITED KINGDOM.

A combination of solid state NMR and molecular dynamics (MD) computer simulations has been used to investigate the structure and dynamics of a series of fluorides. The fluoride fast ion conductor $PbSnF_4$ has one of the highest conductivities measured to date, and is used as an oxygen sensor. Despite this, the structural details and mechanism of conduction are still poorly understood. $PbSnF_4$ adopts a fluorite-related structure consisting of double Sn and Pb layers. The fluoride ions occupy sites between the Pb-Pb and the Pb-Sn layers but the Sn-Sn layers are almost completely vacant. ^{19}F MAS NMR supports a high degree of motion of the fluoride ions, while ^{119}Sn NMR shows that the local environment of the tin is extremely distorted, consistent with the presence of a stereo-active lone pair. $BaSnF_4$ adopts a similar structure, but NMR results show that the tin sites are even more distorted in this compound, and that a number of different fluorine sites are present, each associated with different mobilities. MD simulations using the Polarizable Ion Model were carried out to help explain the NMR results and determine the nature of inter and intra-layer motion of the fluoride ions. These simulations reproduce the M-M, Sn-Sn double layers and the 5-coordinate environment of Sn [1] but show significant differences in the arrangement of fluoride ions around the 5-coordinate tin atoms between the two structures, increased disorder being observed in the Pb system. Conduction occurs primarily in the M-Sn layers. In a second set of materials, the effect of motion on the structure and phase transitions in a series of ReO_3 /perovskite-related materials has been investigated. For example, the rocking of the tilted AlF_6^{3-} octahedra in α - AlF_3 , and the phase transition from a rhombohedral to a cubic structure have been investigated by using MD simulations, X-ray diffraction and NMR.

[1] G. Denes, Y.H. Yu, T. Tyliczaczac, A.P. Hitchcock, J. Solid state chem., 1991, 91, 1.

11:30 AM **GG10.10**

PROTONIC CONDUCTING PROPERTIES OF SOL-GEL DERIVED ORGANIC/INORGANIC NANO-HYBRID MEMBRANE DOPED WITH ACIDIC MOIETIES. Itaru Honma, Shigeki Nomura*, Hitoshi Nakajima, Electrotechnical Laboratory, AIST, Tsukuba, Ibaraki, JAPAN. *Sekisui Chemical Co. Ltd., Osaka, JAPAN.

High temperature protonic conducting polymer membrane has been synthesized through the sol-gel processing of organic/inorganic nanocomposites consisting of SiO_2 /PEO,PPO, PTMO hybrid materials. The hybrid membrane doped with acidic moieties such as 12-phosphotungstic acid (PWA) shows good protonic conductivities

at high temperatures above 100°C. The membrane was found to be thermally stable at high temperatures because of the temperature tolerant inorganic SiO_2 framework in the composite matrix. Protonic conductivities of approximately 10-3 S/cm at 160°C have been achieved at humid condition. The organic/inorganic hybrid membrane can be identified as a remarkable family of proton conducting solid polymer electrolytes which, potentially, provides new technological applications in the high temperature electrochemical devices including electrochromic displays, chemical sensors and fuel cells.

SESSION GG11: THERMO POWER, THERMAL EXPANSION, OPTICAL MATERIALS

Chairs: Arthur W. Sleight and George S. Nolas
Thursday Afternoon, November 30, 2000
Room 304 (Hynes)

1:30 PM ***GG11.1**

"OPEN STRUCTURE" SEMICONDUCTORS: CLATHRATE AND CHANNEL COMPOUNDS FOR LOW THERMAL CONDUCTIVITY THERMOELECTRIC MATERIALS. George S. Nolas, R&D Division, Marlow Industries, Inc., Dallas, TX.

In a good semiconductor the electrons (or holes) propagate through the lattice structure of well ordered atoms without being scattered by the coherent vibrations of the crystal. Thus semiconductors are good conductors of electrons (or holes) and as such have given rise to modern microprocessors that are revolutionizing the way we live. In the same semiconductors the vibrations of the lattice atoms mainly carry the heat. Due to the covalent nature of the bonding in these materials the thermal conductivity is very large. These are therefore poor materials for thermoelectric applications. If the atomic vibrations, or phonons, can be localized so that the heat transfer is essentially an atom-to-atom propagation, then the thermal conduction can be drastically reduced. A semiconductor can, in principle, have the thermal conductivity of a glass. Amorphous semiconductors are of course very poor conductors of electricity therefore one does not want the electrons to propagate through a glass-like material. Instead one wants the electrons to travel as though they only "see" the well-ordered, periodic structure of a crystal while the phonons are scattered by localized disorder within the covalently bonded lattice. "Open structure" semiconductors do, in fact, exist and recent research has given rise to new thermoelectric materials.

2:00 PM **GG11.2**

EVALUATING THE EFFECTS OF MATERIAL COMPOSITION, BOUNDARY CONDITIONS AND LOCALIZED DEFECTS ON THE THERMOELECTRIC PERFORMANCE OF SEMICONDUCTOR SUPERLATTICES. Peter P.F. Radkowski III, Timothy D. Sands, University of California, Graduate Group in Applied Science and Technology, Berkeley, CA.

The charge and heat currents of superlattices are sensitive to material composition, lattice periodicity, temperature, and applied electric field. To evaluate the effects of material composition and nanoscale dimensions on the performance of thermoelectric devices, a compositional superlattice of n-doped polar semiconductor materials is modeled. The electronic band structure is defined by the Kronig-Penney model. Electron scattering is dominated by Frohlich interactions with optical phonons. The optical phonon modes can be associated with the well and barrier heterolayers. Acoustic phonons provide the lattice heat conduction. Because the time scales of electron-phonon and phonon-phonon scattering differ by several orders of magnitude, the electron temperature significantly differs from the lattice temperature. Furthermore, nonequilibrium optical phonon populations may be hotter than acoustic phonons. A benchmark solution is generated by matching electron and phonon boundary conditions. This benchmark is compared to a discrete simulation of the coupled scattering of electrons and phonons. The advantage of the discrete simulation technique is that it can address complex boundary conditions, irregularities in the superlattice periodicity, and localized material defects.

2:15 PM **GG11.3**

STRUCTURE, MAGNETIC AND TRANSPORT PROPERTIES OF ALKALINE EARTH GERMANIUM BASED AND LANTHANIDE GERMANIUM BASED CLATHRATE COMPOUNDS. J. Daniel Bryan, Galen Stucky, University of California - Santa Barbara, Dept of Chemistry and Biochemistry, Santa Barbara, CA.

The quest for more efficient thermoelectric devices has driven the search for new compounds displaying the uniquely balanced transport properties needed for thermoelectric applications. Using a variety of traditional solid state techniques as well as new synthetic techniques we have taken a two-prong approach in this search:(1) synthesis and characterization of new phases of alkaline earth or lanthanide

clathrate compounds; (2) modification of known phases of clathrates by doping using procedures adapted from semiconductor processing technology. Examples from both approaches will be presented. Compounds were characterized by single-crystal x-ray diffraction, and magnetic and transport measurements.

2:30 PM *GG11.4

NEGATIVE THERMAL EXPANSION AND OXYGEN MIGRATION IN FRAMEWORK STRUCTURES. John S.O. Evans, Department of Chemistry, University of Durham, South Road, Durham, UNITED KINGDOM.

There has been considerable recent interest in the structural and physical properties of materials which show the unusual property of negative thermal expansion. Such materials have potential importance in applications where the expansion coefficient of composite bodies needs to be tailored to precise positive, negative or even zero values. A series of recent experiments have shown that cubic zirconium tungstate (ZrW_2O_8) shows large negative thermal expansion over a wide (2-1050 K) temperature range, and have provided significant insight into the physical origins of this phenomenon. The occurrence of negative thermal expansion seems to be closely associated with structural instabilities. Zirconium tungstate has been shown to undergo a number of structural phase transitions, which give further insight into the unusual properties of this material. Under an applied pressure of 0.2 GPa a phase transition involving oxygen migration to a more condensed orthorhombic form occurs; on heating the material to around 450 K a phase transition involving the dynamic migration of oxygen atoms occurs. Oxygen migration at such low temperatures in the solid state is highly unusual. Recent results indicating oxygen migration at much lower temperatures (as low as 200 K) in materials in the $ZrW_{2-x}Mo_xO_8$ family will be presented. The implications of these and other phase transitions in structurally related materials will be discussed.

3:30 PM *GG11.5

NITRIDOSILICATES, SIONS, AND SIALONS - FROM STRUCTURAL CERAMICS TO OPTICAL MATERIALS. Wolfgang Schnick, University of Munich (LMU), Dept of Chemistry, Munich, GERMANY.

The formal substitution of N by O in conventional silicates (oxo-silicates) has led to a novel class of compounds called the nitridosilicates. The most famous representative of these substance class is binary silicon nitride, which is one of the most important non-oxidic ceramic materials. A partial substitution of Si by Al and O by N leads to the oxonitrido-aluminosilicates (so-called sialons) which due to their outstanding materials properties play an important role during sintering processes of silicon nitride ceramic materials. From a structural point of view the manifold group of natural and synthetic oxosilicates (with all their applications) but also the nitridosilicates, the oxonitridosilicates (sions), and the nitridoaluminosilicates, as distinct subgroups derive from the sialons. Therefore a huge manifold of structural possibilities and properties may occur in all of these substance classes. In this presentation a brief outline of the synthesis, structures, and materials properties of novel nitridosilicates, oxonitridosilicates (sions), and the oxonitridoaluminosilicates (sialons) will be presented. Possible applications include advanced structural ceramics (hard materials, micro-structured materials), optical materials (fluorescence, 2-photon absorption, thermoluminescence, NLO), zeolite-analogous framework structures, or layer-like materials.

4:00 PM GG11.6

FILMS OF TRANSPARENT p-TYPE CONDUCTORS WITH THE DELAFOSSITE STRUCTURE. M.K. Jayaraj, A. Draeseke, J. Tate, N. Duan and A.W. Sleight, Center for Advanced Materials Research, Oregon State University, Corvallis, OR.

Thin films of $Cu(Y_{1-x}Ca_x)O_2$ that are p-type conductors with significant transparency in the visible have been prepared by thermal evaporation. Calcium doping was necessary to produce conductive films. The highest conductivity is about 1.0 S/cm, and the average transparency for conducting films about 250nm thick is about 40% - 50% in the visible region and about 70% for a 350-nm film in the infrared. The optical spectra give evidence for a band gap of about 3.5 eV in the more transparent undoped material. Polycrystalline transparent films of $CuScO_{2-x}$ which show p-type electrical conductivity have been prepared by rf sputtering on amorphous substrates. The temperature dependence of the conductivity indicates semiconducting behavior with an apparent room temperature activation energy of 0.11 eV. The highest room temperature conductivity observed was 30 S/cm. Films 110 nm thick show 40% transparency in most of the visible and become much more transparent in the infrared. The p-type behavior of $Cu(Y_{1-x}Ca_x)O_2$ and $CuScO_{2-x}$ films was confirmed by the Seebeck effect.

4:15 PM *GG11.7

NEW MATERIALS FOR HIGH-POWER LASER SYSTEMS. Douglas A. Keszler, Oregon State University, Department of Chemistry, Corvallis, OR.

Continued miniaturization of mechanical and electronic devices, improved manufacturing methods, and unique medical procedures are driving the need for new all solid-state high-power, short-wavelength laser systems. At present, the operational characteristics of these systems are largely limited by the capabilities of nonlinear optical (NLO) materials. In this contribution, I will highlight new NLO materials that have allowed an order-of-magnitude increase in UV laser power over the past few years. The factors limiting the current performance characteristics of these materials will be considered, and the prospects for substantially increasing both wavelength transparency and output powers will be addressed.

4:45 PM GG11.8

SPECTRAL PROPERTIES OF VARIOUS CERMIUM DOPED GARNET PHOSPHORS FOR APPLICATION IN WHITE GaN-BASED LEDS. Jennifer L. Wu, Dept of Chemical Engineering, Steven P. Denbaars, Dept of Materials, Vojislav Srdanov, Dept of Chemistry, University of California-Santa Barbara, Santa Barbara, CA; Henry Weinberg, Symyx Technologies, Santa Clara, CA.

Recently, a renewed research interest has emerged for the development of visible light, down-converting phosphors for application in white light emitting diodes (LEDs). In such devices, a blue GaN LED can act as the primary light source, exciting photoluminescence in a phosphor with subsequent broad-band emission occurring at lower energies. It was recently reported that use of a combinatorial approach to synthesize and screen potential inorganic phosphors for such an application could aid in identifying improved phosphors for blue to yellow down conversion. Using solution chemistry techniques developed by Symyx Technologies, solid state thin-film arrays (libraries) based on the garnet structure $(A_{1-x}B_x)_{3-z}(C_{1-y}D_y)_5O_{12}:Ce^3_z$, where A, B = Y, Gd, Lu, La; C, D = Al, Ga, Sc, Bi; x and y = 0 to 1.0; and z = 0.03, were synthesized. X-ray diffraction was used to select library samples of the crystalline garnet phase. Libraries of these various garnets were then characterized, and their spectral properties compared to traditionally prepared bulk powder phosphors of similar composition. Emission and excitation trends show that as larger cations are substituted for Y (A = Y), emission and excitation are red-shifted and as larger cations are substituted for Al (C = Al), emission and excitation are blue-shifted. If smaller cations are substituted for Y and Al an opposite trend is observed. Lifetimes and quantum efficiencies are also examined for these down-conversion phosphors. Studies show that phosphor composition can be optimized with respect to color point and quantum efficiency. By varying the garnet composition, which controls the color of the white LED, and by taking advantage of the ability to tune the wavelength of blue excitation light through changes in the indium composition of InGaN, a more efficient white LED may be realized.