SYMPOSIUM FF

Solid-State Chemistry of Inorganic Materials V

November 29 - December 2, 2004

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* Invited paper

SESSION FF1: Synthesis of Novel Materials
Chairs: Nathaniel Brese and Cora Lind
Monday Morning, November 29, 2004
Room 200 (Hynes)

8:30 AM *FF1.1
Hydrothermal Synthesis of Alkali and Alkaline Earth Borates for Deep UV Optical Applications. Joseph William Kolis[1], Colin McMillen[1] and Taina Franco[1]; [1]Chemistry, Clemson University, Clemson, South Carolina; [2]Chemistry, Clemson University, Clemson, South Carolina; [3]Chemistry, Clemson University, Clemson, South Carolina.

The demands for deep UV (150-200nm) optical applications are high. Materials must be transparent over a wide range and have high optical damage thresholds. For non linear optical (NLO) applications it must be acentric, polarizable and non-cubic for phase matching. There are very few materials with these characteristics. Metal borates have many attractive properties for deep UV optical applications. They have very wide bandgaps and exceptionally high optical damge thresholds. In particular, they have a greater than average tendency to form acentric crystal structures. They are difficult to grow as high quality single crystals by conventional melt or flux techniques however, as they have a high tendency to form glasses. As amphiprotic oxides however, borates are almost ideal materials for hydrothermal crystal growth. Despite these promising characteristics there has been almost no work done on hydrothermal synthesis and crystal growth of borates. In this talk we will present a series alkali and alkaline earth borates along with their structures and physical properties. In particular, the mixed alkaline earth borates show exceptional promise. For example Sr2Be2B2O7 is reported to have some exceptional NLO properties but crystal growth is problematic. We will present a very promising hydrothermal growth method for this intriguing material. The chemistry of other mixed alkaline earth borates will also be presented. Several lithium borates with exceptionally high bandgaps will also be introduced.

9:00 AM FF1.2
Crystal Chemistry of Some Organically Templated Metal Fluorides. Philip Lightfoot and Nicholas Stephens; Chemistry, Univ. of St Andrews, St Andrews, United Kingdom.

The solvothermal chemistry of metal fluorides is relatively unexplored. In particular, the development of organically-templated metal fluorides is in its infancy, in contrast to the corresponding vast metal oxide and phosphate chemistry. Bentrup et al. have reviewed transition metal chemistry of this type: surprisingly, most of these materials consist of isolated polyhedral units, with very few extended-connectivity lattices produced, and no 3-D connected metal fluoride frameworks. More recently, the groups of OHare, Albrecht-Schmitt and Weller have developed the corresponding uranium, zirconium and berylloflouride chemistry, and several extended chain or layer-type structures have been discovered. We have followed up this work by exploring, inter alia, scandium and yttrium fluoride hydrothermal systems. There is vast scope here for exploring novel structural chemistry, and possibly new properties such as luminescence and non-linear optical behaviour. Some recent results will be reviewed.

9:15 AM FF1.3
Influence of Small Organic or Inorganic Species in the Formation of Vanadium Oxides. Olivier Durupthy, Nathalie Steunou, Thibaud Coradin, Jocelyne Maquet and Jacques Livage; Chimie de la Matiere Condensee, University Paris 6, Paris, Ile de France, France.

A large variety of new vanadium oxide has been synthesized from aqueous solutions at room temperature or under mild hydrothermal conditions. Some of them are currently used as positive electrode for lithium batteries or for catalytic applications. The performance of the materials in applications requires the control over the size, the morphology and the surface structure, which is based on the appropriate control of the parameters that influence nucleation and growth. This can be performed by adding some molecular species or cations that can act as structure-directing agents through cooperative interactions with the inorganic component across an organic-inorganic interface. Therefore, this communication deals with the synthesis of vanadium oxides in the presence of inorganic, organic or bioorganic molecules. These species are added to the vanadium precursor in solution at the earliest stages of the polymerization reactions at a pH close to 2. Without foreign species, these polymerization reactions lead to the formation of a $V_2O_5.nH_2O$ gel whose structure and properties were extensively studied. At first, we typically used some chloride salts (NaCl, CsCl, $CaCl_2$, TMACl) and organic or inorganic bases (NaOH, CsOH, $Ca(OH)_2$, TMAOH) to evaluate the effect of pH and ionic strength on the nucleation and growth of a vanadium oxide. This approach was extended to organic (amines, carboxylic acids) and bioorganic molecules (dipeptides, gelatin) that may complex and reduce vanadium. The vanadium oxides incorporating organic molecules or cations were characterized by X-ray diffraction, Scanning and Transmission electron microscopy and ^{51}V solid-state NMR. In addition, identification of the molecular precursors by ^{51}V NMR spectroscopy in solution allows us to suggest some chemical mechanisms describing the formation of the different oxide networks at room temperature and below pH 7. These mechanisms are of interest in regard to a better understanding of an oxide network formation upon condensation of molecular precursors that is still a matter of debate.

9:30 AM FF1.4
A Synthetic Route to the Confinement of Ternary II-II'-VI Nanomaterials Within a Solid-State Inorganic Framework. Elizabeth A. C. Turner, John F. Corrigan and Yining Huang; Department of Chemistry, The University of Western Ontario, London, Ontario, Canada.

There continues to be a dynamic interest in the field of nanocluster materials research. By limiting the size of a cluster to the nanometer-sized regime, these materials exhibit unique *sizedependent* electronic, physical and optical properties that lie between those of the bulk material and molecular complexes. As a result, these new materials have potential uses in future opto-electronic devices. The difficulty in accessing and maintaining the desired nanosized material lies in the ability to kinetically stabilize discrete size selective particles. In the absence of a chemical capping agent, such as an ancillary surface ligand, the material aggregates to the bulk material. An attractive alternative to the use of surface ligands is the use of mesoporous molecular sieves as hosts for cluster growth and confinement. The framework offers a controlled size environment of regular arrays of mesoporous channels with a desirable diameter for the formation of nanomaterials. The framework should yield the ability to control size, shape and arrangement of the nanoparticles within the mesoporous host. MCM-41 has been used extensively in the synthesis and encapsulation of binary semiconducting nanomaterials, but expansion of this approach to ternary MM'E [E = S, Se, Te] nanomaterials remains relatively unexplored. Our approach to the synthesis of MM'E materials [M, M' = Zn, Cd, Hg; E = S, Se] within the pores of MCM-41 involves the incorporation of metal-chalcogenolate precursors into the porous framework. This is achieved via organic functionalization of the pore walls with a chelating ethylenediamine ligand. Subsequent treatment with solubilized zinc acetate, followed by reaction with $E(SiMe_3)_2$ yields silylated zinc-chalcogenolate moieties within MCM-41. The pendant trimethylsilyl groups can readily react with a second solubilized metal acetate salt [$M(OAc)_2$, M = Cd, Hg] whereby there is generation and elimination of $AcOSiMe_3$ and the formation of Zn-E-M bonding interactions. The entire synthesis is contained within the pores of MCM-41, which have an average pore diameter of 3.5 nm and as a result the observed optical properties of the contained ternary materials exhibit the effects of quantum confinement. The modified MCM-41 materials are characterized by PXRD, nitrogen adsorption, TGA, CP MAS NMR (^{13}C, ^{29}Si, ^{113}Cd), IR and Raman spectroscopies, UV-Vis spectroscopy and TEM and EDX analyses.

9:45 AM FF1.5
Silver cluster formation in mesoporous silica obtained by the Sol-Gel method. Lidia Armelao[1], Gregorio Bottaro[1], Renzo Campostrini[2], Stefano Gialanella[2], Marco Ischia[2], Fabrizia Poli[3], Cinzia Sada[4] and Eugenio Tondello[3]; [1]Chemistry, CNR-ISTM - University of Padova, Padova, Italy; [2]Materials Engeneering, University, Trento, Italy; [3]Chemistry, University, Padova, Italy; [4]Physics, University, Padova, Italy.

In recent years, mesoporous based-silica materials having an ordered and controllable arrangement of pores have gained increasing interest, owing to their potential applications in catalysis and optical devices. The self-assembly of nanoparticles into ordered morphologies represents one of the topics in materials science, as it is expected to originate nanostructured systems with unique physical and chemical properties. At this regard, mesoporous materials are suitable candidates for the loading and encapsulation of metal or semiconductor clusters and nanowires. This work reports the use of mesoporous silica materials as molds for the growth of silver nanoparticles, in order to control their size, shape and organization. In particular, mesoporous silica powders have been synthesized via sol-gel starting from aqueous solutions of TEOS under acidic conditions, and using non-ionic alkyl poly(ethylene oxide) oligomeric (Brij76) as structure-directing agent. The introduction of silver ions in the mesoporous silica network was carried out by vacuum impregnation with solutions of silver acetate. Finally, generation of silver nanoparticles in the porous matrix was performed by annealing between 200 and 600C under inert or reducing atmosphere. The obtained mesoporous systems (pure and Ag-loaded silica) were characterized by X-Ray Diffraction (XRD), N2 BET adsorption and

X-ray Photoelectron Spectroscopy (XPS). Moreover the optical properties of the nanocomposite materials were studied by means of UV-Vis absorption spectroscopy. TEM analysis was performed with the aim to obtain information on both particle size and particle location in the ordered mesoporous matrix. Relevant results concerning the relations between the synthesis and annealing conditions, and particle size are presented and discussed.

10:30 AM *FF1.6
The Synthesis and Characterization of Ultra-incompressible, Hard Transition Metal Borides. Richard B. Kaner[1,2], Robert Cumberland[1], Michelle Weinberger[1], Sarah Tolbert[1], John Gilman[2] and Simon Clark[3]; [1]Chemistry & Biochemistry, University of California, Los Angeles, Los Angeles, California; [2]Materials Science & Engineering, University of California, Los Angeles, Los Angeles, California; [3]Lawrence Berkeley National Laboratory, Berkeley, California.

High bulk modulus, ultra-hard materials are highly sought after due to their usefulness in a wide variety of industrial applications. These include abrasives, cutting tools and coatings where wear prevention, scratch resistance, and surface durability are a priority. Here we report the synthesis and characterization of an ultra incompressible material, osmium diboride (OsB2). X-ray powder diffraction carried out under pressures up to 32 GPa reveal a bulk modulus of 395 GPa based on fitting the unit cell volume to a third-order Birch-Murnaghen equation of state. This value surpasses other hard materials including silicon carbide (248 GPa), sapphire (252 GPa) and cubic boron nitride (367 GPa) and approaches diamond's bulk modulus (442 GPa). In the c-direction, OsB2 is even slightly more incompressible than diamond. In addition to a high bulk modulus, OsB2 is hard. It readily scratches sapphire, and a nanoindentation test indicates a Vicker's Hardness of >3000 kg/mm2. Research on other transition metal borides will be discussed.

11:00 AM FF1.7
Formation of Intermetallic-Ceramic Composites from Nanoreactants in a Self-Sustaining Reaction Regime. Jan A. Puszynski, Jacek Swiatkiewicz, Shivanee R. Dargar and Lori J. Groven; Chemistry & Chemical Engineering Department, South Dakota School of Mines and Technology, Rapid City, South Dakota.

A combustion synthesis, also called self-propagating high-temperature synthesis, has been found to be an effective and economical production method of advanced ceramic and intermetallic compounds. This method is very suitable for the formation of nonstoichiometric compounds, solid solutions, and refractory composites. Many reacting systems, especially those involving elemental reactants, may generate a sufficient amount of energy to be self-sustaining. In such cases, a reacting system, once initiated by a local energy source, generates a high temperature combustion wave, which propagates throughout the reactants forming more thermodynamically stable products. Typically, for most nanosize reactants the combustion front propagates with a velocity of several hundreds of meters per second compared to micron size reactants which is millimeters or centimeters per second. Combustion temperatures are typically in the range of 2000-3800K. Traditional consolidation techniques, such as high temperature pressureless sintering and hot pressing, have several limitations, including high cost, low throughput, and long exposure to high temperatures, which result in dense products with relatively large grain sizes. In order to reduce the average grain size of sintered materials two important factors must be met: i) submicron size of starting powders and ii) low sintering temperature. It was already demonstrated that many metals or ceramic powders may sinter at much lower temperatures if average particle size is in the range of few nanometers. In this presentation, two nanoreactant energetic systems, TiO2-Al and Ni-Al-Al2O3, will be discussed. Simultaneous combustion synthesis and densification experiments, leading to homogeneous and functionally graded products of the above reactions, have been conducted in an uniaxial press with preheating capability up to 1500K and densification pressures up to 200MPa. The gas atmosphere may be vacuum or inert gas. It has been demonstrated in the case of TiO2-Al system that the product titanium aluminide alumina composite still retains its nanostructure despite of short term exposure to higher temperatures and densification force. Up to now, materials with densities up to 90% of the theoretical density were obtained. Currently, there is an effort underway to minimize the effect of sample preheating by increasing the size of densified powders and increasing the exothermicity of the reacting system (Ni-Al-Al2O3). Several techniques have been used to characterize both reactants and products participating in those exothermic reactions, such as DSC, BET,X-ray diffraction,SEM,TEM,and LIBS. This paper will address several key issues associated with simultaneous combustion synthesis and densification, including the effect of initial composition, average particle size of reactants and diluent, temperature-pressure history, and densification force on combustion synthesized product morphology and its residual porosity.

11:15 AM FF1.8
Design, Synthesis, and Applications of Poly(norbornenyldecaborane), a Single-Source Polymeric Boron Carbide Precursor. Xiaolan Wei[1], Daniel T. Welna[2], Jared D. Bender[2], Larry G. Sneddon[1] and Harry R. Allcock[2]; [1]Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania; [2]Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania.

The new organodecaborane polymer, poly(norbornenyldecaborane) (PND), was readily prepared via the ruthenium catalyzed ring opening metathesis polymerization (ROMP) of 6-norbornenyldecaborane. The polymer was isolated as an air-stable white powder with a molecular weight in excess of 32 kDa. Ceramic conversion studies have shown that PND is a processable single-source precursor to boron carbide ceramic materials. Thermogravimetric analysis (TGA) shows that the polymer weight loss begins near 100oC and is essentially complete by 500oC, with a final char yield of 72%. X-ray diffraction (XRD) and diffuse reflectance Fourier Transform (DRIFT) analyses of bulk ceramic conversions of polymer powders indicated that amorphous boron carbide materials were obtained up to 1300oC, while crystalline materials were obtained at higher temperatures. Polymer blends of allylhydridopolycarbosilane(AHPCS)/PND and polyvinylsiloxane (PVS)/PND gave silicon-carbide/boron-carbide and silicon-oxycarbide/boron-carbide composite materials, respectively.

11:30 AM FF1.9
Hydrolysis of Aluminum Metal, Synthesis of Nano Alumina and Sol Gel Processing of Monoliths.
Thiruchitrambalam Manickavasagam[1] and V. R. Palkar[2]; [1]Dept. of Mechanical Engineeirng, Mahalingam College of Engineering and Technology, Pollachi, Tamil Nadu, India; [2]Condensed Matter Physics, Materials Science Group, Tata Institute of Fundamental Research, Mumbai, Maharastra, India.

High purity alumina is usually prepared using various intermediate aluminium compounds such as aluminium nitrate, aluminium alkoxides etc., as precursors. However there are some disadvantages to these methods; basically related to production, cost and environmental pollution. In fact the above mentioned intermediate aluminium compounds themselves are produced from aluminium metal. The present investigation is concerned with examining the feasibility of using aluminium hydroxides prepared by hydrolyzing aluminium metal, for sol gel processing. The study assumes added significance in view of the recent claims of Alcoa that it is possible to produce high purity aluminium metal in large quantities economically. During the present investigation sols were prepared by using various hydroxides, ie., bayerite, gibbsite and pseudo boehmite. Sol gel transition was observed only in the case of pseudo boehmite sol and this was gelated by either forced gelation method to prepare powders or controlled gelation methods to prepare monoliths. Transparent Xerogels (pseudo boehmite) could be prepared b controlled gelation method but the presence of a thin layer of bayerite often resulted in translucency. Crack free monoliths could be prepared by heating the xerogels at a low heating rate(< 1 degree C/min). It was found that sol gel processed boehmite transformed to alpha alumina at a relatively lower temperature (1080 degree C) than the as prepared boehmite which transformed at about 1200 degree C.

11:45 AM FF1.10
Influence of Precursor Design on the Growth of Nano-materials. Sanjay Mathur, CVD Division, Leibniz Institute of New Materials, Saarbruecken, Germany.

Sanjay Mathur Leibniz-Institute of New Materials Saarland University Campus Building 43 A, Im Stadtwald D-66041 Saarbruecken, Germany E-mail: Smathur@inm-gmbh.de Fundamental to the development of nanoscience and nanotechnology is the availability of high-purity materials exhibiting specific properties, tailored shape and microstructure. Despite extensive research in the synthesis and processing of inorganic materials, producing (nano)materials with precise control over chemical composition, morphology and microstructure remains an overarching task. The conventional synthesis of inorganic materials, controlled by diffusion of ionic and atomic species through both reactants and products, is rather crude for the unit-by-unit assembly of nanostructures. Given the inherent limitations of traditional material processing routes, a number of chemistry-based milder approaches (e.g., sol-gel, self-assembly, chemical vapour synthesis, combinatorial and hydrothermal methods) have been put forward, which appear promising especially in terms of synthesis and composition-structure-property relationships. The transformation of molecular compounds (precursors) in solution or gas phase methods to grow extended frameworks from atomically defined units represents a popular strategy to control the materials synthesis. Metal alkoxides, for instance, in view of pre-formed metal-oxygen bonds are efficient precursors to metal oxides. In the context of

molecule-derived materials, the challenge is to develop synthetic rationales for a customized assembly of molecular building blocks from the fundamental components (metals and ligands) that would allow fabrication of suitable precursor to any desired nanomaterial. Since molecular control of materials is not a predictive science, it is difficult to anticipate the phase structure of the resulting solid from the knowledge of the precursor design. Most of the work performed to demonstrate the strength of chemical methods to achieve a better control over the phase purity and composition of the materials is based on an explanation with hindsight, achieved after concluding the experiment. Therefore, we are developing chemical concepts for a designed materials synthesis. This talk will address the question, whether the molecular structure of the precursor species can influence the phase of the final solid product?

SESSION FF2: Non-oxide Systems
Chairs: Mercouri Kanatzidis and Glen Kowach
Monday Afternoon, November 29, 2004
Room 200 (Hynes)

1:30 PM *FF2.1
Synthetic Approaches, Structure Properties Realations, and Applications of Novel Advanced Nitridic Materials.
Wolfgang Schnick, Department of Chemistry & Biochemistry, University of Munich (LMU), Munich, Germany.

Due to their highly crosslinked covalent network structures, the nonmetal nitrides BN, Si_3N_4, or P_3N_5 exhibit promising properties for the development of novel high-performance materials [1]. In combination with further electropositive elements, ternary and multinary compounds with a wide range of condensation degrees are accessible. For the nitridosilicates [2] anionic substructures of SiN_4 tetrahedrons have been identified, where the N atoms are either terminally bound to Si, or they act as bridging atoms between two, three, or even four adjacent Si atoms. The resulting Si/N network structures contain both corner and edge-sharing SiN_4 units. From a formal point of view, the oxonitridosilicates are related to both classic oxosilicates and nitridosilicates. Despite this similarity, these compounds may exhibit structural characteristics that have not been found in the group of oxosilicates or nitridosilicates. As compared to Si/O compounds considerably fewer oxosilicates and nitridosilicates have been investigated so far. However, already this small number of known compounds suggest a much more versatile structural chemistry as compared to the former group of compounds [3] and thus, one has to expect a broad range of promising materials properties. Due to their high thermal and chemical stability, nitridosilicates and oxonitridosilicates have the potential for the development of advanced optical materials with high refractive indices, or the ability for second harmonic generation [4]. Furthermore, nitridosilicates of rare earth elements may exhibit promising magnetic properties [5] or they might be useful as novel phosphors for light conversion applications [6]. [1] W. Schnick, Angew. Chem. Int. Ed. Engl. 1993, 32, 1580. [2] W. Schnick, H. Huppertz, Chem. Eur. J. 1997, 3, 679. [3] H. Huppertz, W. Schnick, Angew. Chem. Int. Ed. Engl. 1996, 35, 1983. [4] H. Lutz, S. Joosten, J. Hoffmann, P. Lehmeier, A. Seilmeier, H. A. Hoeppe, W. Schnick, J. Phys. Chem. Solids 2004, 65, 1285. [5] H.A. Hoeppe, H. Trill, B. D. Mosel, H. Eckert, G. Kotzyba, R. Poettgen, W. Schnick, J. Phys. Chem. Solids 2002, 63, 853. [6] H.A. Hoeppe, H. Lutz, P. Morys, W. Schnick, A. Seilmeier, J. Phys. Chem. Solids 2000, 61, 2001.

2:00 PM FF2.2
Sol-Gel Deposition of Transition Metal and Silicon Nitride Films. Andrew William Jackson and Andrew Lee Hector; School of Chemistry, University of Southampton, Southampton, Hampshire, United Kingdom.

There is an increasing interest in sol-gel synthesis of nitrides.[1,2,3] Transition metal nitrides have high temperature stability and are widely used in applications including hard coatings and high conductivity diffusion barriers. [4,5,6] Silicon nitride is a popular insulator and encapsulating material in electronics and also useful as a low density ceramic.[7] The ability to deposit films of these materials by dip- or spin-coating will increase the range of applications in which they are viable and is an important step toward general sol-gel processing of nitride materials. Silicon nitride sol-gel precursor chemistry is the most developed part of the field[1-3] and we report the deposition of silicon nitride films by dip-coating, using coating sols produced by the ammonolysis of silicon amides. With transition metals, the ammono based analogue of the well established alkoxy route to oxide precursor gels is inherently difficult to control. The basicity of the system and the overwhelming tendency of the starting materials to favour particle growth mean a precipitate rather than a stable, useful emulsion is produced, unless both environment and synthetic pathway are carefully controlled. Hence reports to date of sol-gel routes to transition metal nitrides describe production of powders.[8] We report work on a sol-gel route to titanium nitride with the ammonolysis of titanium amides controlled by temperature and chemical moderators, resulting in stable emulsions useful for dip-coating. Ongoing work within our group is to increase the application of this technique to other transition metals, to develop better coating sols and to investigate the properties of these films. 1. S. Kaskel, K. Schlichte and B. Zibrowius, *Phys.Chem.Chem.Phys.***4**167 (2002). 2. J. Engering and M. Jansen, *Z.Anorg.Allg.Chem.* **629** 913 (2003). 3. J. S. Bradley, R. Rovai and C. W. Lehmann, *Angew.Chem.Int.Ed.* **38** 2036 (1999). 4. F. Levy, P. Hones, P. E. Schmid, R. Sanjines, M. Diserens and C, Wiemer,*Surf.Coat.Tech.* **120 – 121** 284 (1999). 5. P. Baldus, M. Jansen and D. Sporn, *EnergyRev.* **285** 699 (1999). 6. C. H. Winter, *Aldrichchim.Acta* **33** 3 (2000). 7. U. Schubert and N. Huesing, *SynthesisofInorganicMaterials* (Wiley-VCH, Weinheim, 2000). 8. G.M. Brown, L. Maya, *J.Am.Ceram.Soc.* **71** 78 (1988); B. V. Baxter, M. H. Chisholm, V. F. DiStasi, G. J. Gama, A. L. Hector and I. P. Parkin, *Chem.Mater.* **8** 1222 (1996).

2:15 PM FF2.3
Formation and Characterisation of Amorphous Ti_3N_4.
Andrew Lee Hector and Andrew William Jackson; School of Chemistry, University of Southapton, Southampton, United Kingdom.

Only two of the transition elements in Groups 4 to 6 have well characterised, crystalline nitrides with the metal in its highest oxidation state, namely Zr_3N_4 and Ta_3N_5. This is somewhat surprising for such electropositive elements and the expectation would be that others, e.g. Ti_3N_4 should be accessible. In fact many of these materials have been reported, but as amorphous materials where characterisation is based purely on elemental analysis. These are listed in the Table,[1-4] with the formal metal oxidation states. The phases in brackets are amorphous and poorly characterised. The eventual aim of our work is to anneal precursors to transition metal nitrides under high pressures to produce the crystalline nitrides in their highest oxidation states. However, the amorphous phases are readily accessible, for example the precipitate formed by the action of ammonia on $Ti(NMe_2)_4$ in solution decomposes to amorphous Ti_3N_4 on heating to ca 400°C. Further heating at ambient pressure results in nitrogen loss at around 700°C before crystallisation to TiN. Variations in the conditions used for precursor formation have little effect on the temperature at which Ti_3N_4 is formed and decomposes, but do induce changes in the composition. For example precursors with much lower organic content or containing significant amounts of azide can be produced. These are significant points when it comes to minimising the carbon content and maximising nitride content, especially since these reactions have the potential to be used in sol-gel processing of metal nitrides. We will also present work on the characterisation of amorphous Ti_3N_4, using a combination of XPS, EXAFS, IR/Raman spectroscopy and thermogravimetric analysis. The structure is basically a defect form of Rocksalt with one quarter of the Ti sites unoccupied - these vacancies probably explain why this material is thermally unstable at ambient pressure with respect to TiN.
References 1. N. E. Brese and M. O'Keeffe, *Struct.Bonding* **79** 307 (1992). 2. M. Lerch, E. Fueglein and J. Wrba, *Z.Anorg.Allg.Chem.* **622** 367 (1996). 3. W. H. Baur and M. Lerch, *Z.Anorg.Allg.Chem.* **622** 1729 (1996). 4. B. V. Baxter, M. H. Chisholm, V. F. DiStasi, G. J. Gama, A. L. Hector and I. P. Parkin, *Chem.Mater.* **8** 1222 (1996).

2:30 PM FF2.4
Ductile Machinable Ternary Carbides and Nitrides; A New Class of Solids; Kinking Nonlinear Elastic Solids.
Michel W. Barsoum, Anand Murugaiah, Teijun Zhen and Surya R. Kalidindi; Drexel University, Philadelphia, Pennsylvania.

In the past 7 years we have made good progress in understanding the properties of a new class of layered, hexagonal ternary carbides and nitrides with the general formula: Mn+1AXn, where n = 1 to 3, M is an early transition metal, A is an A-group (mostly IIIA and IVA) element and X is either C and/or N. In all of these compounds, XTi6 layers are separated from each other by layers of pure A. These carbide and nitrides, which total over 60, represent a new and hitherto unknown and uncharted class of solids - polycrysalltine nanolaminates - that are a subset of an even larger class of solids best described as kinking nonlinear elastic solids*. These so-called MAX phases combine unusual and sometimes unique chemical, physical electrical and mechanical properties. They combine some of the best attributes of metals and ceramics. Like metals, they are electrically and thermally conductive, most readily machinable (manual hack saw will suffice) not susceptible to thermal shock, plastic at high temperatures, and exceptionally damage tolerant. Like ceramics, some are exceptionlly elastically rigid, lightweight, and most important, maintain their strength to temperatures as high as 1200 C. In the case of Ti3SiC2 it is also creep, fatigue and oxidation resistant. With proper alignment of the grains, they are ductile at ambient temperature. Furthermore, basal planes of Ti3SiC2 possess very low coefficients of friction (0.03) that are quite robust vis-a-vis exposure to the atmosphere. Three

interrelated characteristics distinguish these phases from other layered materials: i) the metallic-like nature of the bonding; ii) basal slip, and only basal slip, is operative down to at least 77K and, iii) they deform by a unique combination of kink and shear band formation together with delaminations. Recently we documented a new physical phenomenon in the deformation of solids**: fully reversible, dislocation-based deformation. We showed that polycrystalline Ti3SiC2 cylinders can be repeatedly compressed - up to 1 GPa- at room temperature and fully recover upon the removal of the load. The stress-strain curves are non-linear, outline fully reversible reproducible closed loops whose size and shape depend on grain size, but not strain rate. The energy dissipated per cycle is of the order of 1 MJ/m3, a value closer to rubber than to crystalline solids. At the grain level we have shown that it is possible to nanoindent grains of Ti3SiC2 with up to 10 GPa stress, dissipate about 25 % of the mechanical energy and not be able to find any trace of the indentation. This hitherto unreported phenomenon is attributed to the formation and annihilation of incipient kink bands. The technological implications of having these naturally nanolayered materials will be discussed. *M. W. Barsoum, A. Murugaiah, S. R. Kalidindi and T. Zhen, Phys. Rev. Letts., in press. **M. W. Barsoum, T. Zhen, S. Kalidindi, M. Radovic and A. Murugaiah, Nature Materials, 2, 107-111 (2003).

2:45 PM FF2.5
Disordered Zinc in Zn4Sb3 with Phonon Glass, Electron Crystal Thermoelectric Properties. Jeff Snyder[1], Mogens Christensen[3], Eiji Nishibori[2], Thierry Caillat[1] and Bo Brummerstedt Iversen[3]; [1]Jet Propulsion Laboratory/California Institute of Technology, Pasadena, California; [2]Department of Applied Physics, Nagoya University, Nagoya, Japan; [3]Department of Chemistry, Aarhus University, Aarhus, Denmark.

The compound Zn4Sb3 is one of the most efficient thermoelectric materials known. Its high efficiency results from an extraordinarily low thermal conductivity in conjunction with the electronic structure of a heavily doped semiconductor. Previous structural studies have been unable to explain this unusual combination of properties. Through a comprehensive structural analysis using single crystal X-ray and powder synchrotron radiation diffraction methods, we have found that both the electronic and thermal properties of Zn4Sb3 can be understood in terms of unique zinc interstitials which have been previously overlooked [Nature Materials, in press]. The identification of Sb3- ions and Sb2- dimers reveals that Zn4Sb3 is a valence semiconductor with ideal stoichiometry Zn13Sb10. In addition, the structure contains significant disorder, with zinc atoms distributed over multiple positions. The discovery of glass-like interstitial sites uncovers a highly effective mechanism for reducing thermal conductivity.

3:30 PM *FF2.6
Structure and Properties of Rare-Earth Transition-Metal Antimonides. Arthur Mar, Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada.

Ternary rare-earth transition-metal antimonides $RE_xM_ySb_z$ provide fertile ground for discovering materials with unusual electrical and magnetic properties such as superconductivity and ferromagnetism. Because their structures often contain low-dimensional features imparted by homoatomic Sb-Sb bonding networks, these properties are typically highly anisotropic. Strong magnetic exchange interactions also develop through coupling of f and d electrons. Examples used to illustrate these structures and properties will be taken from two extensive series of compounds, RE_3TiSb_5 and $RECrSb_3$.

4:00 PM FF2.7
Synthesis and Characterization of Layered and Framework Chalcoarsenates: Tl2SnAs2S6, Tl2SnAs2Se6, Tl8Sn10Sb16Se48, AgEuAsS4 and Eu3As2S8.
Mercouri G. Kanatzidis and Ratnasabapathy G. Iyer; Department of Chemistry, Michigan State University, East Lansing, Michigan.

Recently we began a systematic investigation of the reactivity of main group, transition and rare earth metals in alkali polythioarsenate fluxes. The reactions of Sn in potassium thioarsenate flux yielded us the two-dimensional compound K2SnAs2S6, which is isostructural to the mineral ernigillite, Tl2SnAs2S6. We reasoned that it should be possible to replace the K with Tl, and hence get better semiconducting properties given the more covalent bonding nature of Tl compared to K. We were successful in making Tl2SnAs2S6 and its Se analog. Tl2SnAs2Se6 is particularly interesting due to its low band gap and glass formation property. When we attempted to make Tl2SnSb2Se6, we made a new compound Tl8Sn10Sb16Se48, which is composed of alternating [Sn10Sb4Se28]-4 and [Sb12Se20]-4 layers that are separated by Tl cations. Similarly our reactions with Pb yielded us APbAsS4 (A = Rb, Cs), which are isostructural to APbPS4. Based on our observations in thiophosphate chemistry, we knew that Eu would yield similar structures. We therefore decided to substitute the alkali metals with Ag in the reactions of Eu with arsenic sulfide. We obtained the framework compouds AgEuAsS4 and Eu3As2S8. These compounds belong the general series (Ag3AsS4)n(Eu3As2S8)m with n = 1, m =1 for AgEuAsS4 and n = 0, m = 1 for Eu3As2S8. In addition Eu3As2S8 crystallizes in a new structure type. The structures and some physical properties of these compounds will be presented.

4:15 PM FF2.8
Structures and Properties of Layered Transition Metal Oxysulfides. Simon James Clarke, Zoltan A. Gal, Geoffrey Hyett and Catherine F. Smura; Chemistry, University of Oxford, Oxford, United Kingdom.

A large number of technologically important solid state compounds are oxides. Alternative classes of compound such as sulfides, nitrides and mixed-anion compounds have received little attention. Because of the different chemical requirements of oxygen and its heavier congeners, oxysulfides and oxyselenides often exhibit layered structures with distinct oxide and chalcogenide portions. The electron count and precise structural details of both of these parts of the structure can be tuned by judicious substitution, and because the two parts of the structure are not independent, the composition and structure of the chalcogenide layer will influence the composition and structure of the oxide layer and vice versa. The compounds $A_2MO_2Cu_{2-\delta}E_2$(A = Sr, Ba; M = Mn, Co, E = S, Se) will be discussed. These are composed of MO_2 planar layers and $Cu_{2-\delta}E_2$ antifluorite layers separated by electropositive A^{2+} cations. The $A_2CoO_2Cu_{2-\delta}S_2$ series is shown to be copper deficient (δ= 0.15) with a Co oxidation state of around +2.15. The nature of the large conductivity change between $Sr_2CoO_2Cu_{2-\delta}S_2$ (semiconducting) and $Ba_2CoO_2Cu_{2-\delta}S_2$ (insulating) will be discussed with reference to the structural, magnetic and electronic properties of the series $Sr_{2-x}Ba_xCoO_2Cu_{2-\delta}S_2$ ($0 < x < 2$). A new series of compounds has been identified in which either the oxide layer or the chalcogenide layer is thicker than in the $A_2MO_2Cu_{2-\delta}E_2$ compounds [1]. Chemical tuning of the physical properties in the compounds $A_4Mn_3O_{8-x}Cu_2E_2$ (A = Sr, Ba; E = S, Se) which contain a perovskite manganate slab separated by Cu_2E_2 layers will be discussed with reference to the magnetoresistive manganate oxides. The crystal chemistry and electronic and ionic transport properties of the members of the homologous series $Sr_2MnO_2Cu_{2n-\delta}S_{n+1}$, with n = 2, 3 and thick copper sulfide antifluorite layers separating the Sr_2MnO_2 layers, will be compared with those of the n = 1 member.
[1] N Barrier and S J Clarke Chemical Communications 164 (2003).

4:30 PM FF2.9
Synthesis and characterization of new widegap p-type semiconductors MCuFCh (M=Sr ,Eu Ch=S, Se) with layered structure. Eiji Motomitsu[1], Hiroshi Yanagi[1], Toshio Kamiya[1,2], Masahiro Hirano[2] and Hideo Hosono[1,2]; [1]Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan; [2]Hosono Transparent Electro-Active Materials (TEAM) Project, JST, Kawasaki, Japan.

New wide gap p-type semiconductors MCuFCh (M = Sr, Eu Ch = S, Se) were successfully synthesized by solid state reaction, and their electrical, optical and magnetic properties were characterized.
MF_2, MCh, and Cu_2Ch were used for starting materials. EuF_2 powder was prepared by reduction of EuF_3 in flowing H_2 gas at 1000 ^{0}C for 10h. SrS powder was prepared by reduction of $SrSO_4$ at 950 ^{0}C for 6h. On the other hand, SrSe powder was prepared by the reaction of Sr with Se in an evacuated silica tube at 450 ^{0}C for 5h. The stoichiometric mixtures of starting materials were pressed into pellets and sealed in an evacuated silica tube. In the case of preparing SrCuFCh and EuCuFCh, the pellets were heated at 500 ^{0}C for 4h and at 750 ^{0}C for 4h, respectively.
The powder X-ray diffraction (XRD) patterns of the obtained samples were measured from $2\theta = 5^0$ to 140^0 with Cu Kα line. The crystal structures were refined by the Rietveld method; MCuFCh have a layered structure with tetragonal symmetry, in which $(M_2F_2)^{2+}$ fluoride layers and $(Cu_2Ch_2)^{2-}$ chalcogenide layers are alternately stacked along the c-axis. This layered structure is the same as that of LaCuOCh, which exhibits excitonic absorption and emission even at room temperature. The temperature dependence of electrical conductivities of polycrystalline samples was measured by four-probe method from 2 to 400K. Seebeck measurements were carried out at room temperature. The room temperature conductivities of SrCuFCh and EuCuFCh were 8.4×10^{-5} S/cm and 1.9 S/cm respectively for the sulfide (Ch = S), 3.6×10^{-3} S/cm and 1.5×10^{1} S/cm respectively for the selenide (Ch = Se). Seebeck coefficients of all the samples examined here were positive, indicating that these samples are p-type conductors. The diffuse reflectance spectra were measured in the UV - visible region at room temperature. The estimated band gap energies of SrCuFS and EuCuFS were approximately 3.0eV and 2.2eV, respectively. The temperature dependence of DC magnetic susceptibility for EuCuFCh polycrystalline sample was measured with a SQUID magnetometer in

the temperature range from 5 to 300K. Both EuCuFS and EuCuFSe showed paramagnetic behaviors.

4:45 PM FF2.10
New Magnetic Zintl Phases in the Eu-In-P System.
Jiong Jiang[1], Marilyn M. Olmstead[1], Susan M. Kauzlarich[1] and Peter Klavins[2]; [1]Chemistry Department, University of California, Davis, Davis, California; [2]Physics Department, Univeristy of California, Davis, Davis, California.

The single crystals of two new compounds, Eu3InP3 and Eu3In2P4, were prepared by In flux synthesis. Eu3InP3 crystallizes in the Pnma orthorhombic space group with a = 12.6517(15) Å, b = 4.2683(5) Å, c = 13.5643(14) Å, and Z = 4 while Eu3In2P4 belongs to Pnnm space group, a = 6.6999(6) Å, b = 16.1019(13) Å, c = 4.2725(4) Å, and Z=2. These two compounds are isotypic to main group compounds Sr3InP3 and Sr3In2P4 respectively. Both structures consist distorted In-P tetrahedra and isolated Eu^{2+} ions. In Eu3InP3 these tetrahedra share corners to form one-dimensional chains. The Eu^{2+} ions occupy three different sites and form a complicated network containing some triangles. In Eu3In2P4 they form edge-shared dimers, and these dimers form chains. Eu3InP3 shows unusual magnetic properties: there are three magnetic ordering transitions at 14 K, 13 K, and 10.4 K; the magnetization curve shows steps, with out-of-loop initial magnetization and reversed hysteresis at low field region. Eu3In2P4 antiferromagnetically orders at 14.5 K. Its magnetization curve saturates at around 1T. Eu3InP3 and Eu3In2P4 are both semiconductors.

SESSION FF3: Poster Session: Solid State Posters I
Monday Evening, November 29, 2004
8:00 PM
Exhibition Hall D (Hynes)

FF3.1
Growth of Single Crystal α-Fe_2O_3 from a $CaFe_4O_7$-Based Solvent. Ann Norina Chiaramonti[1], Jason D. Pless[2], Li Liu[2], Jared P. Smit[2], Courtney H. Lanier[1], Kenneth R. Poeppelmeier[2], Peter C. Stair[2] and Laurence D. Marks[1]; [1]Materials Science and Engineering, Institute for Environmental Catalysis, Northwestern University, Evanston, Illinois; [2]Chemistry, Institute for Environmental Catalysis, Northwestern University, Evanston, Illinois.

In this poster, we present results from the successful growth of a large single crystal rod of α-Fe_2O_3 using a hemicalcic ferrite ($CaFe_4O_7$)-based solvent in the optical floating zone furnace in the traveling solvent zone configuration. The as-grown crystal measures 33mm long by 5mm in diameter and was confirmed by powder X-ray diffraction to be phase-pure hematite. TEM analysis revealed the growth direction to be parallel to [001] and the crystalline quality excellent, with no evidence of stacking faults, voids, inclusions, twins, or dislocations. Single crystal growth from the melt in the optical floating zone furnace at constant oxygen partial pressure is an open thermodynamic system, where the path of equilibrium crystallization is constrained to follow the relevant oxygen isobar. To congruently melt and solidify hematite directly, and avoid the magnetite+hematite two phase region of the binary phase diagram (at which the reduction from Fe^{3+} to Fe^{2+} would liberate oxygen and destroy the stability of the growing crystal) pressures approaching 35 atm are needed. Considering this observation, and the fact that the furnace as equipped cannot handle pressures exceeding 9 bar, it was determined that hematite could not be grown directly from the melt using the present setup and a suitable solvent had to be found. $CaFe_4O_7$ is such a solvent. It is a high temperature phase which undergoes a peritectic reaction to form hematite plus liquid, and serves to both lower the temperature at which hematite solidifies from the melt compared to the Fe-O binary system and prevent the reduction of hematite to magnetite at the temperatures and pressures used in single crystal growth. Unique to the growth of hematite in the optical floating zone furnace, we have used the peritectic reaction to our benefit by thermally decomposing an incongruently melting material to grow a large single crystal of an atmospherically sensitive different phase. In contrast to the common method of employing a solvent from within the system of interest (for example, in the case of YIG and high T_c cuprates), we have used a solvent that contains a species which is wholly undesirable in the final product. In a method analogous to the "push-pull" technique for the growth of semiconductor single crystals, we have executed the continuous, large single crystal growth of what is known in incongruently melting systems as the 'first grown material'. Remarkably, TEM and Laue analysis have shown that, except for the first 3mm of growth which is polycrystalline in nature, the entire length of the rod is a single crystal. Finally, inductively coupled plasma-atomic emission spectroscopy (ICP-AES) revealed that the Ca:Fe ratio in the as-grown single crystal is zero, which represents the first time hematite of this three-dimensional size and purity has been synthesized at oxygen pressures of less than 35 atmospheres.

FF3.2
Open-Framework Copper Titanosilicates. Xiqu Wang, Lumei Liu and Jacobson Allan J.; Department of Chemistry and Center for Materials Chemistry, University of Houston, Houston, Texas.

Two prominent examples of microporous titanosilicates are ETS-4 and ETS-10 that have applications in ion-exchange and gas separations (1). Recently we reported a group of microporous copper silicates (2) that have metal oxide octahedral chains similar to those found in ETS-4 and ETS-10. Systematic extension of our synthetic studies has led to a number of new open-framework copper titanosilicates that can be divided into three types. The first type consists of phases obtained by substitution of CuO_4 squares for the separated TiO_5 pyramids of ETS-4. Phase **1** has the space group symmetry C2/m with a = 14.352, b = 13.954, c = 12.173 Å and β = 107.2°. The structure of **1** determined from single crystal X-ray data is closely similar to that reported for ETS-4, but ca. one third TiO_5 pyramids are randomly replaced by CuO_4 squares. Phase **2** has the space group symmetry Cccm with a = 46.402, b = 14.419, c = 13.970 Å. Structural refinements indicate that **2** also has the ETS-4 structure but all the TiO_5 pyramids are replaced by CuO_4 squares which are not randomly disordered. The second type is obtained by substitution of Cu for the Ti atoms in single octahedral chains of titanosilicates. Phase **3** with the composition $Na_8CuTi_3Si_{16}O_{43}$ has the same structure as the mineral narsarsukite, a titanosilicate closely related to ETS-10. Narsarsukite and ETS-10 have the same straight single chains of TiO_6 octahedra which are partially substituted by CuO_5 pyramids in **3**. Phase **4** with the composition $K_4CuTiSi_8O_{21}$ contains separated CuO_5 and TiO_5 tetragonal pyramids that crosslink a new type of silicate double layers to form an open framework. 1. S. M. Kuznicki et. al.: Nature, 412 (2001) 720-724; US Patent 4938939, 1990. 2. X. Wang, L. Liu, A. J. Jacobson: Angew. Chem. Int. Ed., 42 (2003) 2044-2047.

FF3.3
Barium Strontium Titanate Ceramics Prepared by a Reaction-Sintering Process. Yi-Cheng Liou, Jen-Hsien Chen and Chi-Ting Wu; Department of Electronic Engineering, Kun-Shan University of Technology, Tainan Hsien, Taiwan.

Barium strontium titanate (Ba0.7Sr0.3TiO3, BST) ceramics prepared by a reaction-sintering process were investigated. The mixture of raw materials of stoichiometric Ba0.7Sr0.3TiO3 was pressed and sintered into ceramics without any calcination stage conducted. Perovskite BST ceramics were obtained after sintered at 1330-1370oC for 2-6 h. For 6 h sintering at 1350oC, density value 5.68 g/cm3 (99.8% of the theoretical value) was obtained. A diffused ferroelectric-paraelectric transition was observed in Ba0.7Sr0.3TiO3 ceramics sintered at 1330oC for 2 h and disappeared at a longer soak time or a higher sintering temperature.

FF3.4
Preparation of (Pb,Ca)(Fe0.5Nb0.5)1-yTiyO3 Perovskite Ceramics by a Reaction-Sintering Process. Yi-Cheng Liou, Jen-Hsien Chen and Hsueh-Yung Lu; Department of Electronic Engineering, Kun-Shan University of Technology, Tainan Hsien, Taiwan.

(Pb0.45Ca0.55)(Fe0.5Nb0.5)O3 (PCFN) and (Pb0.45Ca0.55)[(Fe0.5Nb0.5)0.9Ti0.1]O3 (PCFNT) perovskite ceramics prepared by a reaction-sintering process were investigated. The mixture of raw materials was pressed and sintered into ceramics without any calcination stage conducted. Perovskite PCFN and PCFNT ceramics were obtained after sintered at 1150-1270oC for 2 h and 4 h. A density of 5.88 g/cm3 was obtained in PCFN for 2 h sintering at 1270oC. For PCFNT, a higher density 6.21 g/cm3 was obtained for 2 h sintering at 1270oC. The reaction-sintering process is proved a simple and effective method in preparing perovskite PCFN and PCFNT ceramics.

FF3.5
Preparation of NiNb2O6 Columbite Ceramics by a Reaction-Sintering Process. Yi-Cheng Liou and Chao-Yang Shiue; Department of Electronic Engineering, Kun-Shan University of Technology, Tainan Hsien, Taiwan.

NiNb2O6 columbite ceramics prepared by a reaction-sintering process were investigated. The mixture of raw materials was pressed and sintered into ceramics without any calcination stage conducted. Columbite NiNb2O6 ceramics were obtained in pellets using 50%Ni(NO3)2-50%NiO (NN1) after sintered at 1250-1450oC for 2 h and 4 h. In pellets using NiO (NN2), columbite NiNb2O6 ceramics were obtained after sintered at 1150-1350oC for 2 h and 4 h. A density of 4.47 g/cm3 was obtained in NN1 for 2 h sintering at 1400oC. For NN2, a higher density 5.62 g/cm3 (99.8% of the theoretical value) was obtained for 2 h sintering at 1300oC. The

reaction-sintering process is proved a simple and effective method in preparing columbite NiNb2O6 ceramics. A higher density could be obtained at lower sintering temperature by using NiO instead of 50%Ni(NO3)2-50%NiO in the reaction with Nb2O5.

FF3.6
The Synthesis, Structure, and Physical Properties of Ce_2PdGa_{10}. Jasmine Nicole Millican[1], Robin T. Macaluso[1], David P. Young[2], Monica Moldovan[2] and Julia Chan[1]; [1]Chemistry, Louisiana State University, Baton Rouge, Louisiana; [2]Physics and Astronomy, Louisiana State University, Baton Rouge, Louisiana.

A new ternary compound, Ce_2PdGa_{10}, has been synthesized using Ga flux and characterized by single-crystal X-ray diffraction. Ce_2PdGa_{10} adopts a tetragonal structure in the $I4/mmm$ space group and is isostructural to Ce_2NiGa_{10}. Lattice parameters are a = 4.3230 (3) Å and c = 26.536 (3) Å, V = 495.91 (7)Å^3 and Z = 2. The compound is metallic ($d\rho/dT > 0$)with the resistance decreasing roughly linearly with temperature from 300 K down to 175 K. The magnetic susceptibility of Ce_2PdGa_{10} is consistent with local moment paramagnetism and no long-range magnetic ordering occurs down to 2 K. We present the structure and physical properties of Ce_2PdGa_{10} and compare them to a structurally related ternary compound, $CePdGa_6$.

FF3.7
Crystal Growth, Characterization and Physical Properties of $PrNiSb_3$, $NdNiSb_3$ and $SmNiSb_3$. Evan Lyle Thomas[1], Robin T. Macaluso[1], Han-Oh Lee[2], Zachary Fisk[2] and Julia Y. Chan[1]; [1]Chemistry, Louisiana State University, Baton Rouge, Louisiana; [2]Physics, University of California, Davis, California.

Single crystals of three new intermetallic ternary compounds in the $LnNiSb_3$ (Ln = Pr, Nd and Sm) family have been synthesized from excess Sb flux and characterized by single crystal X-ray diffraction. $PrNiSb_3$, $NdNiSb_3$ and $SmNiSb_3$ all crystallize in an orthorhombic space group, $Pbcm$ (No. 57), Z = 8, with a = 12.5700(2) Å, b = 6.2010(4) Å, c = 18.670(6) Å, and V = 1431.64(11) Å^3; a = 12.5090(2) Å, b = 6.1940(3) Å, c = 18.3350(6) Å, and V = 1420.61(9) Å^3; and a = 12.3900(1) Å, b = 6.1760(3) Å, c = 18.2650(6) Å, and V = 1397.65(8) Å^3, for Ln = Pr, Nd and Sm, respectively. These compounds consist of rare-earth atoms located above and below layers of nearly square, buckled Sb nets, along with layers of highly distorted edge- and face-sharing $NiSb_6$ octahedra. Resistivity data indicate metallic behavior for all three compounds. Magnetization measurements show antiferromagnetic behavior with T_N = 4.5 K ($PrNiSb_3$), 4.6 K ($NdNiSb_3$) and 2.9 K ($SmNiSb_3$). Effective moments of 3.62 μ_B, 3.90 μ_B and 0.80 μ_B are found for $PrNiSb_3$, $NdNiSb_3$ and $SmNiSb_3$, respectively, and are consistent with Pr^{3+} (f^2), Nd^{3+} (f^3) and Sm^{3+} (f^4).

FF3.8
Preparation of Textured Bismuth Titanate Ceramics by Templated Grain Growth Method Application for Spark Plasma Sintering Method. Keishi Nishio[1], Rena Maeda[1], Yasuo Kogo[1], Tohru Kineri[2] and Atsuo Yasumori[1]; [1]Materials Science and Technology, Tokyo University of Science, Noda-shi, Chiba, Japan; [2]Materials Science & Environment Engineering, Tokyo University of Science, Yamaguchi, Onoda-shi, Yamaguchi, Japan.

Textured bismuth titanate ($Bi_4Ti_3O_{12}$), the simplest and best known compound among the bismuth layer-structure ferroelectrics is interesting because of its peculiar switching behavior resulting from a small c-axis component of the spontaneous polarization and a small coercive force. $Bi_4Ti_3O_{12}$ ceramics was prepared by templated grain growth (TGG) method combined with spark plasma sintering (SPS) method. TGG method has been developed to provide a simper method of creating textured ceramic microstructure. And SPS method enables a compact powder to be sintered under uniform heating to high density at relative lower temperatures and in much shorter sintering periods compared with conventional sintering method. Precursor powder of $Bi_4Ti_3O_{12}$ was obtained by co-precipitation method with Ti alkoxide and Bi oxide as raw materials. Platelet $Bi_4Ti_3O_{12}$ was synthesized from precursor powder by flux method using NaCl and KCl. The obtained platelet $Bi_4Ti_3O_{12}$ has high aspect ratio The ceramics was prepared by treatment using SPS the mixture of the platelet Bi $_4Ti_3O_{12}$ and amorphous precursor powder. As a result, the dense ceramics could be obtained easily without crystalline of amorphous precursor and grains could not be observed growth during the sintering. After heat treatment of the ceramics, high textured and high dense $Bi_4Ti_3O_{12}$ ceramics could be obtained. The ceramics shows high orientation, above 60%, for c-axis direction and high density above 80%.

FF3.9
Preferential Crystallization of β-$FeSi_2$ from Micro-droplets Generated by Laser Ablation. Aiko Narazaki, Tadatake Sato, Yoshizo Kawaguchi and Hiroyuki Niino; Photonics Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan.

Generation of molten micro-droplets is a peculiar feature of laser ablation of solid targets. The droplets had been recognized as a major drawback of laser ablation due to the degradation of a smooth film surface. However, in a different perspective, they have an advantage in the crystallization at lower substrate temperatures compared with other ejected species such as atoms, molecules and ions. On the other hand, β-$FeSi_2$ is a promising eco-friendly semiconductor because of luminescence at 1.55 μm used for optical networking as well as abundant component reserves on the earth and non-toxicity. However, preparation of β-$FeSi_2$ thin films generally required high-temperature multi-processes such as film deposition at $\geq$ 450 °C and following post-annealing at $\geq$ 800 °C from several hours up to a few days. Moreover, it is difficult to prepare β-$FeSi_2$ bulk materials since the semiconducting beta phase undergoes the phase transformation to a high-temperature equilibrium metallic alpha phase above about 950 °C during pulling from a melt or sintering, resulting in the precipitation of the metallic alpha phase. In this work, we succeeded in the room-temperature fabrication of β-$FeSi_2$ microprecipitates by the active use of droplets. Based on micro-Raman spectra, it was confirmed that the molten droplets crystallized preferentially as the low-temperature equilibrium β-$FeSi_2$, not the high-temperature equilibrium alpha phase. One of possible explanations for the preferential crystal growth of the beta phase is as follows. The molten droplets were cooled down rapidly mainly due to thermal radiation and heat conduction to the substrate, resulting in a super-cooled liquid. Solidification from this super-cooled liquid possibly accompanies the crystallization in a non-equilibrium process. This non-equilibrium crystallization leads to the preferential precipitation of β phase, not the equilibrium α phase. Consequently, this technique is effective for preparing crystalline materials at room temperature as well as preferential crystal growth of low-temperature equilibrium β phase.

FF3.10
Nitridation analysis of Silicon powder compacts using TG system and preparation of High Strength Sintered Reaction Bonded Silicon Nitride. Seiji Nakahata and Michimasa Miyamaga; Sumitomo Electric Industries, Itami, Japan.

Sintered Reaction bonded silicon nitride (SRBSN) has been expected to apply to engineering material because of the low shrinkage, high dimensional accuracy, and the low cost of raw silicon powder. However the RBSN has not been used widely since it is difficult to control the nitriding process because of low nitrogen diffusivity in silicon or silicon nitride which is created on silicon surface during nitriding process and further fact that the SRBSN has low density and low strength (< 0.5 GPa). We focus on the developing of a new process to satisfy both of short nitriding time (< 10 hours) and high strength SRBSN (> 1 GPa). A new TG (Thermogravimetry) system, which is able to measure the weight change of silicon powder compacts during nitridation under 0.4 MPa in nitrogen atmosphere, was installed in a furnace to investigate nitriding kinetics. Firstly, to search a new nitriding additive and estimate nitriding time and temperature, silicon powder was mixed with or without various additives and pressed into rectangular shape with 5 x 8 x 46 mm. The obtained silicon powder compacts were analyzed using TG system during nitriding. It was clear that some additives, such as Cupper, Chromium, Lanthanoid oxide, promoted the nitridation and the nitridation ratio was achieved over 98% after only 5 hours nitridation while silicon powder compacts without additives was nitrided only 35 %. Secondly, to measure the strength of SRBSN after sintering, silicon powder was mixed with nitriding additives as mentioned above and 5 wt% Y2O3 and 2.8 wt% Al2O3 as sintering additives. The obtained powder was pressed into same shapes as described above. These compacts were nitrided for 5 hours at 0.4 MPa in nitrogen atmosphere, then sintered for 3 hours at 1750, 1800, 1850 C, respectively. Three bending strength of obtained sintered bodies were measured after grinding. The strength of the SRBSN with Cupper and Chromium were around 0.5 GPa, on the other hand, the SRBSN with Lanthanoid oxide, which is sintered at 1850 C, had 1 GPa. We will show the microstructure of sintered bodies and propose the nitridation mechanism of our new additives in this presentation.

FF3.11
Low Temperature Synthesis of Nano ZnO with Controlled Size and Shape. Po-Yi Wu[1], Feng Zhang[2] and Siu-Wai Chan[1]; [1]Program of Materials Science & Engineering, Department of Applied Physics and Applied Mathematics, Columbia University, New York, New York; [2]Headway Technologies, Inc., Milpitas, California.

An effective chemical process is discovered for synthesizing zinc oxide particles near room temperature with controlled size and shape.

Nanoparticles of crystalline zinc oxide have been prepared by mixing zinc nitrate (Zn(NO3)2) and hexamethylenetetramine (HMT) aqueous solutions at various temperatures, and concentrations. Transmission electron microscopy (TEM) and X-ray diffraction (XRD) investigation shows that particles of specific shape, size, and size-distribution exist for different preparation conditions. Four specific types of particles are produced controllably including sub-micron rods, nano-wires, nano-rods and equiaxis nanoparticles. An effective chemical process is discovered for synthesizing zinc oxide particles near room temperature with controlled size and shape.

FF3.12

Description of the Phosphorescence Mechanism of ZnS:Cu by Band Structure Calculations. Frederic Clabau[1], Xavier Rocquefelte[1], Philippe Deniard[1], Thierry Le Mercier[2], Myung-Hwan Whangbo[3] and Stephane Jobic[1]; [1]LCS, IMN-CNRS, Nantes, France; [2]Rhodia Electronics and Catalysis, CRA, Aubervilliers, France; [3]Department of Chemistry, North Carolina State University, Raleigh, North Carolina.

Phosphorescent materials are semiconducting or insulating phosphors, containing in their forbidden band some discrete levels associated with chemical (dopants) and/or physical imperfections (vacancies, interstitial) of the network host. Under the effect of an external excitation (absorption of the solar UV electromagnetic radiation for example), electrons and/or holes are trapped in these punctual defects. The probability of direct transition from these levels towards the starting level being very weak, this metastable state is maintained as long as a sufficient energy (detrapping energy) is not provided to the system. If this energy is thermal energy at ambient temperature, one speaks about phosphorescence. There is then progressive release of the trapped charge carriers, followed by a differed light emission due to a radiative recombination. A few years ago, the discovery of very efficient phosphorescent materials (SrAl2O4:Eu2+,Dy3+, CaAl2O4:Eu2+,Nd3+, Y2O2S:Eu3+,Mg,Ti) has revived the interest carried out to this phenomenon. The more widely used phosphorescent compound remains ZnS:Cu+. Nevertheless, its phosphorescence mechanism, as for all other phosphorescent materials thereafter discovered, is not properly described in chemical terms and, to some aspects, the trapping and detrapping processes have to be proven. Moreover, the use of ZnS:Cu+ as fluorescent (emission time in the order of a microsecond) and phosphorescent (emission time in the order of an hour) material versus the nature of the co-dopant remains unexplained. Band structure calculations, performed within the scope of the DFT with the VASP code, made possible the positioning, in the forbidden band, of the electronic levels associated with all the defects found in the phosphor. The role of all these defects can thus be discussed.

FF3.13

Ag-B Thin Films Prepared by Magnetron Sputtering. Oren Metz[1], Joshua Pelleg[1], Misha Sinder[1], Roni Schneck[1] and Vladimir Sokolovsky[2]; [1]Materials Engineering, Ben Gurion University of the Negev, Beer Sheva, Israel; [2]Physics, Ben Gurion University of the Negev, Beer Sheva, Negev, Israel.

The discovery of the new superconductor MgB2 with critical temperature of T = 39 K stimulated great activity in search for materials with higher Tc. Theoretical works [1, 2] predicted the possibility of obtaining such superconducting materials in other borides also, in particular in AgB2. It was predicted in these works that diborides of metals having the AlB2 type structure, among them AgB2, may have superconductivity with a Tc higher than 39K. In an early very short report the lattice parameters of AgB2 were evaluated in a synthesized specimen [3]. However, no other indication exists that AgB2 was ever produced. We report the preliminary results of our attempts to prepare AgB2 films. Thin films of Ag-B were produced by magnetron cosputtering in Ar ambient from two separate targets that of B and Ag on Si (100) substrates. The specimens were subjected to X-ray, SEM, XPS, Auger analysis and optical microscope investigation. Resistivity measurements in a wide temperature range were measured. No superconductivity was observed in the range 10-300 K on the basis of resistivity measurements. Preliminary results indicate that AgB2 might be an unstable phase. [1] S. K. Kwon, S. J. Youn, K. S. Kim, and B.I. Min, cond-mat/0106483 (2001) [2] I. R. Schein, N. I. Medvedeva, and A. L. Ivanovskii, Phys. of Solid State, 43, 2213 (2001) [3] W. Obrowski, Naturwissenschaften, 48, 428 (1961).

FF3.14

Single Crystal Characterization of $Ba_8Al_{16}Si_{30}$. Peter Klavins[2], Cathie Condron[1] and Susan Kauzlarich[1]; [1]Chemistry, UC Davis, Davis, California; [2]Physics, UC Davis, Davis, California.

Single crystals of $Ba_8Al_{16}Si_{30}$ were prepared utilizing the molten flux growth method. Single crystal x-ray diffraction studies confirm $Ba_8Al_{16}Si_{30}$ adopts the clathrate (I) structure type, space group $Pn-3m$, with $a = 10.6079(12)$ Å and Z = 1. The polyhedral structure is built of Si_{20} pentagonal dodecahedra occupied by six Ba ($2a$) atoms, and Si_{24} tetrakaidecahedra occupied by two Ba ($6d$) atoms. The Ba atoms at the $6d$ site form a linear chain through the structure and are separated by hexagonal windows. In this way, the linear chains may provide a pathway for 1-D transport. In order to understand the role structure plays in determining electronic properties, single crystal x-ray diffraction, microprobe analysis and solid state NMR studies have been preformed, as well as temperature dependent susceptibility and conductivity measurements. The structure and properties of Ba8Al16Si30 will be presented and compared with previously reported data for bulk measurements.

FF3.15

Spectroscopic Probe into Carbon Nitride Synthesized via High Density Plasma Sputtering. Mayuko Koga[1], Takashi Yokota[2], Nagahiro Saito[3], Yasushi Inoue[1] and Osamu Takai[1]; [1]EcoTopia Science Institute, Nagoya University, Nagoya, Japan; [2]Department of Physical Science and Engineering, School of Engineering, Nagoya University, Nagoya, Japan; [3]Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University, Nagoya, Japan.

Carbon nitride has attracted great interests due to its theoretically-expected extreme properties, such as hardness, high heat conductivity and high chemical stability. There are many studies on the synthesis of carbon nitride films. However, the optimum fabrication method has not been confirmed yet. We propose helicon wave excited plasma is a powerful tool for fabrication of carbon nitride films because high concentration of atomic nitrogen due to high plasma density and low plasma potential. Therefore, we have developed a new device and tried to fabricate carbon nitride films via reactive plasma sputter synthesis. The system consists of two magnetic coils, one turn antenna connected to RF power source, matching box, quartz discharge tube and reactor chamber made by aluminum. We can change the mode of plasma from inductively coupled plasma mode to helicon wave excited plasma mode by turning on the magnetic coil. The nitrogen gas is introduced into the chamber after evacuating with a turbo-molecular pump and a rotary pump. Carbon nitride films are deposited on silicon wafers by high density plasma sputtering of carbon target. Electron density and electron temperature are measured with Langumuir probe. Plasma components are investigated by using the optical emission spectroscopy. The carbon nitride films are characterized by X-ray photoelectron spectroscopy, X-ray diffraction spectroscopy and Fourier-transform infrared spectroscopy. The properties of carbon nitride films are discussed from the viewpoint of the effect of helicon wave plasma.

FF3.16

The Effect of Terminal Ligands on the Dimensionality and Topology of Metal Dicarboxylate Coordination Structures. Long Pan[1], Nancy Ching[1], Xiaoying Huang[1], Jing Li[1], Tan Yuen[2] and C.L. Lin[2]; [1]Department of Chemistry and Chemical Biology, Rutgers University, Piscataway, New Jersey; [2]Department of Physics, Temple University, Philadelphia, Pennsylvania.

Incorporation of multidentate dicarboxylate and monodentate (terminal) ligands to the synthesis of metal organic coordination polymers offers excellent opportunities for designing and building new types of crystal structures. These structures can be modified by changing the functional groups of the terminal ligands to achieve the desired architecture and topology aimed at specific applications. In this presentation, we describe four new cobalt coordination structures obtained based on such a strategy. Solvo- or hydro-thermal reactions of 4,4'-biphenyldicarboxylate acid (H2bpdc) and cobalt (II) salt with several pyridine derivatives generated a 1D zigzag chain structure when 3-methylpyridine (3-pic) was used, a 1D helical chain structure and a 2D interpenetrating grid structure when 4-methylpyridine (4-pic) was used, and a 2D non-interpenetrating network structure while longer 4-benzylpyridine(4-Bzpy) was used. The magnetic properties of selected structures were investigated and the results will be discussed.

FF3.17

High Throughput Synthesis of Pigments by Solution Deposition. Stuart James Henderson, Andrew Lee Hector and Mark Timothy Weller; School of Chemistry, University of Southampton, Southampton, Hampshire, United Kingdom.

The application of high throughput methods for the synthesis and screening of inorganic materials is an area of growing interest.[1,2] The ability to rapidly assess the properties of large numbers of discreet compounds prepared using small quantities of reagents make these techniques attractive for both industrial and academic research. Much of the literature focuses on the preparation of thin film arrays by vapour deposition.[3,4] However, such samples may not give a true indication of the material's properties when prepared as a bulk powder. Libraries of powdered catalysts and phosphor materials

prepared from solutions have been shown to be an effective lower cost route to novel inorganic materials.[5,6] We report the development of high throughput techniques, which use a commercially available liquid handling robot and a simple masking system to produce crystalline samples. This general approach can be used to synthesise materials using a variety of sol-gel methods, from solutions of metal salts or alkoxides. Libraries are prepared on alumina tiles, using a Teflon/stainless steel masking system to create discrete sample spots. The paper will describe how we have applied these methods to oxide and oxynitride pigments by firing in air or high purity ammonia. Initially known systems were investigated to establish the validity of the process. These include spinel based chromite materials (e.g $CuCr_2O_4$) and tantalum containing oxynitride compounds (e.g $LaTaON_2$[7]). The arrays are screened by X-ray diffraction and basic colour measurement to identify promising candidates, which can then be scaled up to produce bulk samples for more complete analysis. 1. B. Jandeleit, T. S. Powers, D. J. Schaefer, H. W. Turner, W. H. Weinberg, *Angew.Chem.Int.Ed.* **38** 2494 (1999). 2. X. D. Xiang, Y. K. Yoo, *J.Phys. : Condens.Matter.* **14** R49-R78 (2002). 3. T. X. Sun, *Biotechnol.Bioeng.* **61** 193 (1999). 4. H. Koinuma, I. Takeuchi, R. B. Van Dover, *MRSBull.* **27** 301 (2002). 5. P. J. Mcginn, H. M. Reichenbach, *J.Mater.Res.* **16** 967 (2001). 6. H. D. Park, S. Y. Seo, K. S. Sohn, *Electrochem.Solid – StateLett.* **4** H26-H29 (2001). 7. M. Jansen, H. P. Letschert, *Nature* **404** 980 (2000).

FF3.18

Magnetic Structure of K_2NiF_4-type Iron(III) Oxide Halides. Andrew Lee Hector, School of Chemistry, University of Southapton, Southampton, United Kingdom.

Materials with the K_2NiF_4 structure and a magnetic atom on the B site are examples of a pseudo-2D square lattice. The nearest neighbour interactions are very strong and, with iron(III), usually lead to xy antiferromagnetic coupling. The layer stacking is more complex since the B site in one layer is above the centre of a square of B sites in the preceding layer. Collinear structures would lead to two ferro- and two antiferromagnetic interactions, all with identical pathways. Hence subsequent layers have orthogonal stacking.[1] We have used powder neutron diffraction at 2K to study the magnetic structures of A_2FeO_3X where A is Ca or Sr and X is Cl or Br. There are two common magnetic structures for K_2NiF_4-type xy antiferromagnets, those of La_2NiO_4 and La_2CuO_4,[2] here we find the former. These two structure types vary in the layer stacking sequence - In La_2NiO_4 there is a net ferromagnetic moment on each (110) type plane, whereas in La_2CuO_4 the moments cancel out completely. In Sr_2FeO_3F we find a more complex situation. The reflections corresponding to the La_2NiO_4 magnetic structure are present from 2K to ambient temperature, but a further set of peaks decays from 2K to around 60K. These correspond to a magnetic structure with a doubled c-axis. We demonstrate that this is due to a magnetic structure in which La_2NiO_4- and La_2CuO_4-type stacking alternate, and suggest possible explanations for this behaviour. To our knowledge this is the only example of this magnetic structure type. The only other example of a K_2NiF_4-type material with a magnetic structure requiring c-axis doubling is Ca_2MnO_4 and this is an Ising antiferromagnet.[3,4] However its doubled magnetic structure may have the same basis as that of Sr_2FeO_3F. References 1. S. Skanthakumar, J. W. Lynn, J. L. Peng and Y. Li, *Phys.Rev.B* **47** 6173 (1993). 2. D. Petigrand, S. V. Maleyev, Ph. Bourges and A. S. Ivanov, *Phys.Rev.B* **59** 1079 (1999). 3. D. E. Cox, G. Shirane, R. J. Birgeneau and J. B. MacChesney, *Phys.Rev.* **188** 930 (1969). 4. K. Tezuka, M. Inamura, Y. Hinatsu, Y. Shimojo and Y. Morii, *J.SolidStateChem.* **145** 705 (1999).

FF3.19

Fine Structure of Chemical Bonding State in Amorphous Carbon Nitride. Yasushi Kobayashi[1], Nagahiro Saito[2,1], Yasushi Inoue[3,1] and Osamu Takai[3,1]; [1]Department of Materials, Nagoya University, Nagoya, Japan; [2]Department of Molecular Design and Engineering, Nagoya University, Nagoya, Japan; [3]EcoTopia Science Institute, Nagoya University, Nagoya, Japan.

Amorphous carbon nitride (a-CNx) films have a potential of mechanical coating material with super hardness and high wear resistance. Therefore many researchers have investigated a-CNx films from various views. The detail of the chemical bonding state has not been understood yet although the chemical bonding states have a great effect on the mechanical property. In this study, the correlation between mechanical properties, in particular, hardness, and chemical bonding in a-CNx was focused. In order to reveal the chemical bonding state, solid-state nuclear magnetic resonance (NMR), electron energy loss spectroscopy (EELS), electron spin resonance (ESR), infrared (IR) spectroscopy, Raman spectroscopy and x-ray photoelectron spectroscopy (XPS) were used. a-CNx films were prepared from inductively coupled plasma chemical vapor deposition (ICP-CVD). Substrate bias voltage was treated as a process parameter. The ratio of sp2-C to sp3-C hybrid orbital (sp2-C/sp3-C) was derived from NMR and EELS spectra. From NMR results, the ratio in the films was over 1. Thus this shows that sp2-C hybrid orbital was main chemical bonding state. However the ratio of sp3-hybridized C increased with the increase of substrate bias voltage. The chemical bonding state derived from NMR measurement was also evaluated compared with that from other method. Results of other analyses will be shown in the presentation.

FF3.20

Fabrication of Anatase TiO_2 Thin Films using Pulsed DC Magnetron Sputtering. I. A. Al-Homoudi[1], Gregory W. Auner[2], G. Newaz[1], R. Naik[3], L. Rimai[2] and R. Baird[2]; [1]Mechanical Engineering, Wayne State University, Detroit, Michigan; [2]Electrical and Computer Engineering, Wayne State University, Detroit, Michigan; [3]Physics and Astronomy, Wayne State University, Detroit, Michigan.

TiO2 is a markedly inert, stable compound found in nature in three crystalline forms rutile, anatase (both tetragonal) and brookite (orthorhombic). According to thermodynamics analysis, rutile is thermally the most stable, where anatase becomes more stable than rutile when the particle size decreases below c.a. 14 nm. The surface free energy and surface stress play important roles in the thermodynamic phase stability, which is a function of particle size. This study deals with structural and morphological evolution of amorphous/crystalline anatase TiO2 thin films, fabricated using magnetron sputtering. TiO2 thin films were deposited using pulsed D.C. magnetron reactive sputtering on glass substrates. Thin films (500-1000 nm) of TiO2 were deposited using a Ti source in Ar+O2 gas mixture with different parameters of power (350-500W), substrate temperature (25øC-400øC), growth pressure (3.5-4.5) and oxygen gas flows (2.5-3.5 sccm). The x-ray diffractions in 2Θ ranges between 20 and 90 degrees, show amorphous and/or anatase phase depending upon the deposition conditions. The films were found to be amorphous at lower substrate temperature and at lower powers. The grain size and RMS roughness of the films were characterized using Atomic Force Microscopy (AFM). The RMS roughness was found to be higher for films prepared with higher power and at higher temperature. The sample with 4 mTorr, 400W of power, a substrate temperature of 250øC with 3.5 sccm of oxygen flow has the best crystalline quality. The temperature dependent electrical conductivity measurement in air for the above film shows an exponential increase in conductivity with temperature. The correlation between the microstructure and electrical conductivity of TiO2 film will be presented.

FF3.21

The Development of F-free Mold Flux in Continuous Casting of Ultra Low Carbon Steel. Soon-Yong Choi[1], Se-Young Choi[1] and Jung-Wook Cho[2]; [1]School of New Materials Science and Engineering, Yonsei University, Seoul, South Korea; [2]Kwangyang Steelmaking Research Team, POSCO, Cheonnam, South Korea.

Mold fluxes play a crucial role in aspects of the efficiency of the continuous casting of steel and the surface quality of the steel product. Especially, the surface quality depends on viscosity and heat transfer of the infiltrated mold flux between the mold wall and the solidified steel shell, and the crystallization of mold flux strongly influence heat transfer because heat transfer is influenced substantially by the thermal resistance at the interface between mold flux film and copper mold. Mold fluxes usually contain the following major constituents: CaO-SiO2-Al2O3-Na2O-CaF2. Among the chemical compositions of mold flux, the roles of fluorine are the control of viscosity and solidification temperature. However, the fluorine leads to the corrosion of casting facilities and the environmental pollution. Therefore, the elimination of fluorine in the mold flux is considered to be urgently necessary. In this work, we investigated the glass system of CaO-SiO2-Al2O3-Na2O-B2O3 as F-free mold flux instead of commercial mold flux. Physical properties such as viscosity, thermal conductivity and crystallization behavior were observed and compared with commercial mold flux used in continuous casting of ultra low carbon steel. As a result, physical properties of prepared F-free mold flux were similar to the commercial mold flux and we find the adequate application possibility in continuous casting of ultra low carbon steel.

FF3.22

Correlation between Growth Parameters, Optical Properties and Material Chemistry of Thick Silicon Oxynitride Films. Sudipto Naskar[1,2], Lindsey N. Yadon[1], Christopher A. Bower[1], Scott Wolter[2], Jeffrey T. Glass[2] and Brian R. Stoner[1,2]; [1]MCNC-RDI, Research Triangle Park, North Carolina; [2]Electrical and Computer Engineering, Duke University, Durham, North Carolina.

The importance of silicon oxynitride (SiOxNy) material for optoelectronic device applications is ever increasing owing to its tunable refractive index. In this research, the influence of deposition conditions on film properties and the correlation of the deposition and properties with film composition and bonding has been investigated. Thick SiOxNy films are being deposited in a PECVD reactor using

silane (SiH4) and nitrous oxide (N2O) as precursor gases. To investigate the influence of deposition conditions on film properties, a three-dimensional parameter space has been constructed with flow ratio, frequency switching ratio and power as the coordinate axes. Several different SiOxNy films have been deposited at varying conditions within the parameter space. The temperature and pressure were maintained at 350 C and 1 Torr during all the experimental runs. The films were characterized for refractive index, growth rate and stress values. While the refractive index and the thickness were measured using prism-coupling technique, stress buildup is determined using bow measurements. For materials characterizations, X-ray diffraction studies and X-ray photoelectron spectroscopy studies are under investigation. The materials analysis is being used to determine the correlation between growth parameters and material chemistry. In addition, the correlation between material chemistry and refractive index and stress values are also being investigated. A summary of this analysis will be included in this presentation.

FF3.23
Ion Beam Sputter Deposition of Composition Spread Metal Thin Films. Parhat Ahmet[1], Shinjiro Yagyu[1], Michiko Yoshitake[1] and Toyohiro Chikyow[1,2]; [1]National Institute for Materials Science, Tsukuba, Japan; [2]CREST-Japan Science and Technology, Tokyo, Japan.

We have developed a fully automated composition spread thin film deposition system based on ion beam sputtering. The system has the capability of rapid fabrication of ternary composition spread metal thin films by sequential sputtering three different target materials while a horizontal moving mask controls the thicknesses of deposited thin film in each specific region on a substrate. We have applied the deposition system to rapid establish ternary phase diagrams of metal thin films. Our system has equipped with a rotate-able substrate holder system, a horizontal moving mask system, and a multi-target exchange system. Metal thin films were fabricated by sputtering metal target materials using an Ar+ ion gun. Atomically intermixing between different compositions in the thin films can be achieved by adjusting the deposited film thickness to several Angstrom in each deposition sequence and the desired film thickness can be obtained by repeating the deposition sequence. A computer controls the whole deposition process. System constructions and the obtained results on several ternary metal thin film systems fabricated using the new deposition system will be presented.

FF3.24
Development of Alkali-Alumino-Borosilicate Glass for PDP Substrate by Float Process. Jin-Woo Kim[1], Dae-Sung Kim[1], Se-Young Choi[1] and Ki-Dong Kim[2]; [1]School of New Materials Science and Engineering, Yonsei University, Seoul, South Korea; [2]Dept. of Materials Science and Engineering, Kunsan University, Kunsan, South Korea.

The glass substrate of the PDP devices plays an important role in sealing and preventing the major parts in PDP and also transmitting image. The PDP development process which has repeatedly heat-treatment at temperature range 450 600°C requires that the glass substrate has high stability without deformation after heat-treatment and similar coefficient of thermal expansion(CTE) with electrodes. However the commercial glass substrate contains high alkali contents, which would cause deformation of the glass substrate or chemical reaction with other parts in PDP processing through the elution of alkali elements. In addition, the commercial substrate glass is manufactured by float process, so the substrate glass would be affected by tin. In the mean time, float glass that contains Sn2+ can decrease optical transmittance and electrical conductivity of ITO electrode by diffusion of Sn2+ from float glass to transparent conducting oxide during the process. In this study, the low alkali containing glass substrates were prepared based on Alkali-Alumino-Borosilicate glass system; SiO2-B2O3-ZrO2-Al2O3-R2O(Na2O+K2O)-RO(MgO+CaO+SrO+BaO)-ZnO-TiO2. Then, their thermal and physical properties were characterized by using DTA, TMA, Rotation Cylinder Viscometer, hardness, strength and UV- Visible transmittance. In order to investigate effect of Sn, EPMA and UV- Visible transmittance were used.

FF3.25
Preparation and Characterization of Porous TiO_2-SiO_2 Mixed Oxide. Ang Thiam Peng, Zhong Ziyi and Highfield James; Institute of Chemical and Engineering Sciences, Singapore, Singapore.

A study on the comparison of porous TiO_2-SiO_2 mixed oxide synthesized via amine directed method is reported. The amine capping groups used are octylamine, dodecylamine, octyldecylamine, aniline and isobutylamine. The mixed oxide is characterized with x-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), infrared spectroscopy (IR), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and Brunauer-Emmett-Teller analysis (BET). While XRD, SEM and TEM provide the structural information of the mixed oxide, BET probes into the surface area of these compounds. IR indicated the chemical mixing of both oxides. The BET results suggested that high surface area can be obtained by the mixed oxide prepared in this manner.

FF3.26
Effect of Al Additions on the Synthesis of Single-Phase Ti_3SiC_2. ZhengMing Sun[1,2], Songlan Yang[2] and Michel W. Barsoum[1]; [1]Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania; [2]National Institute of Advanced Industrial Science and Technology, Nagoya, Japan.

Ti_3SiC_2 is the most studied ternary of the MAX phase family of compounds (viz. $M_{n+1}AX_n$ where, M: early transition metal, A: group A element, X: C and/or N, n=1-3). The MAX phases have received added attention recently due to their unique combination of both metal- and ceramic-like properties. Applications of Ti_3SiC_2 compound in various fields are presently under way. However, one processing challenge has been how to process the material without secondary phases such as TiC. Pulse discharge sintering (PDS) has been applied to the reactive sintering of Ti_3SiC_2 considerably improving purity when starting with 2Ti/2Si/3TiC powders. However, the processing window remained narrow and most importantly, the sintering temperature was still high. In order to enhance both, the effects of adding a quaternary element, Al, was considered. To that effect, compositions of 3Ti-SiC-C-xAl powders with mole fractions of x varying for 0 to 0.20 were mixed and sintered with PDS, at temperatures ranging from 1200 °C to 1350 °C. During the 15 min of sintering time, a uniaxial pressure of 50 MPa was applied to a 20 mm diameter disc. Characterization of the samples revealed that for the starting powder mixture without Al, the maximum Ti_3SiC_2 content was 85 vol. %, with TiC as the main secondary phase. With increasing x content the Ti_3SiC_2 content increased to a maximum of 100% at x=0.15; at x = 0.2, the Ti_3SiC_2 content was reduced slightly. Furthermore, at x= 0.15 single-phase samples of Ti_3SiC_2 can be synthesized at a temperature as low as 1200 °C, when the PDS process is employed. Careful analysis of the sintered product revealed a higher Al concentration at the grain boundaries. This low sintering temperature is probably related to the formation of a liquid phase. Why the presence of Al inhibited the formation of TiC is not clear at this time.

FF3.27
Second+order Optical Effects in $LaFe_4Sb_{12}$. Kazimierz J. Plucinski[1], K. Nouneh[3,4], R. Viennois[3,6], Ivan V. Kityk[2,4], F. Terki[3], S. Charar[3], S. Benet[4], J. Ebothe[5], D. Ravot[5] and J. C. Tedanac[3]; [1]Electronics, Military University of Technology, Warsaw, Poland; [2]Inst. of Physics, Ped. University, Czestochowa, Poland; [3]Univ. Montpellier, Montpellier; [4]Univ. d'Perpignan, Perpignan, France; [5]Univ. de Reims, Reims, France; [6]Max-Planck Institut, Dresden, Germany.

Thermoelectric materials have recently attracted a considerable amount of interest. Among these, a new group called "filled" skutterudite composites of unit-formula RM_4X_{12} (where R is the rare- or alkaline-earth or actinide element; M = Fe, Ru or Os; X = P, As or Sb) should be a subject of specific attention because of their extremely large figure of merit $Z = (S^2\sigma / k)$, that is the main requirement for thermoelectric applications. S is the Seebeck coefficient; σ the electrical conductivity and $k = k_e + k_l$, the thermal conductivity, which respectively includes both electronic and phonon contributions. Besides, these filled ternary compounds exhibit a large variety of electronic properties, where the magnetic behavior is dominated by the particular 4f electronic configuration of rare earth elements. To increase the figure of merit, it is necessary to enhance the power-factor $S^2\sigma$ (characteristic of semiconductors strongly doped) and to reduce the phonon thermal conductivity. The study of electron-phonon anharmonic interactions existing in these compounds will be useful in reducing thermal conductivity. In the present paper, the PISHG is used as a main tool for studying very weak electron-phonon anaharmonic interactions enhanced by low-temperature ordering including spin alignment. A correlation between the temperature dependence of the resistivity, Seebeck coefficient and photoinduced second harmonic generation (PISHG) were found in a specific skutterudite compound, $LaFe_4Sb_{12}$. These results, found here for the first time, correlate well with the appearance of PISHG at low temperatures, which is caused by electron-phonon anharmonicity with the other above properties of transport. We observed two maxima of the PISHG at temperatures 14.5 K and 16.5 K. The PISHG signal increases substantially below 30 K. In the same temperature range, a non-Fermi liquid (NFL) behaviour developed in the resistivity. Pump-probe time dependence of the $LaFe_4Sb_{12}$, shows almost parallel shift of the PISHG with temperature. At the same time, the study of transport properties may indicate the crucial role of the van Hove singularities for the electronic

density of states. Then, the change of sign of the Seebeck coefficient S near 90 K and its maximum about 40 K may be caused by a kind of competition between two mechanisms - the first being connected with the trapping of the heavy fermions by the polarons and the second - with the activation of the carriers between particular trapping and localised levels. These effects are of a particular interest for non-equilibrium spin-phonon interactions contributing to the second-order susceptibility and can explain the PISHG signal observed.

FF3.28
Low-Temperature Formation of Epitaxial Metal Thin Films by way of Hydrogen Reduction of Epitaxially Grown Oxide Thin Films. Akifumi Matsuda[1], Shusaku Akiba[1], Takashi Okada[1], Mamoru Yoshimoto[1], Keisuke Saito[2], Kouji Koyama[3], Atsuko Takeuchi[3], Kouhei Hamaya[4] and Yoshitaka Kitamoto[4]; [1]Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Kanagawa, Japan; [2]Bruker AXS, Yokohama, Kanagawa, Japan; [3]Namiki Precision Jewel Co., Ltd., Adachi-ku, Tokyo, Japan; [4]Interdisciplinary Graduate School of Sci. and Eng., Tokyo Institute of Technology, Yokohama, Kanagawa, Japan.

Compared with the polycrystal bulky materials, the resulting products of epitaxially (single crystal like) grown various metal films, can induce unique electronic, optical, and magnetic properties and also enhance their advantages which are undoubtedly important for the development of much applications. Epitaxial metal films are mostly grown by thermal evaporation and magnetron sputtering using metal sources, which methods need high temperatures at least around 700°C. Here we report a newly developed method to prepare epitaxial metal thin films at low temperatures from hydrogen reduction of the metal oxide sources. We used the ultrasmooth sapphire (0001) substrates which have atomic steps of 0.2 nm in height and atomically flat terraces of 50-100 nm in width. In experimentals, NiO films were deposited onto the substrates at room temperature (20°C) by pulsed laser deposition (PLD) method using a sintered NiO ceramic target. Thin films were found to be NiO (111) epitaxially grown on sapphire (0001) by x-ray diffraction (XRD) and reflection high-energy electron diffraction (RHEED) measurements. The specimens were then annealed for an hour in hydrogen gas ambient, to reduce whole antiferromagnetic NiO into ferromagnetic Ni metal. As a result, after annealing even at 300°C, oxygen atoms in NiO were beard off and complete reductions were achieved. It is noted that RHEED and XRD observations clearly showed entire disappearing of NiO (111) and formation of epitaxial Ni (111) films. Further experimentals are conducted for other metal oxides such as CoO or MnO. For nanotechnology, this novel process named as Metal Oxide-Reduction-Epitaxy (MORE) method was applied for development of nanostructured metal such as metal nanowires, that is, resulting in Ni metal nanowires from NiO nanowire array grown on sapphire. The obtained epitaxial Ni metal nanowires are expected to be used as magnetic sensing device and high performance electrode or catalytic nanotemplates for the growth of CNTs and ultra-high density magnetic recording devices.

FF3.29
Metalorganic Chelated Films Grown via Layer-By-Layer Self-Assembly In Solution and In Vacuum. Ritesh Tipnis[1], Faquir Jain[2] and Fotios Papadimitrakopoulos[3]; [1]Nanomaterials Optoelectronics Laboratory, Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, Connecticut; [2]Nanomaterials Optoelectronics Laboratory, Electrical and Computer Engineering, University of Connecticut, Storrs, Connecticut; [3]Nanomaterials Optoelectronics Laboratory, Department of Chemistry, Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, Connecticut.

The non-aqueous layer-by-layer growth of metalorganic assemblies using coordination chemistry has shown an enormous potential in obtaining facile growth of highly ordered thin films, suitable for semiconductor applications. Our group has previously demonstrated the layer-by-layer growth of 8,8′-dihydroxy-5,5′-biquinoline (bisquinoline) with different zinc precursors which gave rise to films which although uniform, did not show any long-range order. This could be attributed to conformational diastereomerism of the organic ligands and inclusion of metal precursors and byproducts in the primary structure. Due to these problems we have turned our attention to a more rigid molecule, 2,5-dihydroxy-1,4-benzoquinone and have also endeavored into assembly techniques that limit the inclusion of byproducts in the assembled structures. We have successfully grown these supramolecular architectures in solution phase and have obtained a timely and a monotonic film growth, as observed by UV/VIS spectroscopy. To further improve the film characteristics and achieve a closely packed configuration, we have ventured into growing these films in vapor phase and under high vacuum. FTIR spectroscopy confirmed the film growth according to the proposed model, especially by observing the shifts in specific peaks due to the chelated structures. Atomic force microscopy shows the films grown in vacuum to be much smoother than those grown in solution, whilst maintaining their insoluble and intractable nature. Due to the chemical bonding between the substrates and the oligomeric chelates, these films have excellent mechanical integrity, which could find potential applications in the semiconductor industry.

FF3.30
Interfacial Synthesis of Anion Substituted Layered Cobalt Hydroxide with Novel Optoelectronic Properties. Kristian M. Roth[1,2] and Daniel E. Morse[1,2]; [1]California Nanosystems Institute, UCSB, Santa Barbara, California; [2]Institute for Collaborative Biotechnologies, UCSB, Santa Barbara, California.

The layered transition metal hydroxide based compound $Co_2(OH)_{3-x}(A^{-n})_{x/n}\cdot zH_2O$ with various anions (A) substituted in the interstitial space between layers has been synthesized using a room temperature vapor diffusion process. The novel method used to synthesize this material was inspired by biological systems that utilize interfacial forces to impart order on the resulting material and operate at room temperature and pressure. The crystal morphology depends strongly on the surface tension of the mother liquor. When coupled with the unique wetting properties of the layered hydroxide, this method results in the formation of sheets 2 μm thick at a water/air interface. The resulting material was characterized by TOF-mass spectrometry, XRD, XPS, UV/Vis and electron microscopy. The product is easily removed from the reaction vessel in intact sheets (1-3 cm^2) for connection to a variety of electrode geometries and materials. Large polycrystalline sheets of this material are electrically conductive without sintering and photoconductivity has been observed upon radiation with visible light along with the generation of a small photovoltage. The effects of synthesis surface tension on the morphological and electrooptic properties will be discussed.

FF3.31
Magnetic Properties of Li3Fe2(PO4)3 Nasicon-Like Compounds. Atmane Aitsalah[1], Pavel Jozwiak[2], Jerzy Garbaczyk[2], Francois Gendron[1] and Christian M. Julien[1]; [1]LMDH, University P et M Curie, Paris, France; [2]Faculty of Physics, University of Technology, Warsawx, Poland.

A tremendous resurgence of interest has been displayed in lithium metal phosphates because they contain both mobile Li cations and redox-active metal sites shrouded within a rigid phosphate framework. Lithium iron phosphates with the nasicon-like structure possess large tunnels which allow the Li+ fast-ionic transport. They are considered such as candidate materials for positive electrodes in rechargeable lithium batteries. The framework of nasicon materials may be described as a stacking of corner-sharing [Me2P3O18] "lantern" units parallel to the c-direction. Fundamentally, these materials present many questions that relate to the transport of electrons and lithium ions within the lattice. The understanding of physical phenomena such as magnetic properties is critical to the search for new materials. In this work we study the magnetic properties of Li3Fe2(PO4)3 phases using SQUID and ESR measurements. Li3Fe2(PO4)3 compounds were synthesized using wet-chemical technique from nitrate precursors. Following a series of thermal treatments (pre-heated at 400 C for 4 h and final synthesis at 700 C for 12 h in Ar ambient), the resulting nasicon-like material crystallizes in the orthorhombic system (Pcan space group). Magnetic susceptibility measurements show the deviation from the Curie-Weiss type dependency at low temperatures while electron spin resonance yields information about the immediate environment and the oxidation state of transition metal ions in the nasicon framework.

FF3.32
Structural and Magnetic Properties of Glassy Phosphates with Nasicon Structure. Pavel Jozwiak[1], Jerzy Garbaczyk[1], Francois Gendron[2] and Christian M. Julien[2]; [1]Faculty of Physics, University of Technology, Warsaw, Poland; [2]LMDH, University P et M Curie, Paris, France.

Recently, transition metal-based compound containing compact tetrahedral polyanion structural units have been investigated intensively as potential positive electrode materials for lithium-ion batteries. Among the lithium metal polyphosphate family, Li3Me(PO4)3 (Me=Fe, V, Mo) compounds crystallize with the nasicon-like structure. They are considered as stable, non toxic and green materials. However, materials display very different voltage-composition curves as a result of their structural differences. Our report concerns the structural and magnetic properties of nasicon phases including either iron, vanadium, or molybdenum transition-metal cations are investigated. Samples were synthesized by rapid quenching technique. Their structural properties of amorphous materials were investigated by spectroscopic probes such as Raman and FTIR. Their magnetic properties were measured using a SQUID apparatus in the temperature range 2-300 K. Vibrational features of

vitreous nasicon materials show similarity with those of the Li2O-V2O5-P2O5 glass system. The spectrum of Li3Me2(PO4)3 is dominated by two very strong and broad bands located in mid-infrared in the far-infrared range. A third band is attributed to the P-O-P ring of the P2O5 glass former. Studies of the magnetic susceptibility of Fe and V compounds as a function of temperature show that the room-temperature behaviour follows a Curie-Weiss model with well-defined magnetic moments associated with the transition metal sites and a negative Curie temperature consistent with the behaviour of an antiferromagnetic material at temperatures above its Neel point. For the Mo compounds, a dissimilar behaviour is observed; this material behaves as paramagnetic in the whole range of temperature.

FF3.33
Synthesis of Nanocrystalline B_4C and Low Temperature Hot Pressing. Simone Herth, Robert H. Doremus, Will Joost and Richard W. Siegel; Rensselaer Nanotechnology Center, Rensselaer Polytechnic Institute, Troy, New York.

B_4C can be sintered to full density only at extreme high temperatures. For lowering the sintering temperature, it is essential to reduce the particle size, which increases the surface area of the powder. B_4C of a grain size of 50 nm to 100 nm was successfully synthesized by the carbothermal reaction route 2 B_2O_3 + 7 C -> B_4C + 6 CO. Amorphous B_2O_3 was filled into a graphite crucible and covered with a graphite foil. Carbon black (grade 5333, Asbury Carbon), characterized as amorphous carbon with a small particle size, was put onto this graphite foil leading to an 100% excess of B_2O_3 according to the reaction equation. In order to remove moisture from the carbon powder, the carbon black was stored in an oven at about 82 øC for at least 12 hrs, ground, and put in the oven for at least additional 12 hrs before using. The crucible was annealed in a vacuum furnace at different temperatures and times at a pressure of about 10^{-3} mbar. X-ray studies of the grain size revealed average values of about 20 to 30 nm nearly independently from the annealing temperature. Additional characterization with electron microscopy shows an increase of the grain size from about 50 nm to 100 nm for annealing times of 30 minutes to 8 hrs. First results of hot pressed samples using the synthesized nanocrystalline B_4C will be shown.

FF3.34
The Synthesis of III-V Semiconductor InSb Quantum Dots by Solvothermal Reduction Reactions. Shira Black, Monica De Lezaeta, Margaret Lam, Baohe Chang and Bonnie L. Gersten; Department of Chemistry and Biochemistry, Queens College, CUNY, Flushing, New York.

The synthesis of quantum dots of the III-V semiconductor indium antimonide (InSb) by the solvothermal reduction method was investigated. InSb is a material with a large carrier mobility and a high sensitivity in the wavelength range (3-5 mm) which makes it a candidate material for applications as a quantum dot material for infrared (IR) detectors. In this study In and Sb chloride and acetate precursors were placed in an ethylenediamine solvent for 4-24 hours at 120-220oC in an autoclave. The particles were characterized by transmission electron microscopy (TEM), x-ray diffraction (XRD), and dynamic light scattering (DLS). It was found that InSb with small amounts of Sb precipitated. The particles size was found to be nano-clustered aggregates. In the future, the absorbance spectra of these powders will be investigated.

FF3.35
Preparation of Ni Nano Particles using The Polyol Process. Seon-Mi Yoon, Samsung Adv Inst of Tech, Yongin-City, Gyunggi-Do, South Korea.

The Ni nano particles are prepared by the chemically controlled polyol process, using OH dornor and water. In the previous research, it showed that the particle size depends on nucleating agent. But in this research the particle size depends strongly on amounts of basic solution rather than nucleating agent. The nucleating agents are more expensive than basic source becuase most of them are nobel metal. The nano powders could be applied to multilayer ceramic capacitor(MLCC) and recording.

SESSION FF4: Electronic, Magnetic, Optical, and Other Functional Materials
Chairs: Mercouri Kanatzidis and Jing Li
Tuesday Morning, November 30, 2004
Room 200 (Hynes)

8:30 AM *FF4.1
Hydrazinium Precursor Approach for Preparing High-Mobility Metal Chalcogenide Films. David B. Mitzi, Matthew Copel, Conal E. Murray, Laura L. Kosbar and Ali Afzali; IBM T. J. Watson Research Center, Yorktown Heights, New York.

The effort to identify low-cost solution-based deposition techniques for thin-film field-effect transistor (TFT) fabrication has accelerated in recent years, as a result of new applications potentially enabled by the alternative technologies (e.g., flexible displays, electronic newspapers, smart cards / fabric). Paramount to this search is the need to identify processes that simultaneously offer high-throughput deposition (e.g., spin coating, printing, stamping), as well as continuous high-mobility films. In this talk, we discuss a new approach for spin-coating ultrathin semiconducting films based on the low-temperature decomposition of highly soluble hydrazinium precursors of main group metal (e.g., Ge, Sn, In, Sb) chalcogenides. The process involves synthesizing the hydrazinium precursor by dissolving the metal chalcogenide in hydrazine with added chalcogen (S, Se), spin coating thin films of the precursor using an appropriate solvent and decomposing the precursor film to the targeted semiconductor using a low-temperature anneal (200 - 380 °C). The resulting metal chalcogenide films are only a few unit cells thick, with remarkably large mobilities (>10 cm^2/V-s) – an order of magnitude better than previous studies involving high-throughput solution-based deposition. Several of the hydrazinium precursors have been structurally characterized, including $(N_2H_5)_4Sn_2S_6$, $(N_2H_4)_3(N_2H_5)_4Sn_2Se_6$ and $(N_2H_5)_4Ge_2Se_6$ and each is shown to consist of dimers of edge-sharing MX_4 (M = Sn or Ge; X = S or Se) tetrahedra, separated by hydrazinium cations. Dimensional reduction of the extended metal chalcogenide framework into small isolated anionic species accounts for the high degree of solubility of the precursors in selected solvents (e.g., hydrazine, hydrazine/water, amines). The small size of the hydrazinium counter-cation (and correspondingly the relatively small film volume loss during the decomposition step) likely also contributes to the high quality and continuity of the resulting ultrathin metal chalcogenide films deposited using the new approach.

9:00 AM *FF4.2
Chalcogenide Tetrahedral Clusters and Open Frameworks. Pingyun Feng[1], Nanfeng Zheng[1] and Xianhui Bu[2]; [1]Chemistry, University of California at Riverside, Riverside, California; [2]Chemistry and Biochemistry, California State University of Long Beach, Long Beach, California.

Open framework chalcogenides represent an interesting class of materials that combines uniform porosity with high electrical conductivity and tunable optical properties. They consist of single-sized tetrahedral clusters that act as molecular building blocks in the formation of well-ordered superlattices from zero to three dimensions. Tetrahedral clusters can be joined directly to produce purely inorganic frameworks or by multidentate organic ligands to form inorganic-organic hybrid frameworks. A number of main-group and transition metals have been incorporated into clusters to allow the modification of structural and physical properties. The structural analysis based on single crystals reveals detailed information that could help the structural elucidation of larger colloidal nanostructures. The synthesis, structures, and various properties such as porosity, photoluminescence, tunable bandgap, and fast ion conductivity will be discussed.

9:30 AM FF4.3
Synthesis and Characterization of Metal-Organic Frameworks and Metal-Organic Polyhedra Containing Oligo-thiophene Units. Zheng Ni[1], Abderrahim Yassar[2] and Omar Yaghi[1]; [1]Department of Chemistry, the University of Michigan, Ann Arbor, Michigan; [2]ITODYS, Universite Paris 7, Paris, France.

A series of 3-dimensional Metal-Organic Frameworks (MOFs) and 0-dimensional Metal-Organic Polyhedral structures (MOPs) were synthesized by using solvothermal reactions of oligo-thiophene dicarboxylic acid with metal salts (mainly copper, zinc and lathanides). These compounds have been analyzed by X-ray diffraction (single crystal and powder), UV-vis, IR, fluorescence spectroscopy, thermal gravimetric analysis and elemental analysis. The important interactions between the oligo-thiophene units in these compounds were elucidated based on single crystal structures. These oligo-thiophene-containing MOFs and MOPs represent a unique type of materials potentially combining the properties of crystallinity, porosity and electrical activity. A preliminary study of the porosity and conductivity of these materials will also be presented.

9:45 AM FF4.4
In-situ Study of Reduction of CuO Nanoparticles. Jenna Pike[1], Siu-Wai Chan[1], Feng Zhang[1], Jonathan C. Hanson[2] and Xianqin Wang[2]; [1]Applied Physics and Applied Mathematics, Columbia University, New York, New York; [2]Department of Chemistry, Brookhaven National Lab, Upton, New York.

CuO is widely used as a catalyst in many reactions, and the CO oxidation activiy of CuO and its suboxide Cu_2O has been the subject

of many studies. Synchrotron-based time-resolved X-ray diffraction (TR-XRD) was used to investigate the reduction of CuO nanoparticles with CO gas. The in-situ experiments show that under a normal supply of CO, monoclinic CuO nanoparticles form a stable intermediate cubic phase, Cu_2O, rather than a direct transformation to metallic, cubic Cu, as has been observed for bulk CuO particles. Copper oxide nanoparticles are prepared by mixing aqueous solutions of copper nitrate and hexamethylenetetramine (HMT) at 50C. Transmission electron microscope (TEM) results show that the shape and size of the CuO nanoparticles are controlled by varying the HMT concentration. An increase in HMT concentration results in a decreased nanoparticle aspect ratio. In addition, the less acicular CuO particles reduce more quickly to Cu_2O. These results indicate the relationship among morphology, particle size, and reduction behavior may have significant consequences for the use of CuO nanoparticles in catalytic applications.

10:30 AM *FF4.5
Crystal Growth and Physical Properties of $Ln_3Co_4Sn_{13}$ (Ln = La, Ce) and Tb_4MGa_{12} (M = Pd, Pt). Julia Y. Chan, Evan L. Thomas, Willa Williams, Andrew N. Bankston and Vanessa Kemp; Chemistry, Louisiana State University, Baton Rouge, Louisiana.

To gain a better understanding of the interplay between structure and physical properties, we have grown large single crystals (up to 1 cm^3) of several new rare earth intermetallics including $Ln_3Co_4Sn_{13}$ (Ln = La, Ce) and Tb_4MGa_{12} (M = Pd, Pt). $Ln_3Co_4Sn_{13}$ (Ln = La, Ce) are cubic with space group $Pm3n$ with a 9.6410(5)$\AA$ and 9.6010(6)$\AA$, respectively. $Ln_3Co_4Sn_{13}$ consist of interpenetrating A15-like $SnLn_3$ and trigonal prismatic $RhSn_3$ sublattices, in addition to Ln cuboctahedra and $SnSn_{12}$ icosahedra. The Sn compounds will also be compared to Tb_4MGa_{12} (M = Pd, Pt). The Tb compounds crystallize in the cubic space group $Im-3m$, with Z = 2 and lattice parameters: a = 8.5940(5) $\AA$ and a = 8.587(11) $\AA$ for Tb_4PdGa_{12} and Tb_4PtGa_{12}, respectively. The crystal structure consists of corner-sharing MGa_6 octahedra and $TbGa_3$ cuboctahedra. Magnetic measurements suggest that Tb_4PdGa_{12} is an antiferromagnetic metamagnet with a Neel temperature of 16 K, while the Pt analog orders at T_N = 12 K. The structures of these materials and the role of rare earth coordination with respect to the physical properties will be discussed.

11:00 AM FF4.6
Pressure Tuning of Thermoelectric Materials: Computation and Experiment. Thomas Scheidemantel[1,2,3], John Badding[2,3], Jorge Sofo[1,3], Gerald Mahan[1,3], Francis DiSalvo[4], Jinfang Meng[2,3], Timo Thonhauser[1,3] and Michael Mcguire[4]; [1]Department of Physics, The Pennsylvania State University, University Park, Pennsylvania; [2]Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania; [3]Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania; [4]Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York.

The conventional means of searching for new materials, in this case efficient thermoelectrics, is to synthesize a large number of compounds and investigate each in detail as a function of materials parameters, such as preparation conditions and doping levels. Each compound thus represents one point in a phase space determined by electronic and structural parameters. With the use of pressure one can continuously adjust the interaction parameters and follow the change in properties for each compound. Thus a much larger volume of this interaction phase space can be "scanned" in a short time without the large effort necessary to produce the thousands of materials necessary to do so with the conventional approach. We have demonstrated that antimony bismuth telluride can be pressure tuned to exhibit a high thermoelectric power and an associated thermoelectric figure of merit that is at least a factor of two higher than any known material at ambient pressure. This demonstration that higher ZT is possible under pressure is a valuable "existence proof". Our current research goals are now focused on chemical modification of the semiconductors that have been successfully pressure tuned with the goal of obtaining improved thermoelectric properties at atmospheric pressure. Recent studies of antimony bismuth telluride alloyed with selenium and arsenic at ambient and high pressure has provided valuable information about this high ZT. This new understanding suggests future research directions for ambient pressure chemical tuning. We have also implemented methods for calculating transport coefficients from first-principles calculations, providing a means to estimate the thermoelectric properties of a compound with input of only the lattice parameters and structure. We use the band structure calculated using the powerful FLAPW method within density functional theory. As a preliminary test, bismuth telluride was studied because its transport properties are well documented. Our calculations are in very good agreement with published results. We also used this method to explore the improvements in the thermoelectric power in the alloys discussed above. Calculations using ambient pressure and high pressure (hydrostatic and non-hydrostatic) structures may provide insight into these increases in thermopower.

11:15 AM FF4.7
Inducing Magnetism in Wide Band Gap Hosts. Ram Seshadri[1], Aditi S. Risbud[1] and Gavin Lawes[2]; [1]Materials Department, University of California, Santa Barbara, California; [2]Los Alamos National Laboratories, Los Alamos, New Mexico.

We have used precursor routes to prepare magnetic transition metal ion (tM) substituted wurtzite ZnO powders with up to 15% tM substitution (tM = Co^{2+} and Mn^{2+}) on the cation site. Careful magnetic studies reveal that these samples show no cooperative magnetic ordering, and certainly no ferromagnetism. Instead, the nearest-neighbor coupling is actually antiferromagnetic. Modeling of the temperature dependence of the magnetic susceptibility indicates the difficulty in inducing ferromagnetism, in keeping with the results of density functional calculations. We have then tried the alternate strategy of inducing dilute *ferrimagnetism* in wide band gap spinel hosts with two cations sites. This approach has been more successful: dilute magnets based on tM substitution in spinel $ZnGa_2O_4$ seem promising, displaying magnetic hysteresis in nearly transparent samples.

11:30 AM FF4.8
Synthesis and Properties of [B/C] Layered Compounds. Takao Mori, [1]National Institute for Materials Science, Tsukuba, Japan; [2]PRESTO, Japan Science and Technology Agency, Kawaguchi, Japan.

Metal borocarbide compounds containing boron and carbon mixed 2D layers are interesting materials. Structurally, a wide variation in the coordination of the [B/C] layer is exhibited depending on the type/size of metal atoms sandwiched in between, even for compounds with the same stoichiometry [1,2]. We have been interested in these compounds ever since we discovered the first [B/C] graphite intercalation-like compound, $Sc_2B_{1.1}C_{3.2}$ which has a $[B_1C_2]_\infty$ graphitic layer [3]. In topics of recent interest, high temperature ferromagnetism was reported in the [B/C] CaB_2C_2 compound, which has similarities to the well known doped CaB_6 [4]. Synthesis of completely Fe-free CaB_2C_2 was successfully carried out and it was found that the magnetism is actually diamagnetic [5]. In another topic, the discovery of superconductivity in MgB_2 [6] has engendered an enormous amount of work throughout the world, because of the relatively high temperature of the transition, T_C = 39 K, and the simple structure of the binary compound. However, new developments are eagerly awaited since there have not been any well established reports of a sizable increase of T_C by doping of MgB_2 itself, nor any reports of similar MB_2-type compounds exhibiting high temperature superconductivity. We have focused on the [B/C] compounds MgB_2C_2 and LiBC, which have similar features in the band structure to MgB_2. Results of our investigation into the synthesis and hole-doping of these compounds will be presented. [1] J. Bauer *et.al*, Coord. Chem. Rev. 178 (1998) 723. [2] P. Rogl, Phase Diagrams of Ternary Metal-Boron-Carbon Systems, ASM (1998). [3] T. Mori *et.al*, Phys. Rev. B 62 (2000) 7587. [4] D. P. Young *et.al*, Nature 397 (1999) 412. [5] T. Mori *et.al*, J. Phys. Soc. Jpn. 71 (2002) 1789. [6] J. Nagamatsu *et.al*, Nature 410 (2001) 63.

11:45 AM FF4.9
First-Order Raman Scattering from the M_n+1AX_n Phases. Jonathan E. Spanier[1], Surojit Gupta[1], Maher Amer[2] and Michel W. Barsoum[1]; [1]Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania; [2]Dept. of Mechanical and Materials Engineering, Wright State University, Dayton, Ohio.

We report on the Raman spectra of Ti_3SiC_2, M_2AlC (211), (M=Ti, V, Cr and Nb) and Ti_4AlN_3 as representative compounds from the family of $M_{n+1}AX_n$ phases, and present an analysis of the spectra based on symmetry considerations and from results of first principles calculations of phonon frequencies. Unlike other metallic systems having Raman-active phonons, the MAX phases exhibit relatively intense and narrow Raman scattering features. The agreement between the experimental and theoretical mode energies is excellent. The identification of the modes enables application of Raman scattering as a diagnostic tool for the detailed study of the structural and physical properties of this family of compounds and their engineered solid solutions.

SESSION FF5/K5: Joint Session: Solid State Chemistry of Ionics Conductors
Chairs: Nathaniel Brese and Harry Tuller
Tuesday Afternoon, November 30, 2004
Republic B (Sheraton)

1:30 PM *FF5.1/K5.1

NMR Investigations of Ionic Conduction Mechanisms in Oxides and Fluorides: Applications to Pyrochlores, Perovskites, Aurivillius Phases and Fluorites. Namjum Kim, John L. Palumbo, Stephen A. Boyd and Clare P. Grey; Chemistry, SUNY Stony Brook, Stony Brook, New York.

Solid state NMR may be used to correlate local structure with the dynamics that occur in ionic conductors. For example, in studies of α-$Bi_4V_2O_{11}$, we have shown that ^{17}O MAS NMR may be used to (i) distinguish between oxygen ions in the $[Bi_2O_2]^{2+}$ and vanadium oxide (perovskite) layers, and (ii) detect the mobility of the ions in the perovskite layers. $^{17}O/^{51}V$ double resonance NMR experiments, which probe proximity between different nuclei, were used to confirm the assignments of the resonances and as an additional probe of oxygen mobility. Two-dimensional NMR may be used to detect much slower motion, allowing a wider range of oxide-ion conductors to be studied with ^{17}O NMR. Applications of this approach to study motion in Nb^{5+} -doped Bi_2WO_6 and Ca^{2+}-doped $Y_2Ti_2O_7$ will be shown. In more recent work, we are investigating the effect that particle size has on local structure and conductivity of doped fluorides.

2:00 PM FF5.2/K5.2

Structure Specificity of Nanocrystalline Praseodymia Doped Ceria. Vladislav A. Sadykov[1], Vladimir I. Voronin[2], Alexander N. Petrov[3], Yulia V. Frolova[1], Vladimir I. Zaikovskii[1], Holger Borchert[1] and Stylianos Neophytides[4]; [1]Heterogeneous catalysis, Boreskov Institute of Catalysis, Novosibirsk, Russian Federation; [2]Institute of Metals Physics, Ural Branch of RAS, Ekaterinburg, Russian Federation; [3]Chemical Department, Ural State University, Ekaterinburg, Russian Federation; [4]Institute of Chemical Engineering & High Temperature Processes, Patras, Greece.

Praseodymia doped ceria possessing a high mixed conductivity is of a great interest for such application as fuel cell electrodes, oxygen separation membranes, sensors etc. However, up to day neutron diffraction studies of this system have not bee available. In this work, nanocrystalline samples of praseodymia doped ceria (x Pr =0-0.5) prepared by Pechini route and calcined under air at 500-1300 C were studied by using TEM and neutron diffraction methods. The neutron diffraction studies were performed at room temperatures with the use of a D7a neutron diffractometer installed at the horizontal channel of an IVV-2M reactor. The structural parameters were refined by the Rietveld full-profile method with the Fullprof program package. The charge state of Pr in samples was characterized by XPS. TEM revealed a good crystallinity of nanodomains (typical sizes 50-100 A) disorderly stacked into platelets. Within studied doping range, all samples were found to be single-phase fluorites. The lattice constant goes through the maximum at x =0.3. This trend correlates with variation of the diffraction peaks half-width and intensity of diffraction background corresponding to an admixture with a high non-elastic thermal neutron scattering cross-section (such as hydroxyls, water etc). This behavior was explained by existence of both Pr3+ and Pr4+ cations in samples as revealed by XPS. At higher Pr content Pr4+/Pr3+ ratio increases which explains decreasing of the lattice constant due to smaller size of Pr4+ cation. The surface layer hydroxylation leading to the increase of O/Me ratio up to 2.2 was demonstrated by XPS, while the lattice hydroxyls were detected by FTIRS. Domain boundaries could be hydroxylated as well due to their loose structure. For all nanocrystalline samples, Rietveld structure refinement has not revealed any substantial deviations of the O/Me occupation factors ratio from 2, though it does not exclude simultaneous presence of both cation and anion vacancies in the lattice. Decline of a mean Pr-O distance with Pr content approaching that of Ce4+-O was revealed correlating with the increase of Pr4+ content for heavily-doped samples. For a given Pr content, the lattice constant declines with calcination temperature reaching at 1300 C values typical for dense coarse-grained systems due to oxidation of Pr3+ to Pr4+ and dehydroxylation of a sample. Based upon all these results, the structural model for the nanocrystalline praseodymium doped ceria is suggested. This includes existence of both cation and anion vacancies in the lattice filled in part by dissociated water species. The relative stability of this defect structure is ensured by a high value of the free surface and developed domain boundaries network. This work is in part supported by INTAS 01-2162 and ISTC 2529 Projects. DAAD postdoctoral research scholarship to H.B. is acknowledged.

2:15 PM FF5.3/K5.3

Measurement of the Transport Mechanism of YSZ and CGO Thin Films with Nanometer-Sized Grain Structure. Joshua L. Hertz, Anja Bieberle and Harry L. Tuller; Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Micro-solid oxide fuel cells hold promise as portable power sources with energy densities considerably above that exhibited by batteries. However, the use of thin film processing schemes often produces films with nanometer-scale grain sizes. Others have reported transport mechanism changes in zirconia and ceria-based materials at these size scales, often leading to decreases in activation energy1,2. In this work, thin film yttria-stabilized zirconia [YSZ] and cerium gadolinium oxide [CGO] solid electrolytes were sputtered onto insulating substrates over a range of temperatures. Films were produced with a range of grain sizes, ranging from as small as 10-20 nm for those sputtered at room temperature. For reference, polished samples of single crystal and bulk, poly-crystalline YSZ were also used. Platinum, platinum-YSZ cermet and gold film electrodes were then sputtered on top and lithographically patterned to give interdigitated electrodes with well-controlled geometry. Electrode patterns with variable separation distances and triple phase boundary lengths, ranging over nearly two orders of magnitude, were used. Impedance spectroscopy was carried out on these samples at controlled temperatures, DC bias and oxygen partial pressures. The microstructure and chemistry of the films were characterized by XRD, TEM, AFM, WDS and RBS. Correlating the measured electrochemical performance data with sample morphology, geometry, composition and measurement environment provided insight into the transport mechanism of the films as well as the reaction pathways at the electrodes. This work was supported by the DoD Multidisciplinary University Research Initiative (MURI) program administered by the Army Research Office under Grant DAAD19-01-1-0566. 1. P. Mondal, A. Klein, W. Jaegermann and H. Hahn, Solid State Ionics, 118, 331 (1999). 2. Y. Li, M. Liu, J. Gong, Y. Chen, Z. Tang and Z. Zhang, Mat. Sci. and Eng. B, 103, 108 (2003).

2:30 PM *FF5.4/K5.4

Ion Conduction - Bulk vs. Interface. Joachim Maier, Solid State Chemistry I, Max Planck Institute for Solid State Research, Stuttgart, Germany.

The first part of the talk gives a brief overview on fundamentals of ion conduction in the bulk of solids, in particular on the dependence of charge carrier concentrations on materials and control parameters. The second part highlights the modifications in charge carrier concentrations that are due to the presence of interfaces, and discusses in how far the purposeful introduction of interfaces can be used as a materials design parameter. The third part discusses true size effects, i. e. effects in which neighboring interfaces perceive each other. It is shown that nano-ionics is of similar perspective for Solid State Ionics as nano-electronics is for the field of electronics. Size reduction leads to a variety of anomalies in terms of ion conduction, mixed conduction, and charge storage that can be understood in terms of defect chemistry and can be used in terms of electrochemical devices.

3:30 PM *FF5.5/K5.5

Ionic Transport Properties of Mixed Conducting Perovskite Oxides. Werner Sitte and Edith Bucher; Department of General, Analytical and Physical Chemistry, University of Leoben, Leoben, Austria.

Mixed ionic-electronic conducting oxides are of interest as potential candidates for solid oxide fuel cell cathodes, oxygen permeable membranes, or sensors. At high temperatures and low oxygen partial pressures these transition metal oxides exhibit large concentrations of vacant oxygen sites, inducing high ionic conductivity and high oxygen diffusivity. However, with increasing oxygen deficit, vacancy association in microdomains within the disordered matrix is assumed. The degree of ordering in the oxygen sublattice controls the number and mobility of ionic charge carriers available for oxygen transport. Experimental evidence for order-disorder transitions has been reported for a number of compounds in the (La,Sr)(Co,Fe)O3-δ system. Measurements of the oxygen transport properties, i.e. the temperature and pO2-dependences of the ionic conductivity and the kinetic parameters for oxygen exchange (chemical diffusion coefficient, surface oxygen exchange coefficient) are used to gain insight into oxygen vacancy ordering and formation of defect clusters in La1-xSrxCoO3-δ (x=0.4, 0.6) and La1-xSrxFeO3-δ (x=0.6) [1]. Additionally, selected samples quenched from the T- and pO2-conditions of interest are studied on the nanometer scale by transmission electron microscopy in order to elucidate the microstructure [2]. It is concluded that ordering leads to progressive immobilization of oxygen vacancies and consequentially to a decrease of the ionic conductivity with increasing oxygen nonstoichiometry in La1-xSrxCoO3-δ (x=0.4, 0.6). Similar effects are believed to be responsible for the decrease of the chemical diffusion coefficient of La1-xSrxCoO3-δ (x=0.6) with decreasing oxygen partial pressure. Microdomains with vacancy ordered structures could be detected by analytical electron microscopy in highly oxygen-deficient samples of La0.4Sr0.6CoO3-δ. High resolution transmission electron microscopy revealed a superstructure within the oxygen sublattice in domains of about 100 nm in size. References 1. E. Bucher, A. Benisek, W. Sitte, Solid State Ionics 157 (2003) 39-44. 2. E. Bucher, W. Sitte, I. Rom, I. Papst, W. Grogger, F. Hofer, Solid State Ionics 152-153 (2002) 417-421.

4:00 PM FF5.6/K5.6

Defect Chemical Role of Mn in Gd-Doped CeO_2 (GDC). Sang-Hyun Park and Han-Ill Yoo; School of Materials Science and Engineering, Seoul National University, Seoul, South Korea.

It has been known that addition of a small amount of Mn remarkably accelerates sintering of Gd-doped CeO_2, that is, rendering the sintering possible at much lower temperature than otherwise. This phenomenon is generally understood as being due to Mn acting as acceptors to increase the concentration of charge compensating oxygen vacancies and hence to enhance the mass transport. In this case, one would even expect that the electrolytic domain of GDC may be enlarged towards the reducing atmosphere because Mn tends to be more effective as acceptors due to its ever reducing valence down to +2 (or Mn_{Ce}") with decreasing oxygen activity. In order to elucidate the defect chemical role of Mn in GDC, we examined the electrical conductivity on 5 m/o Mn-doped GDC in association with XRD and EPMA analyses. It has been found that Mn addition does neither enhance the ionic conductivity nor enlarge the electrolytic domain width towards reducing atmosphere, indicating that Mn is by no means so effective an acceptor as expected. Furthermore, despite that the specimens are X-ray-wise pure, rastered EPMA results revealed at grain boundaries the isolated packets with Mn enriched. It is, thus, suggested that the solubility limit of Mn in GDC is likely no more than 1 m/o and the sintering enhancement is likely due to a liquid phase at grain boundaries due to the enriched Mn.

4:15 PM FF5.7/K5.7

Growth and Characterization of Highly Oriented Pure and Gd2O3 Doped CeO2(111) on ZrO2(111)/Al2O3(0001) System. Debasis Bera[1,2], S. Seal[1], S. Azad[2], C. M. Wang[2], V. Shutthanandan[2], D. E. McCready[2], M. H. Engelhard[2] and S. Thevuthasan[2]; [1]MMAE, University of Central Florida, Orlando, Florida; [2]Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington.

Epitaxial growth of ceria on insulator substrates has been the focus of materials research in the recent years due to its applications in technological devices such as sensors, solid oxide fuel cells, batteries and three-way catalysts of automobiles. Highly oriented pure and Gd2O3 doped ceria films have been grown on pure and ZrO2(111) buffered Al2O3(0001) substrates using oxygen plasma-assisted molecular beam epitaxy (OPA-MBE). These films were characterized by several surface and bulk sensitive capabilities. The Ceria films grown on pure Al2O3(0001) substrate show polycrystalline features due to structural deformations resulting from the large lattice mismatch between the Al2O3(0001) substrate and the ceria film. However, the ceria films grown on a thin layer of ZrO2(111), which is grown as a buffer layer on top of Al2O3(0001), appears to be epitaxial and highly oriented. This is presumably due to the much smaller lattice mismatch between cubic zirconia and ceria compared to the substantial differences between the lattice parameters of Al2O3(0001) and ceria. Oxygen ionic conductivity in Gd2O3 doped ceria films has been measured as a function of Gd concentration and these results will be compared with the ion conductance of the polycrystalline ceria films. Inter-diffusion of elements at the CeO2/ZrO2 interface has been studied using high resolution transmission electron microscopy (HRTEM) and x-ray photoelectron spectroscopy (XPS) depth profiling. Detailed discussion of these results, along with the Rutherford backscattering spectrometry results will be presented.

4:30 PM FF5.8/K5.8

Morphology and Electrochemistry of Hydrothermally Synthesized Olivine Phosphates. Brian L. Ellis, Subramanya P. Herle, Young-Ho Rho, William R. M. Makahnouk and Linda F. Nazar; Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada.

Among the many positive electrode materials being studied for rechargeable lithium batteries, $LiFePO_4$ is a promising material based on its low environmental impact and low cost of the raw materials. However, the material has a low inherent electrical conductivity, limiting its electrochemical performance thus far. Two of the most critical solutions in producing $LiFePO_4$ that exhibits close to theoretical capacity at high rates have been found to be coating the crystallites with carbon (or another conductive coating) and reduction of the particle size to reduce the transport path length. We report here novel synthetic methods based on hydrothermal synthesis in the presence of solution additives, which result in very small crystallite, single-phase $LiFePO_4$. The $LiFePO_4$ products are produced either directly by hydrothermal synthesis, or by coating the precursor crystallites with various agents, followed by heat treatment at 600øC-800 øC under reducing atmospheres. The morphology of the end product can be controlled by the manipulation of the concentration of precursors, pH, hydrothermal pressure and the nature of the additive. Control of these factors results in crystallites with an average size of between 500 - 700nm, and a narrow particle size distribution. Morphology and particle size distribution of the hydrothermal product are maintained during heat treatment at higher temperatures, as the additive remains on the surface of the crystallite and hence limits particle sintering. The effects of morphology and particle size on electrochemical performance will be described.

4:45 PM FF5.9/K5.9

Vibrational Features of Polyphosphates used as Lithium Intercalation Materials. Christian M. Julien[1], Pavel Jozwiak[2,1], Jerzy Garbaczyk[2] and Michel Massot[3]; [1]LMDH, University P et M Curie, Paris, France; [2]Faculty of Physics, University of Technology, Warsaw, Poland; [3]LPMC, University P et M Curie, Paris, France.

Among the huge family of compounds constituted by phospho-oxide polyanions, the polyphosphates can be sub-classified into orthophosphates characterized by (PO4)3- isolated units, pyro- and diphosphates in which P2O7 groups are formed by two shared corner (PO4)3- units, and triphosphates (n=3) where three (PO4)3- units form (P3O10)5- anions. The adaptability of PO4 tetrahedra and P2O7 groups of interest possess an open framework that houses interstitial lithium ions. Thus, lithium transition-metal phosphates built from MeO6 octahedra linked to PO4 tetrahedra are candidates as positive electrodes for Li-ion batteries. We present here the results obtained from structural characterisation using X-ray diffractometry and local probe such as Raman and FTIR spectroscopy. Vibrational features and local cationic environments in different structures including both crystalline and glassy form of phospho-olivines LiMePO4, pyrophosphates LiMe1.5P2O7, and Nasicon-like Li3Me2(PO4)3 frameworks are presented. The infrared and Raman spectra of these materials are interpreted using factor group analysis and molecular model. Spectroscopic data show the fingerprint of the various frameworks and the possibility of obtaining direct information about the configuration of (PO4)3- polyanions and of P-O-P bridges.

SESSION FF6: Poster Session: Solid State Posters II
Tuesday Evening, November 30, 2004
8:00 PM
Exhibition Hall D (Hynes)

FF6.1

A Model of New Spin Gap Materials: A Novel Vanadate Compound BaCu2V2O8. He Zhangzhen, Kyomen Toru and Itoh Mitsuru; Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan.

The inorganic compounds of copper oxides with Cu2+ are found that their structural feathers are well defined toward quasi-one-dimensional spin systems, in which the Cu2+ ions are bridged by oxygen ions. In terms of the properties of known inorganic spin gap compound and the features of their compositions, a suitable model that aids the search for new spin gap materials has been proposed. The model compounds, formulated as MmCu2X2On, may be new spin gap materials. The model suggests that investigation for a new spin gap material would be profitably conducted by focusing on borates, phosphates, silicates, vanadates, and germandates. For example, recently, a novel vanadate compound, BaCu2V2O8 was found to have a nonmagnetic ground state with a large spin gap of about 230 K. the structure and growth of crystal should be also discussed.

FF6.2

The Effect of Dopant Additions on the Microstructural Characteristics of Boron Fibers. James V. Marzik[1], Raymond J. Suplinskas[1], William J. Croft[2], Warren J. MoberlyChan[2], John D. DeFouw[3] and David C. Dunand[3]; [1]Specialty Materials, Inc., Lowell, Massachusetts; [2]Harvard University, Cambridge, Massachusetts; [3]Northwestern University, Evanston, Illinois.

Boron fibers made by a commercial chemical vapor deposition (CVD) process have been used as precursors for the formation of magnesium diboride superconducting wires. Prior to a reaction with magnesium, the addition of dopants such as carbon and titanium to the boron fiber has been shown to enhance the superconducting properties of MgB2. These dopants also influence the kinetics of the reaction with magnesium. In this study, the effect of dopant additions on the microstructure of boron fibers was investigated using powder x-ray diffraction and scanning electron microscopy (SEM). Dopant levels and distribution were measured using energy dispersive x-ray spectroscopy (SEM/EDS). Additionally, bundles of boron fibers were pressure infiltrated with molten magnesium and heat treated at elevated temperatures. The microstructure and microchemistry of the fiber-metal interface was investigated by transmission electron microscopy (TEM) and electron probe microanalysis (EPMA).

FF6.3

Study Of Electrical, Chemical And Structural Characteristics Of Superconductor Thin Film Obtained By Polymeric Precursors Method. Claudio Luiz Carvalho[1], Raphael Otavio Peruzzi[1] and Durval Rodrigues Junior[3]; [1]Physics and Chemistry, Universidade Estadual Paulista, Ilha Solteira, SP, Brazil; [2]Physics and Chemistry, Universidade Estadual Paulista, Ilha Solteira, SP, Brazil; [3]Materials Engineering, Faculdade de Engenharia Quimica de Lorena, Lorena, SP, Brazil.

Superconductor films of BSCCO system have been grown by dip coating technique with good success. Chemical method allow us to growth up superconductor thin films of high temperature with a great advantage to get as better control about stoichiometry, large areas and so cheaper than another methods. There is a great technological interest in the growth oriented superconductor films due anisotropic characteristics of superconductor materials of high critical temperature, in general the cuprates, as we know that the orientation may increase the electrical transport properties. Based on this, the polymeric precursors method has been used to obtain thin films of BSCCO system. In this work we have applied that method together the deposition technique known as dip coating to obtain superconductor thin films Bi-based, specificly, $Bi_{1.6}Pb_{0.4}Sr_{2.0}Ca_{2.0}Cu_{3.0O}O_{x+\delta}$, also known as 2223 phase with critical temperature around 110 K. The films with multilayers have been grown up on crystalline substrates of $LaAlO_3$ and orientation (100) after heat treated around 790°C - 820°C in lapse time of 1 hour in controlled atmosphere. XRD measurements have shown the presence of crystalline phase 2212 with critical temperature around 85 K with (001) orientation, as well small fraction of 2223 phase. SEM has shown a low uniformity and some cracks that maybe relation with the applied heat treatment, WDS have also used to study the films composition. Different heat treatments have been used with the aim to increase the percentage of 2223 phase. Measurements of resistivity confirmed the presence at least two crystalline phase, 2212 and 2223, with T_c around 85 K and 110 K, respectively.

FF6.4

The electronic structure and polaronic conductivity of olivine phosphates. Thomas Maxisch, Fei Zhou, Kisuk Kang, Dane Morgan and Gerbrand Ceder; DMSE, MIT, Cambridge, Massachusetts.

Materials with the olivine Li_xMPO_4 (M = Fe, Mn) structure form an important class of new materials for rechargeable Li batteries. There is significant interest in their electronic properties because of the importance of electronic conductivity in batteries for high rate applications. Using ab initio DFT+U methods which have been found to be well suited for these correlated-electron systems, the electronic structure of several Li_xMPO_4 compounds has been determined. The calculated optical band gap value of $LiFePO_4$(E_g= 3.8 eV) is in good agreement with experimental values, but in sharp contrast to those of LDA or GGA simulations. It is argued that correlated-electron methods are necessary for accurate prediction of many properties of olivine materials because of the localized nature of valence electrons in these systems. Additionally, evidence has been found that electronic transport can be explained can be explained in terms of nearest-neighbor electron hopping accompanied by a local, short-range crystal distortion forming small polarons. Our calculations reveal a spontaneous formation of localized small polarons in these materials. By evaluating the totalfree energy along a hopping path, it is possible to determine the polaron hopping barriers which are in good agreement with values deduced from conductivity measurements. Therefore it is argued that calculations from first principles are appropriate to describe electronic transport in these materials. Implications for rate behavior and electronic conductivity of Li_xMPO_4 compounds will be discussed.

FF6.5

Does the Mercury Dope Boron Carbide? Carolina C. Ilie, Snjezana Balaz, Luis G. Rosa, Bernard Doudin and Peter A. Dowben; Physics and Astronomy, UNL, Lincoln, Nebraska.

Hg and alkali metal mixtures with molecules have a long history in the study of non-metal to metal transitions. Using photoemission and electron energy loss spectroscopy, we have investigated the changes in the electronic structure of molecularly adsorbed orthocarborane films as a function of Hg co-adsorption. Two scenarios for co-adsorption of Hg and the icosahedral molecule closo-1, 2 dicarbadodecaborane (orthocarborane) are considered. The mercury atoms may form a lattice which weakly interacts with orthocarborane lattice, or Hg may form a layer between the Cu substrate and orthocarborane molecular film [1]. Mercury $5d_{5/2}$ shallow core level widths in photoemission suggest interaction with the molecular film, but the binding energies of the molecular orbitals induced photoemission feature suggest that the interaction is weak. Hg interaction with the closo-carborane molecule is seen to be repulsive. [1] D. N. McIlroy, Jiandi Zhang, P. A. Dowben, P. Xu and D. Heskett, Surface Science 328, 47-57 (1995).

FF6.6

Intensity Dependence of Photoluminescence in Zinc Oxide. Wensheng Shi, Bin Cheng and Edward T. Samulski; Chemistry, University of North Carolina, Chapel Hill, North Carolina.

Photoluminescence from zinc oxide nano-sized particles, rods, and miro-sized particles and a single crystal were measured under various conditions of the UV excitation light. Both the band-gap emission and the deep-level emission were observed from all of the zinc oxide samples. Both kinds of emissions from the different dimensional zinc oxide samples strongly depended on the density of the excitation light. Our results indicated that the intensity ratio of the band gap emission and deep level emission from a zinc oxide could not be employed to evaluate the quality of the zinc oxide.

FF6.7

Heterogeneous Solid State Reduction of Organic Electron Acceptors by Inorganic Electrides. Andrew S. Ichimura and Shungo Miyabe; Chemistry and Biochemistry, San Francisco State University, San Francisco, California.

Alkali metal-doped siliceous zeolites (M@SZ; M=Na-Cs), also called inorganic electrides, are prepared by the addition of alkali metals to the zeolite from the gas phase. They have physical properties in common with organic complexant based electrides, such as the presence of stoichiometric amounts of trapped electrons and a one-to-one electron/cation ratio.1,2 Because inorganic electrides are heat tolerant in vacuo to 473 K (complexant based electrides decompose above 233 K), these materials may have applications that take advantage of their physical properties and chemical reactivity. The present work explores the reductive properties of zeolite based electrides. Two silica zeolites, ITQ-4 (IFR) and siliceous zeolite-Y, with 1-D and 3-D void space topologies, respectively, were used as hosts for the alkali metal. Preliminary experiments tested the hypothesis that materials, such as cesium-doped ITQ-4 (Cs@ITQ-4), would effectively reduce electron acceptors, such as p-benzoquinone and biphenyl, to their radical anions. EPR and reflectance UV-vis-NIR measurements clearly demonstrate the presence of paramagnetic monoreduced products. EPR, ENDOR, and reflectance spectroscopy (IR, UV-vis-NIR) were used to study the reduction products of ketones and arylhalides by M@ITQ-4 and M@zeolite-Y, M=Rb,Cs. Ab initio quantum chemistry computations are used to identify fundamental frequencies of the reduced species and predict possible molecular arrangements of the substrates within the zeolite pores. 1. Ichimura, A. S.; Dye, J. L.; Camblor, M. A.; Villaescusa, L. A. J. Am. Chem. Soc. 2002, 124, 1170-1171. 2. Wernette, D. P.; Ichimura, A. S.; Urbin, S. A.; Dye, J. L. Chem. Mater., 2003, 15(7), 1441-1448. – – – – –

FF6.8

Synthesis and Low Temperature Physical Properties of Metal Substituted $CoSr_2YCu_2O_y$. Masahiro Shiraki[1], Jun-ichi Shimoyama[1,2], Shigeru Horii[1] and Kohji Kishio[1]; [1]Department of Superconductivity, University of Tokyo, Bunkyo-ku, Tokyo, Japan; [2]PRESTO, Japan Science and Technology Corporation (JST), Kawaguchi, Saitama, Japan.

$CoSr_2YCu_2O_y$(Co1212) is one of the layered cuprates having similar crystal structure to that of a well-known 90 K-class high-T_c superconductor $YBa_2Cu_3O_y$. In the Co1212, Co ions have tetrahedral coordination at the CoO layer and the oxygen content, y, is quite stable at 7.0[1], resulting in poor carrier concentration for superconductivity which was confirmed by thermoelectric power measurement at 290 K[2]. Therefore, introduction of excess oxygen sites in the CoO layer accompanying hole carrier generation is attempted in the present study in order to find new superconductors derived from Co1212. For modifying the local crystal structure of CoO layer, small amount of high valence metals, such as Ti, Mo and Re substituted for Co. Sintered bulk samples with nominal compositions of $(Co_{1-x}M_x)Sr_2YCu_2O_y$ (M = Ti, Mo, Re; $0 \leq x \leq 0.2$) were synthesized by solid-state reactions in air. These substituted samples were found to have large oxygen nonstoichiometry through the thermogravimetric measurements, suggesting that a large amount of excess oxygen was introduced in the (Co, M)O layer. Since these substituted metals form robust octahedron, MO_6, hole carriers can be generated even by higher valence metal substitution, which usually accompanies electron doping effect. In fact, small thermoelectric powers with positive sign were observed for these substituted samples after oxygen annealing, suggesting that hole carriers were successfully doped at the CuO_2 plane. The estimated hole concentration was enough for superconductivity particularly for partially Ca substituted samples, $(Co_{0.9}Mo_{0.1})Sr_2(Y_{1-z}Ca_z)Cu_2O_y$ ($0 \leq z \leq 0.5$), however, all these substituted samples did not show superconducting transition down to 4.2 K in both resistivity and magnetization measurements possibly due to partial substitution of Co to the CuO_2 plane. Another attempt for introduction of excess oxygen to the CoO layer was made

by Ba substitution for Sr site. A series samples with starting compositions of $Co(Sr_{1-x}Ba_x)_2YCu_2O_y (0 \leq x \leq 0.5)$ were prepared also by the solid-state reactions in air. Thermogravimetric measurements revealed that the partial Ba substituted samples have excess oxygen as is in the case of $CoBa_2YCu_2O_y$, resulting in remarkably lowered electric resistivity due to hole doping. Furthermore, partially Cu substituted sample, $(Co_{0.5}Cu_{0.5})(Sr_{0.5}Ba_{0.5})_2YCu_2O_y$, showed bulk superconductivity with high T_c 75 K. Various attempts for improving superconducting properties of the present system, such as Ca substitution for Y site and high pressure oxygen annealing, are undergoing. [1] T. Nagai, *etal.*, *J. SolidStateChem.* **176** (2003) 213. [2] J. L. Tallon, *etal.*, *PhysRev. B* **51** (1995) 12911.

FF6.9

Magnetic Properties of New One-Dimensional Vanadium Oxide with Hollandite Structure. Natasha A. Chernova, J. Katana Ngala, Peter Y. Zavalij and M. Stanley Whittingham; Institute for Materials Research, SUNY-Binghamton, Binghamton, New York.

A novel hollandite-type vanadium oxide $V_{7.22}O_8(OH)_8(Cl)_{0.77}(H_3O)_{2.34}$ was synthesized hydrothermally in the presence of triethylmethyl ammonium cation as the organic template. This is the first hollandite-type structure with anions, namely, the chloride ions, in the tunnels of the structure. The compound was characterized by the X-ray diffraction, infrared spectroscopy and thermal gravimetric analysis. The magnetic properties were studied using Quantum Design MPMS XL SQUID Magnetometer. The temperature dependences of dc susceptibility were measured from 2 to 300 K at various magnetic fields (0 to 5000 Oe) under field-cooled FC and zero-field-cooled ZFC conditions. The ac susceptibilities were studied from 2 to 30 K with the ac field amplitude 4 Oe, ac frequencies varying from 0.05 to 1000 Hz in the absence of dc field and in the co-applied dc fields. The temperature dependence of the dc susceptibility at 1000 Oe follows the Curie-Weiss law at higher temperatures; below 250 K a deviation from the Curie-Weiss behavior is observed; around 25 K the susceptibility increases by about two orders of magnitude that indicates a magnetic phase transition. From the fit of the high-temperature susceptibilities to the Curie-Weiss law, the Curie constant is (7.71±0.04) emu K/mol, consistent with 3+ vanadium oxidation state, and the Curie-Weiss temperature is −(500±2) K, indicating a strong antiferromagnetic exchange between the vanadium ions. The temperature dependences of the dc susceptibilities measured under the FC and ZFC conditions deviate below the magnetic phase transition. With the increasing magnetic field the difference between the FC and ZFC curves decreases and the deviation point shifts to the lower temperatures. At low fields, a small susceptibility maximum is observed at about 7 K. Both real and imaginary components of ac susceptibility show two maxima at about 7 and 17 K, as well as pronounced frequency dependence below 25 K. The high-temperature maximum shifts toward the low temperatures when the frequency is decreased. The relative temperature shift per decade of frequency is consistent with the spin-glass behavior. The analysis of frequency dependences of the ac susceptibility reveals the presence of three relaxation processes. The temperature dependences of their relaxation times were determined using the Cole-Cole analysis. The first relaxation process dominates at around the phase transition temperature 17 K. The temperature dependence of its relaxation time is well described within the droplet model for spin glasses. The other two processes are observed in the frozen phase; their origin is discussed. The magnetic properties observed differ significantly from that of other Hollandite-type vanadium oxides containing K^+, Ba^{2+}, Bi^{3+} cations. The nature of this difference is discussed in terms of structural deviations and the variations of the vanadium oxidation states in the compounds.

FF6.10

Dramatically Enhanced Thermoelectric Properties of $Ca_3Co_4O_y$ by Large Amount of RE Substitution. Yuuki Sugiura[1], Shigeru Horii[1], Taichi Okamoto[1], Kenji D. Otzschi[1], Jun-ichi Shimoyama[1,2] and Kohji Kishio[1]; [1]Department of Applied Chemistry, School of Engineering, University of Tokyo, Tokyo, Japan; [2]PRESTO, Japan Science and Technology Corporation (JST), Kawaguchi, Saitama, Japan.

Among various layered cobaltites, $(Ca_2CoO_{3-\delta})_{0.62}CoO_2$ [$Ca_3Co_4O_9$; Ca349] is one of the promising candidates as for new thermoelectric materials up to high temperatures, because its single crystal recorded high thermoelectric performance with a figure of merit $ZT > 1$ [1]. The Ca349 has an alternate layer stacking structure consisted of CdI_2-type CoO_2 conduction layers and rock salt-type $Ca_2CoO_{3-\delta}$ blocking layers along the c-axis. Therefore, c-axis alignment technique is necessary for reducing electrical resistivity, ρ, of its polycrystalline bulks. Since the Ca349 has large anisotropy in its magnetization ($\chi_{ab} < \chi_c$), strongly c-axis aligned bulks of Ca349 were successfully synthesized by magnetic alignment technique in our previous studies [2]. On the other hand, partial substitution of high-valent metals, such as Re, Mo and Nb, for Co in the blocking layer was found to be effective for enhancement of Seebeck coefficient,S, by lowering valence of Co and suppression of oxygen nonstoichiometry [3]. Similar effects on S and oxygen nonstoichiometry of the Ca349 have been expected for partial substitution of rare earth elements, RE, for Ca site, however, their substitution level was limited below 10% in the reported studies, resulting in slight improvements in thermoelectric properties. In the present study, we have attempted to increase substitution level of RE in the Ca349 polycrystalline bulks and found that quarter part of Ca site can be replaced by several RE elements by sintering under flowing oxygen atmosphere. $[(Ca_{1.5}RE_{0.5})CoO_{3-\delta}]_{0.62}CoO_2$ (RE = Y, Sm, Eu, Tb, Dy, Ho and Lu) bulks showed apparently higher S than that of undoped Ca349. Thermogravimetric analyses revealed that oxygen nonstoichiometry is strongly suppressed as was in the case of high valent metal substituted Ca349. These RE substituted samples showed higher ρ at low temperatures, however, it decreased with an increase of temperatures and became almost identical to that of undoped Ca349 at high temperatures. In addition, thermal conductivity were found to be dramatically lowered by the large amount of RE substitution, resulting large enhancement of ZT was achieved particularly at high temperatures 1000 K. Thermoelectric properties of magnetically aligned bulks will be also reported. [1] R. Funahashi *etal.*, *Jpn.J.Appl.Phys.* **39** (2000) L1127. [2] S. Horii *etal.*, *Jpn.J.Appl.Phys.* **42** (2003) 7018. [3] K. Fujie *etal.*, *Mat.Res.Soc.Symp.Proc.* **793** (2004).

FF6.11

Superconductivity in three layer (3L) sodium cobalt oxyhydrate. Maw-Lin Foo[1], Tomasz Klimczuk[3,1], Lu Li[2], Nai-Phuan Ong[2] and Robert J. Cava[1]; [1]Chemistry, Princeton University, Princeton, New Jersey; [2]Physics, Princeton University, Princeton, New Jersey; [3]Applied Physics and Mathematics, Gdansk University of Technology, Gdansk, Poland.

The observation of superconductivity at 4.3 K in a new crystalline form of sodium cobalt oxyhydrate Na0.3CoO2*1.3H2O is reported. The new superconductor has three layers of CoO6 octahedra per crystallographic unit cell, in contrast to the previously reported two-layer superconductor (Takada et al. Nature March 2003, v422, p53). The three-layer cell occurs because the relative orientations of neighboring CoO2 layers are distinctly different from what is seen in the two-layer superconducting phase. This type of structural difference in materials that are otherwise chemically and structurally identical is not attainable in the layered copper oxide superconductors. The similarity in Tc of the new three-layer and the previously reported two-layer superconductor implies that superconductivity is highly two dimensional in nature and not dependent on the relative orientation of the CoO2 layers. The synthesis, stability and physical characterization of the new phase are described.

FF6.12

Growth of Yb:Y_2O_3 Single Crystals by the Micro-Pulling-Down Method. Andrey Novoselov[1,2], Ji-Hun Mun[1], Akira Yoshikawa[1], Georges Boulon[3] and Tsuguo Fukuda[1]; [1]Division of Advanced Crystal Materials, Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan; [2]Japan Science and Technology Agency, Sendai, Japan; [3]Laboratory of Physical Chemistry of Luminiscent Materials, Claude Bernard/Lyon 1 University, Lyon, France.

The rare-earth sesquioxides (RE_2O_3, RE=La-Lu, Y and Sc) are promising host materials for solid-state lasers due to their low phonon energy. It was reported that Y_2O_3 has higher thermal conductivity than that of widely employed $Y_3Al_5O_{12}$. The existence of RE site is also preferable to dope with other RE, which can work as emission center for various wavelengths. In spite of these favorable properties, because of the extremely high melting temperature exceeds 2400 °C, the bulk single crystal growth technology for sesquioxide has not been well established yet. Undoped and Yb-doped yttrium oxide single crystals have been grown by the micro-pulling-down method using rhenium crucible. Growth atmosphere was Ar+H_2 flow to prevent rhenium oxidation. Ceramic Y_2O_3 rod was used as a seed for initial experiment and then single crystalline seed was prepared from the initial growth attempts. Chemical composition was analyzed by electron probe micro analysis. Results of the single crystal growth experiments along with optical properties characterization will be presented and discussed.

FF6.13

Electrospinning, Pyrolysis, and Characterization of Boron Carbide Nanofibers Prepared from Poly (norbornenyldecaborane), a Single-Source Polymeric Ceramic Precursor. Daniel T. Welna[1], Xiaolan Wei[2], Jared D. Bender[1], Larry G. Sneddon[2] and Harry R. Allcock[1]; [1]Chemistry, The Pennsylvania University, University Park, Pennsylvania; [2]Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania.

Electrostatic spinning is a proven technique, which has been used in the fabrication of fibers in the nanoscale domain. Boron carbide nanofibers were fabricated via the electrostatic spinning of poly(norbornenyldecaborane) (PND), a single-source polymeric ceramic precursor. Formation of the PND nanofibers was followed by ceramic conversions at temperatures ranging from 1000øC to 1650øC. The spun polymer fibers and the obtained ceramic fibers were characterized by scanning electron microscopy (SEM), x-ray diffraction (XRD), and diffuse reflectance infrared Fourier Transform (DRIFT) spectroscopy. SEM analysis showed the retention of the nanostructure between the pre- and post-pyrolyzed nanofibers. XRD and DRIFT spectroscopy were used to monitor ceramic conversion and indicate crystallinity. Thermogravimetric analysis (TGA) was used to monitor weight loss of the nanofibers during the ceramic conversion process. In addition, boron carbide/silicon carbide composite ceramic nanofibers were fabricated via the electrostatic spinning of a PND/allylhydridopolycarbosilane (AHPCS) cosolution and subsequently characterized.

FF6.14
Multi-Scale Structure-Property Relations in the Ta2O5-TiO2 System. Geoff Brennecka[1,2] and David Payne[1,2]; [1]Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois; [2]Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois.

Tantalum oxide (Ta2O5) has received a great deal of attention over the past decade as a possible high dielectric constant (K) material compatible with integrated circuit manufacture. The vast majority of these studies have focused on the processing and properties of thin films of the material in its amorphous (K 40) or low-temperature orthorhombic (K 60) form. Bulk samples of the high-temperature monoclinic phase, meanwhile, have been reported to exhibit a room temperature dielectric constant >300, when stabilized with 8mol% TiO2. The current study investigates the relationships among crystallographic phase, microstructure, and properties, focusing on processing approaches that result in improved dielectric performance for both bulk samples and thin films. The development of the unique microstructures observed in this system and the associated effects on properties will be discussed at length.

FF6.15
Crystallochemistry of Thortveitite-Like and Thortveitite-Type Compounds. Erick Adrian Juarez-Arellano, Lauro Bucio and Eligio Orozco; UNAM, Mexico City, Mexico.

The vertiginous rise of science and technology has produced the research and development of different materials presenting valuable physical properties. Silicates, germanates and phosphates in general, offer a great opportunity to obtain very interesting physical properties in a built crystal structure by associating a transition 3d metal or/and 4f rare earth element with covalent phosphorous, silicon, germanium or even arsenic and vanadium as well. In silicates, germanates, phosphates, arsenates and vanadates having the general formula M2X2O7 there is often the thortveitite-like crystal structure. They are composed of Mn+ cations (rare earth, transition metals, divalent or trivalent elements) in octahedral coordination, and X2O72n- anions (X = Si+4, Ge+4, P+5, As+5 and V+5). The frameworks of these phases are built up from corner-sharing MO6 octahedra forming a hexagonal disposition on layers interspersed with layers of X2O7 groups in staggered conformation. Among these layered structures, we have reported the synthesis and crystal structure of monoclinic pyrogermanates FeInGe2O7, InYGe2O7 and In1.08Gd0.92Ge2O7 being configurationally isotypic with the Sc2Si2O7 thortveitite structure reported by Zachariasen. In these cases the octahedral sites are occupied by two trivalent cations keeping the crystal symmetry given by the space group C2/m (No. 12) as in thortveitite. For InYGe2O7 and In1.08Gd0.92Ge2O7 a remarkable photo-luminescence effect when irradiated with 3 MeV ?-particles and during X ray diffraction measurements has been reported. For InTbGe2O7, also reported by us, the space group symmetry is C2/c showing a thortveitite-like structure. The phase formation along the RFeGe2O7 series has been found to be dependent on the size of rare earth R3+ cation generating three different monoclinic crystal structures. The first one, type I, being isotypic with thortveitite structure as in the FeInGe2O7 and YInGe2O7 compounds already exposed. The type II, having the NdAlGe2O7 structure, S.G. P21/c (No. 14) and Z = 4 for FeRGe2O7 with R = La to Gd; and finally, the type III YFeGe2O7 thortveitite-like structure, S.G. P21/m (No. 11) and Z = 4 for FeRGe2O7 with R = Y, Tb-Yb. In this last case, besides the octahedral sites (occupied by Fe3+) there are seven-coordinated sites occupied by the R3+ cation. Antiferromagnetic transitions have been observed around 2K in compounds that show the type II structure while they are around 42 K for type III compounds. No evidence of any magnetic transition has been observed for the type I structure (thortveitite) in germanates. However, for the thortveitite-like Cu2P2O7, Mn2P2O7 and Co2P2O7 compounds antiferromagnetic ordering below 26, 14 and 10.2 has been reported. In this article we present the mean features and structural relationships between all this thorveitite and thortveitite-like compounds both those synthesised and characterised in our laboratory and some others reported in the literature.

FF6.16
Effect of the Local Structure on the Spontaneous and Stimulated Emission Probabilities of Tm3+ in TeO2-ZnO Glass. Gonul Ozen[1,4], Idris Kabalci[1], Alphan Sennaroglu[2], Adnan Kurt[2], John M. Collins[3], Xuesheng Chen[3], Ottavio Forte[4] and Baldassare DiBartolo[4]; [1]Physics Department, Istanbul Technical University, Istanbul, Turkey; [2]Department of Physics and Electrical Electronics Engineering, Koc University, Istanbul, Turkey; [3]Department of Physics and Astronomy, Wheaton College, Norton, Massachusetts; [4]Department of Physics, Boston College, Chestnut Hill, Massachusetts.

Technological development of the optical telecommunications based on the growth of technologies of fiber fabrication and the laser diode has enabled efficient pumping of rare earth ions such as praseodymium, erbium. In these systems, there are a number of interesting relationships between the active ions and the host glass. Among these glasses with low phonon energies are of interest as hosts for infrared and infrared to visible upconversion lasers. Since the oxide glasses such as silicate, borate and phosphate glasses have high phonon energies the multiphonon relaxations become dominant. On the other hand there are some oxide glasses with low phonon energies such as tellurite and gallate in which the upconversion fluoresecence of erbium was observed. Further more tellurite glasses compared with silicate, borate and fluoride glasses show many desirable features including mechanical strength and chemical durability. This presentation reports our findings for the effect of the glass composition on the local environment of the thulium ions in the glass structure and its spontaneous and stimulated emission probabilities in the infrared region at room temperature. Absorption measurements in the UV/VIS/NIR region were used to determine spontaneous emission probabilities for the 4f-4f transitions of the thulium ion. Six bands corresponding to the absorptions of the 1G2, 3F2, 3F3, 3F4, 3H5, 3H4 from the ground level were observed. Integrated absorption cross-section of each band except that of 3H5 level was found to vary with the glass composition. Luminescence spectra of the samples were measured upon 785nm using a diode laser. Two emission bands centered about 100nm and 1900nm were observed. Spontaneous emission cross-sections together with the luminescence spectra measured upon 785 nm excitation were used to determine the stimulated emission cross-sections of these emissions. The effect of the glass composition on the Jodd-Ofelt Parameters and therefore on the spontaneous and the stimulated emission cross sections for the metastable levels of thulium ions will be discussed in detail.

FF6.17
Thermoelectric Applications of Novel Compounds. Shawna R. Brown[1], Cathie L. Condron[1], Susan M. Kauzlarich[1], G. Jeff Snyder[2] and Franck S. Gascoin[2]; [1]Chemistry, UCDavis, Davis, California; [2]Thermoelectric Materials and Devices Team, Jet Propulsion Laboratory - California Institute of Technology, Pasadena, California.

The compounds A14MnSb11 and A14-xMxMnSb11 (A and M = Yb, Ca, Zn) have been synthesized by two high temperature methods (1100 oC); Sn flux in Al2O3 crucibles, and welded Ta tubes sealed in quartz ampoules. These compounds are isostructural to the known Zintl compound, Ca14AlSb11 which crystallizes in a body-centered tetragonal unit cell in the space group I41/acd, with Z=8. They are small band-gap, semiconducting materials that contain heavy elements, large unit cells and structural complexity. Seebeck, thermal conductivity, electrical resistivity, and TG/DTA measurements are used to identify improved thermoelectric properties and thermal stability. The properties of the compounds will be compared to other promising thermoelectric materials.

FF6.18
Ferroelectric Properties of Pr Doped SBT Polycrystals. Jorge Mata, Alejandro Duran, Eduardo Martinez, Jesus Siqueiros and Jesus Heiras; Depto. Prop. Opticas, Centro de Ciencias de la Materia Condensada -UNAM, Ensenada, Baja California, Mexico.

In this study the structure and the dielectric properties of Pr-doped $Sr_xPr_{1-x}Bi_2Ta_2O_9$(SBT-Pr) have been investigated. Polycrystalline samples with x = 0, 0.01, 0.05, 0.10, 0.15, 0.20 were synthesized by the conventional solid-state reaction. The objectives of this work are: a) to study the crystal structure and determine with high precision the composition and chemical occupancies of the three Pr, Sr and Bi crystallographic sites using the Rietveld refinement technique. b) to measure the dielectric response of the synthesized ceramics in order to

relate composition, microstructure and electrical properties. For each composition a structural analysis of the ferroelectric orthorhombic phase has been performed from the XRD X-ray powder diffraction at several temperatures. Grain size and morphology were investigated by Scanning Electron Microscopy (SEM). The addition of the Pr^{3+} atoms results in a cationic disorder on Bi^{3+} and Sr^{2+} crystallographic sites. In this Aurivillius structure, the Pr atoms occupy the Sr sites. The dielectric constant has been measured as a function of the temperature and experimental results suggest that the position and the shape of the dielectric anomaly strongly depend upon the composition and the route used to elaborate the samples. This work was partially supported by grants of DGAPA-UNAM, Proj. IN100903 Proj. IN116703-3 and CoNaCyT Proj. 40604-F.

FF6.19
Effect of Mn Doping on the Structural and Dielectric Properties and Raman Spectra of $SrBi_2Ta_2O_9$. T. Sookawee[1], L. Pdungsap[1], P. Winotai[1], R. Suryanarayanan[2], Vaman M. Naik[3] and R. Naik[4]; [1]Department of Chemistry, Mahidol University, Bangkok, Thailand; [2]LPCS, Universite Paris-Sud, Orsay, France; [3]Natural Sciences, U Michigan-Dearborn, Dearborn, Michigan; [4]Department of Physics, Wayne State University, Detroit, Michigan.

$SrBi_2Ta_2O_9$ (SBT) samples without and with Mn(SBT:Mn) doping have been prepared by sol-gel technique. Scanning electron microscopu, x-ray diffraction (XRD), dielectric measurements as a function of frequency and Raman spectra have been carried out. In the case of SBT, the dielectric constant (ϵ) was found to be very sensitive to excees Bi additions. Highest value of ϵ =120 was obtained when 20 mole % of Bi was added to the starting composition. This sample also showed the largest area of the hysteresis loop. In the case of Mn doped samples, the XRD spectra revealed an unknown phase when the concentration of Mn exceeded about 2.5 mole percent. The value of ϵ increased from about 125 to 140 for very small additions of Mn content (<0.5 mole percent) but decreased to 120 and less when the concentration exceeded 1.5%. The value of e remained constant as a function of frequency from 60 to 85000 cps. The intensity of the Raman bands at 208 and 812 cm $^{-1}$ was very sensitive to Mn additions. For example, the intensity of the 208 cm $^{-1}$ band increased for 0.2 mole percent of Mn, reached a maximum for 1% and dramatically decreased for Mn concentrations greater than 5%. The correlation between XRD, Raman, Mn concentration and the value of ϵ will be discussed.

FF6.20
Abstract Withdrawn

FF6.21
Internal Oxidation in Solid Solutions Bi2.1-xPbxSr2-y Ca1-zRy+zCu2O8+δ (R = Y, Nd or La).
Alexey Viktorovich Garshev[1], Alex Valerievich Knotko[2], Maxim Nikolaevich Pulkin[1], Dmitry Ivanovich Kirdyankin[1], Andrey V. Geyer[1] and Valery Ivanovich Putlayev[2,1]; [1]Department of Materials Science, Moscow State University, Moscow, Russian Federation; [2]Department of Chemistry, Moscow State University, Moscow, Russian Federation.

Internal oxidation of Bi2.1-xPbxSr2-yCa1-zRy+zCu2O8+δ solid solutions is a prospective way to create nanocomposites 'superconducting matrix - nonsuperconducting inclusions'. To control the process one can perform simultaneous substitution in different cation sites (e.g., Bi on Pb and Ca or Sr on rare earth elements). Solid solutions of Bi2-xPbxSr2CaCu2O8+d with substitution of Sr or Ca by Y, Nd or La were fabricated at 760 - 790°C in N2-flow. The samples were tested with chemical analysis, XRD, TEM, TG, XANES and AC-susceptibility measurement. It was shown with the help of iodometric titration and XANES, that the increase of lead content in the solid solution decreased the over-stoihiometric oxygen amount, but did not increase the hole concentration in the [CuO2] layer of the Bi2Sr2CaCu2O8 structure related to superconducting properties of the solutions. Such a fact is likely to be connected with the electronic exchange between the [CuO2] and [Bi2O2] layers. With the same time, doping of the Pb - containing solid solutions with Y decreases the hole concentration in the [CuO2] layer. The two-stage oxidation process of solid solutions Bi2-xPbxSr2CaCu2O8+δ was found earlier by us in air at 650 - 750°C. The first stage was assigned to oxygen redistribution and the second - to a cationic diffusion. The substitution of Ca by Y or Nd significantly decelerates of the first stage of the oxidation and therefore allows to escape a coarsening of spinodal-like precipitates. Oxidation kinetics of the solid solutions with low Pb content demonstrated incubation period followed by formation of equiaxed nanosized particles. This fact is probably related with relatively small difference of the oxygen activities in the oxidized phase and air. Variation in homogeneity range and the rate of secondary phase precipitation for Pb - containing solid solutions based on Bi-2212 with substitution of Ca by Y, Nd and La was established. This effect can be related to a different distribution of different rare earth elements over cation sites of Bi-2212 structure due to distinction in their ionic radiuses. This work was supported by Russian Foundation for Basic Research (grant 02-03-33270a).Authors are thankful to Prof R.S. Liu (Department of Chemistry, National Taiwan University, Taipei 106, Taiwan) for the carrying out the XANES experiments.

FF6.22
Effects of Substitutions at the Ruthenium, Strontium and Gadolinium Sites in the RuSr2GdCu2O8 Compound.
Mohamed Abatal[1], Elizabeth Chavira[1], Valentin Garcia[2], J. C. Perez[2], Claude Filippini[3] and Jean Luis Tholence[3]; [1]ESYC, IIM-UNAM, Mexico, D. F. , Mexico; [2]IF-LRT, Puebla, Puebla, Mexico; [3]LEPES, CNRS, Grenoble, France.

We have successfully obtained a solid solution up to x = 0.4 for Ru1-xSr2GdCu2+xO8, x = 0.1 for Ru(Sr2-xCax)GdCu2O8 and x = 0.7 for RuSr2(Gd1-xLnx)Cu2O8 systems, where Ln = Dy, Ho, Er, Yb and Lu. All systems have been synthesized by solid state reaction method at ambient pressure. These systems are isomorphous to the RuSr2GdCu2O8 composition. The singles phases have been characterized by X-ray powder diffraction (XRD) and Energy Dispersive X-ray Spectroscopy (EDX) analysis. Studies by Scanning Electron Microscopy (SEM) gives a particle size around 1 to 10 micrometer. We report also the results of the temperature dependence of the electrical resistivity of the samples annealing in oxygen flux during 6, 12 and 41h. The AC magnetic susceptibilty measurements indicate that the Ru1-xSr2GdCu2+xO8 system, with $0 < x < 0.4$ is ferromagnetic, with TCurie = 125-145 K. We acknowledge the financial supported from the PAPIIT-UNAM-IN102203, IX108104 and CONACyT 33630-E.

FF6.23
Abstract Withdrawn

FF6.24
Order and disorder on pyrochlores formed in K-W-Sb-O system. Dmitry A. Zakharyevich, Anton Artemyev and Vladimir A. Burmistrov; Condensed Matter Physics, Chelyabinsk State Univ., Chelyabinsk, Russian Federation.

We present the results of studies on formation and stability conditions of pyrochlore phase in K-W-Sb-O sysyem

FF6.25
Improved CMR Properties of $La_{2-2x}Sr_{1+2x}Mn_2O_7$ Achieved by High-Temperature Post Annealing. Yuui Yokota[1], Jun-ichi Shimoyama[1,2], Shigeru Horii[1] and Kohji Kishio[1]; [1]Department of Superconductivity, School of Engineering, University of Tokyo, Bunkyo-ku, Tokyo, Japan; [2]PRESTO, Japan Science and Technology Corporation (JST), Kawaguchi, Saitama, Japan.

Since the discovery of colossal magnetoresistance (CMR) effect, $La_{2-2x}Sr_{1+2x}Mn_2O_7$ [(La,Sr)327]has been under the spotlight[1] as for a new functional material in future. For its practical application, however, there are several problems, such as high resistivity and small magnetoresistance at room temperatures to be overcome. Mechanisms of CMR effect of the (La,Sr)327 have been well clarified through large number of studies on its physical properties using single crystalline samples. In almost all of these studies, as-grown single crystals were used and, therefore, post-annealing effects on CMR properties have not been understood at all, while oxygen nonstoichiometry as well as occupancy ratio of La and Sr in perovskite block and rock salt-layer are supposed to be changed by annealing conditions. In the present study, post-annealing effects on the low temperature physical properties were systematically studied for (La,Sr) 327 single crystals. Crystal boules with starting compositions of $La_{2-2x}Sr_{1+2x}Mn_2O_7$($x$ = 0.3, 0.35, 0.4) were grown by the floating zone method under flowing oxygen. Small rectangular crystals cut from the crystal boules were annealed at 1000 1400°C for 20 300 h in air, then cooled in the furnace. Post annealing at 1000°C was found to improve sharpness of ferromagnetic transition without changing absolute values of resistivity and magnetization. On the other hand, post-annealing above 1300°C was quite effective to lower in-plane resistivity of the (La,Sr)327 single crystals. With an increase of annealing time, in-plane resistivity decreased systematically over one order of magnitude and saturated after annealing for 100 h. Ferromagnetic transition temperature 130 K was slightly increased approximately 5 K. In addition, magnetization above transition temperature was systematically increased by the high-temperature annealing up to 300 h, suggesting that ferromagnetic ordering was developed even at high temperatures including the room temperature. Powder X-ray diffraction and Reitveld analyses revealed that occupancy ratio of La and Sr were gradually changed by post-annealing. In the as-grown single crystals, La ions preferentially existed in the perovskite blocks, while most of La ions moved to the rock salt layer after the high-temperature annealing for long time. Mechanisms for cation exchange between La and Sr by annealing and

resulting improved CMR effect will be reported. [1] Y. Morimoto *etal.*, *Nature* **380** (1996) 141

SESSION FF7: Solid State Theory
Chairs: Martin Jansen and Ram Seshadri
Wednesday Morning, December 1, 2004
Room 200 (Hynes)

8:30 AM *FF7.1
From Configuration Space to Thermodynamic Space: Predicting New Inorganic Solids via Exploration of Their Energy Landscapes. J. Christian Schoen and Martin Jansen; MPI Solid State Research, Stuttgart, Germany.

Predicting the structure of not-yet synthesized crystalline compounds in a given chemical system, requires information about the possible stable structures, their thermodynamic weight, and their kinetic stability as function of thermodynamic parameters such as pressure, temperature and composition. At a given pressure and composition, such (meta)stable compounds correspond to locally ergodic regions on the enthalpy landscape of the system surrounded by sufficiently high energetic and entropic barriers (1,2). In general, location, size and stability of locally ergodic regions change as a function of temperature. The identification of such regions requires the global exploration of the energy (p=0) and enthalpy landscapes of the chemical system (1,2), where, due to new synthesis methods (3), landscapes with negative pressures should be included. Since such a global landscape investigation is not yet feasible using ab initio energy calculations, one uses empirical potentials at this stage followed by a refinement of the structure candidates on ab initio level. Following this general stepping stone approach, for a wide range of pressures and compositions, we first determine as many local minima of the corresponding enthalpy landscapes as possible, using various global optimization procedures. Next, we employ the threshold algorithm to determine their stability, and use swarms of stochastic quench runs, to find the so-called characteristic regions of the landscapes, which serve as further candidates for locally ergodic regions. Finally, we perform local optimizations of the structure candidates using ab initio energy functions within the Hartree-Fock and DFT approximations (4). For those compounds with low enthalpies in various pressure ranges, we then calculate the local free enthalpy by taking free energy contributions of the phonons and, if applicable, the entropy of mixing into account. This allows us to identify the thermodynamically preferred structure as function of temperature, pressure, and composition. Examples will be drawn from various binary and ternary ionic compounds, such as the alkaline metal sulfides, and the system Ca/Si/Br. (1) J. C. Schon, M. Jansen, Angew. Chem. Int. Ed. 35:1286 (1996) (2) J. C. Schon, M. Jansen, Z. Krist. 216:307,361 (2001) (3) D. Fischer, M. Jansen, J. Am. Chem. Soc. 124:3488 (2002) (4) J. C. Schon, Z. Cancarevic, M. Jansen, J. Chem. Phys., in press (2004)

9:00 AM *FF7.2
Origin of ferromagnetism in novel spintronic oxides. Nicola A. Spaldin, Priya Gopal and Rebecca Janisch; Materials Department, UCSB, Santa Barbara, California.

Recent reports of high temperature ferromagnetism in transition-metal-doped oxides have generated considerable interest, both in determining the fundamental physics driving the ferromagnetic interactions and in exploring possible applications in spintronic devices. Here we use first-principles density functional theory to investigate the origin of ferromagnetism in two systems; ZnO doped with a range of transition metals, and Co-doped TiO_2. Our results indicate that substitution of host cations by magnetic transition metal cations alone does not lead to strong ferromagnetism. We explore other possible origins for the reported ferromagnetism, including the incorporation of n- or p-type carriers, and the influence of oxygen vacancies and grain boundaries. Finally we comment on the possibility of creating a novel multifunctional oxide by combining ferromagnetism with the well-established piezoelectricity of wurtzite-structure ZnO.

9:30 AM FF7.3
Charge Transfer in Mixed 3d/4d Transition Metal Oxides. I-W. Chen[1], F. Huang[1] and Wojciech Dmowski[2]; [1]Materials Science and Engineering, University of Pennsylvania, Philaelphia, Pennsylvania; [2]Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee.

Mixed valency is a common phenomenon in solid state chemistry and its prediction has been largely empirical. In this study, we developed a rigorous approach based on the Zaanen-Sawartzky-Allen scheme which was originally proposed to classify Mott-Hubbard insulator versus charge transfer insulator. The basic parameter in this scheme is the charge transfer energy from O2p to the Fermi level, which typically lies in the metal d-manifold for transition metal oxides. This quantity is experimentally measurable using various spectroscopic techniques; it can also be quantified by first principles calculation. Based on this information, we have predicted the charge transfer in various transition metal oxides of mixed 3d/4d metals. We verified these predictions using near edge fine structure, which determines the valence state of cations. Manifestation of the charge transfer effect and the closely related resonance scattering effect, found in cation ordering and impurity-induced magnetic moment, is described.

9:45 AM FF7.4
The Contribution To Bond Valences By Lone Electron Pairs. Xiqu Wang[1] and Friedrich Liebau[2]; [1]Department of Chemistry, University of Houston, Houston, Texas; [2]Institut Geowissenschaften, Universitaet zu Kiel, Kiel, Germany.

Many inorganic materials containing cations with lone pair electrons (LEP) have interesting physical properties such as ferroelectricity, semiconductivity and superconductivity. The effect of LEPs on these properties remains a fundamental open question in materials science. Our previous studies[1] found a correlation between the stereo chemical activity of the LEP and bond valence sums (BVS) calculated according to the bond valence model.[2] BVS values calculated for lone-pair cations are found increasingly higher than their formal valences as the retraction of the LEP from the nucleus is more pronounced. The increase in BVS is interpreted as a continuous increase of an effective valence of an atom that is a measure of its actual ability to bind other atoms without changing its formal valence. Therefore, different crystallographic sites of the same ion in a structure may have different effective valences that can be approximated by the BVS values. The effective valence can be related to material properties as shown for the conduction paths in the semiconducting cetineite-type phases.[3] Our statistic study shows that the stereo activity of LEP of a lone-pair cation may cause the BVS value for the cation to be up to ca. 1.0 v.u. higher than their formal valences. How the LEP of a lone-pair cation affects the effective valence of other atoms in a structure is studied by bond valence calculations for specific structures. For structures rich in alkali cations, it is found that the high effective valence of the lone-pair cations tend to be balanced by low effective valence of alkali cations. For example, in the structure of Na_4SnO_3,[4] the BVS values for Sn^{2+}, Na^{+} and O^{2-} ions are 2.78, 0.53-0.85 and 1.86-1.99 v.u., respectively. In particular the Na(1) site with a BVS value 0.53 v.u. is coordinated by two oxygen atoms and four LEPs from four Sn atoms in a distorted octahedral configuration. The LEPs of the lone-pair cations reduce the effective valence of the alkali cations by participating their coordination spheres. This is similar to a hydrogen bond, the lone-pair cations act as electron pair donors and the alkali cations as acceptors. The LEP transfers bonding power or effective valence from the alkali cation to the surrounding lone pair cations. For structures rich in lone-pair cations where the lone-pair cation coordination polyhedra tend to be interconnected, the high effective valence of the lone-pair cations tend to be balanced by high effective valence of the bridging anions, probably due to local pressure caused by repulsion between lone electron pairs and bonding electron pairs. 1. Wang, X; Liebau, F.: Acta Cryst. B52 (1996) 7-15; Z. Kristallogr. 211 (1996) 437-439. 2. Brown, I. D.: Acta Cryst. B 41 (1992) 553-572. 3. Liebau, F.: Z. Kristallogr. 215 (2000) 381-383. 4. Nowitzki, B., Hoppe, R.: Z. Anorg. Allg. Chem., 515 (1984) 114-126.

10:30 AM *FF7.5
Shape Measures, Shape Maps and Polyhedral Interconversion Paths in the Solid State. Santiago Alvarez[1], Pere Alemany[2], Miquel Llunell[2], David Casanova[1] and Jordi Cirera[1]; [1]Departament de Quimica Inorganica, Universitat de Barcelona, Barcelona, Spain; [2]Departament de Quimica Fisica, Universitat de Barcelona, Barcelona, Spain.

The definition of shape and symmetry as continuous properties provides us with accurate stereochemical description of the coordination polyhedron of a given atom in a molecular or solid state structure in terms of a wide set of reference shapes, such as Platonic, Archimedean, Johnson and Catalan polyhedra. The shape measures of a particular structure relative to two alternative polyhedra can be plotted in a shape map that provides hints on the type of distortion from ideality present in that structure, and the minimal distortion interconversion pathway between two polyhedra is univocally defined in such a map. Recent studies aimed at systematic structural studies [1] and at analyzing magneto-structural relationships [2] will be discussed, with special emphasis in the field of solid state structures. A prospective of future developments such as automatic shape clasification and symmetry measures of the electron density will be outlined. [1] S. Alvarez, M. Llunell, J. Chem. Soc., Dalton Trans., 3288 (2000); S. Keinan, D. Avnir, J. Chem. Soc., Dalton Trans., 941 (2001); S. Alvarez, D. Avnir, M. Llunell, M. Pinsky, New J. Chem., 22, 996 (2002); D. Casanova, P. Alemany, J. M. Bofill, S. Alvarez, Chem. Eur. J., 9, 1281 (2003). J. Cirera, P. Alemany, S. Alvarez,

Chem. Eur. J., 10, 190-207 (2004) [2] S. Alvarez, J. Am. Chem. Soc., 125, 6795 (2003).

11:00 AM FF7.6

The RÔle of Defects in Photographic Latent Image Formation. Dan J. Wilson, A. A. Sokol, S. A. French and C. R. A. Catlow; Davy Faraday Research Laboratory, The Royal Institution of Great Britain, London, United Kingdom.

One of the major challenges for over 30 years in the physics and chemistry of defects in ionic crystals has been the development of a detailed and quantitative understanding of defects in silver halides (AgX). The problem is of course central to the photographic industry as it is the interaction between defects and photoelectrons that forms the basis of the photographic process. Early studies of bulk charged defects [1,2], based on interatomic potential methods achieved a measure of success, but only when ad-hoc adjustments were made to the potential parameters. We therefore report a new study using density functional theory of the structure and energies of bulk defects in the silver halides. The localisation of photoelectrons and corresponding holes at these defects has been studied, along with the corresponding relaxation of the lattice. Due to the large surface/volume ratio of the micron-sized AgX crystallites in a photographic film, many of their salient properties derive from surface properties. Moreover, despite a number of concerted theoretical studies on the role of silver clusters [3] and chemical sensitizers [4] in the photographic process, the key issue of latent image formation remains unresolved. The dynamics of interstitial cations near the surface, and the role of environmental adsorbates such as H_2, O_2, and H_2O on latent image formation are the focus of this work. We have applied state-of-the-art static, and novel dynamical, QM/MM embedding methods, and have found valuable new insights into this long-standing problem. [1] Catlow C. R. A., Corish J. and Jacobs P. W. M., *J.Phys.C*, **12**, 3433 (1979). [2] Baetzold R. C., Catlow C. R. A., Corish J., Healy F. M., Jacobs P. W. M., Leslie M. and Tan Y. T., *J.Phys.Chem.Solids*, **50(8)**, 791 (1989). [3] Baetzold R. C., *J.Phys.Chem.B*, **105**, 3577-3586 (2001). [4] Marchetti A. P., Lushington K., Baetzold R. C., *J.Phys.Chem.B*, **107**, 136-146 (2003).

11:15 AM FF7.7

Analysis of the Complex Refractive Index of Inorganic Solids and Determination of the Relevant Parameters Governing n and k. Stephane Jobic[1], Xavier Rocquefelte[1], Fabrice Goubin[1] and Myung-Hwan Whangbo[2]; [1]LCS, IMN-CNRS, Nantes, France; [2]Department of Chemistry, North Carolina State University, Raleigh, North Carolina.

The development of new pigments and particulate-based sunscreens requires the knowledge of the optical properties of inorganic materials, namely, the refractive index n and the extinction coefficient k. These two quantities, which depend on the wavelength λ of the impinging light, form the complex refractive index $N(\lambda) = n(\lambda) + i\,k(\lambda)$. The opacity (i.e., the light scattering power) and the color strength (i.e., the light absorbing capacity) of inorganic materials depend on n and k, respectively. Typically, light scattering has to be minimized in the visible region for UV absorbers (low n index) while the opposite is requested for pigments (high n index). Alternatively, the interaction of light with materials can be discussed in terms of the complex dielectric function $\epsilon(\lambda) = \epsilon1(\lambda) + i\,\epsilon2(\lambda)$, which describes the linear response of the electronic structure of an insulating material to the electrical field of the incident radiation with a wavelength λ. The real part $\epsilon1(\lambda)$ is related to the electronic polarizability of the material, and the imaginary part $\epsilon2(\lambda)$ is associated with the electronic absorption of the material. n and k are related to $\epsilon1$ and $\epsilon2$ as follows: $\epsilon1=n^2-k^2$, $\epsilon2=2nk$. $\epsilon2$ is related to $\epsilon1$ via the Kramers-Kronig relation. Consequently, if $\epsilon2(\lambda)$ is determined experimentally or theoretically, n and k can be deduced. A relation between the electronic energy band structure and optical constant $\epsilon2(E)$ exists which takes into account the the electric dipolar momentum. Thus, on the basis of first principles electronic structure calculations, the dielectric functions and the complex refractive indices of the solid materials may be determined and discussed in terms of ionicity, structure, compactness, and the main factors which governed these values can be deduced. Our discussion will lie on new results acquired on borates and oxydes of cerium and the various allotropic forms of TiO2. Related references: F. Goubin, Y. Montardi, P. Deniard, X. Rocquefelte, R. Brec, S. Jobic, J. Solid State Chem., 177, 89-100, 2004 F. Goubin, X. Rocquefelte, M.-H. Whangbo, Y. Montardi, R. Brec, S. Jobic, Chem. Matter., 16, 662-669, 2004 X. Rocquefelte, G. Goubin, S. Jobic, H.-J. Koo and M.-H. Whangbo, Inorg. Chem., 43, 2246-2251, 2004

11:30 AM FF7.8

Transformations among near-degenerate phases: why platinum dioxides show poor crystallinity. Shuping Zhuo[1,2] and Karl Sohlberg[1]; [1]Department of Chemistry, Drexel University, Philadelphia, Pennsylvania; [2]School of Chemical Engineering, Shandong University of Technology, Zibo, Shandong, China.

The platinum dioxides have been poorly characterized due to poor crystallinity. PtO2 phases are studied here with first-principles-based thermodynamics. The phase transformations are then studied with first-principles-based kinetics calculations. Three polymorphs are found to be nearly energy degenerate. The beta- (CaCl2) structure is the most stable, while the beta'- (rutile) structure represents an unstable fixed point on the potential energy surface, or is barely bound. The alpha- (CdI2) structure is a true metastable phase, but the alpha- to beta-PtO2 conversion barrier is high. These results reconcile seemingly contradictory findings and answer longstanding questions about PtO2

11:45 AM FF7.9

Chemical and Physical Hardnesses of Solids. John Joseph Gilman, MSE, UCLA, Los Angeles, California.

A measure of chemical stability for molecules (atoms) is chemical hardness. This is a scalar and therefore inadequate for solids unless it is modified. The reason is that isotropic solids have two types of stability; size and shape. The elastic bulk modulus measures the former, while the elastic shear modulus measures the latter. Less symmetric solids require the full elasticity tensor to describe their stabilities. The formal definition of chemical hardness is that it is the derivative of of the electronic chemical potential with respect to the number of valence electrons. Here the electronic chemical potential is the change in energy of a molecule with a change in the number of valence electrons. Since the elastic moduli depend om valence electron densities, it might be expected tha they would depend on chemical hardness densities (energy / volume). This is indeed the case. Therefore, a physical hardness can be defined that is proportional (and sometimes equal) to the chemical hardness. Data that verify this are presented. The relationshipt between the two types of hardness depends on the type of chemical bonding. For simple metals, where the bonding is non-local (i.e., approximately spherically symmetric) the bulk modulus is proportinal to the chemical hardness density. For covalent crystals, where the bonding is localized, the bulk moduli are not proportional to the the chemical hardness density, but the octahedral shear modulu are. In this case the indetation hardnesses (and therefore the Moh hardnesses) are proportional to the chemical hardness densities. One implication of these findings is that chemical hardnesses should be related to the band gaps of covalent crystals, since they are related to the LUMO-HOMO gaps of molecules. Data indicate that this is indeed the case. Another implication is that the chemical potential of a solid is, in general, a second order tensor that is related to the deformation tensors (strains) through the fourth order tensor of elasticity coefficients.

SESSION FF8: Nanomaterials with High Aspect Ratios
Chairs: Susan Kauzlarich and Jing Li
Wednesday Afternoon, December 1, 2004
Room 200 (Hynes)

1:30 PM *FF8.1

Shape-Controlled Synthesis of Nanostructured Materials. Younan Xia, Department of Chemistry, Univ. of Washington, Seattle, Washington.

I will discuss a number of strategies that my group has demnonstrated in the past couple of years for synthesizing or fabricating nanostructured materials with well-controlled shapes, sizes, and properties. In the first example, I will show how the anisotropic structure of a solid material can be used to control the growth of group-IV semiconductirs (Se, Te, and their alloys) into uniform, nanometer-sized wires, rods, and tubes. In the second system, I will demonstrate how a polymer capping reagent can be added to the polyol synthesis to confine the growth of metals (e.g., Ag, Au, Pt, Pd, and their alloys) into uniform nanowires, cubes, and spheres with well-controlled dimensions and surface plasmon resonance (SPR) features. My discussion will be mainly based on poly(vinyl pyrrolidone), PVP, a water-soluable polymer. In the third example, I will illustrate how these well-defined nanostructures can be used as physical or chemical templates to direct the formation of new types of funational nanostructures having well-defined shapes. For example, the galvanic replacement reaction between the silver nanocubes and an aqueous chloroauric acid solution can be used to generate gold nanostructures with hollow interiors and porous surfaces, and thus tunable SPR peaks extanding into the near IR region. I will focus on the mechanism associated with each synthetic method, as well as its potential extension to other materials.

2:00 PM *FF8.2

High Pressure Fabrication of Extreme Aspect Ratio Semiconductor Micro and Nanostructures. John V. Badding[1,3],

Pier J.A. Sazio[2], Thomas J. Scheidemantel[1,3], Neil F. Baril[1,3], Venkatraman Gopalan[3] and DongJin Won[3]; [1]Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania; [2]Optoelectronics Research Centre, University of Southampton, Southampton, Hampshire, United Kingdom; [3]Materials Research Institute, Pennsylvania State University, University Park, Pennsylvania.

Extreme aspect ratio semiconductor nanostructures are currently the subject of considerable scientific and technological interest. High pressure fluids are well suited for the synthesis of such extreme aspect ratio structures because of their ability to penetrate well into nanoscale pores within a host. Using high pressure fluids and suitable precursors, we have fabricated organized arrays of several different types of extreme aspect ratio nanowires and microwires. We have characterized both the electronic and photonic properties of these structures, which are expected to have wide ranging application.

2:30 PM FF8.3
Synthesis of InP and InAs Quantum Rods Using Myristic Acid. Itzik Shweky[1], Assaf Aharoni[1], Eli Rothenberg[1], Taleb Mokari[1], Inna Popov[2], Moshe Nadler[1] and Uri Banin[1]; [1]Institute of Chemistry The Farkas Center for Light Induced processes and the Center for Nanoscience and Nanotechnology, The Hebrew University of Jerusalem, Jerusalem, Israel; [2]The unit for Nanocharacterization, The Hebrew University of Jerusalem, Jerusalem, Israel.

The development of solution based synthesis approaches for preparing nanocrystals of III-V semiconductor presents a significant & important challenge especially with relation to shape control to achieve rod growth. To this end, a novel approach for synthesis of soluble semiconductor quantum rods using metal nanoparticles to direct and catalyze one-dimensional growth is developed. The synthesis method is useful in particular for III-V semiconductor with cubic lattice, where the utilization of surfactant-controlled rod-growth is not easily realized. The growth takes place via the solution liquid solid (SLS) mechanism where proper precursors are injected into a coordinating solvent as we reported in earlier work for InAs nanorods. Herein, we report the synthesis of high quality InP nanorods using different precursors and surfactants with gold nanoparticles as the catalysts in the SLS growth mode. A similar route was successfully developed for the growth of InAs nanorods. We find that the amount of Au catalyst in the reaction is an important parameter to achieving shape control. Transmission electron microscope (TEM) images of InP and InAs nanocrystals revealed that the crystals are mostly rod-shape. XRD measurements, absorption & PL spectra were preformed for the nanorods characterization.

2:45 PM FF8.4
Low-Temperature Solution-Phase Conversion of MnP Nanoparticles to Nanowires: Implications for Dimensionality Control in Nanoscale Phosphides. Kanchana Somaskandan[1], Georgy M. Tsoi[2,3], Lowell Wenger[3,2] and Stephanie Brock[1]; [1]Chemistry, Wayne State University, Detroit, Michigan; [2]Physics, Wayne State University, Detroit, Michigan; [3]Physics, University of Alabama, Birmingham, Alabama.

The evolution of shape in nanoscale materials remains a poorly understood phenomenon, despite the promise of enhanced or directional physical properties in materials with engineered anisotropy. We have developed a methodology for the preparation of discrete ferromagnetic MnP spherical nanoparticles from $Mn_2(CO)_{10}$ and $P(SiMe_3)_3$ in coordinating solvents. These particles demonstrate expected size-dependent blocking temperatures, but unexpectedly do not show the low-temperature metamagnetic transition observed in bulk samples. Recently, we have found that low-temperature post-treatment of these spherical nanoparticles in pyridine at 80 °C results in continued growth of the spherical nanoparticles, as well as their transformation to nanorods and, ultimately, wires. Here we will discuss possible mechanisms for rod-growth as well as the potential of this methodology for the development of other shapes and/or nanostructures in MnP and phosphides in general. Additionally, the influence of shape anisotropy on blocking temperature, coercivity, and recovery of the metamagnetic transition in MnP nanoparticles will be presented.

3:30 PM FF8.5
Mo_2C Nanowires and Ribbons on Si Substrates via Two-Step Vapor Phase Growth. Loucas Tsakalakos, Lauraine Denault, Michael Larsen, Yan Gao, Paul Wilson and Joleyn Balch; GE Global Research, Niskayuna, New York.

Transition metal carbides are an interesting class of electronic materials owing to their high electrical conductivity at room temperature, which is only slightly lower than that of their constituent transition metal elements. For example, the room temperature electrical resistivity of bulk Mo_2C is 70 μW-cm compared to that of Mo (4.85 μW-cm), whereas that of NbC is 50 μW-cm as compared to 15.2 μW-cm for Nb. Indeed, the temperature dependent resistivity of many transition metal carbides suggests metallic like conduction. Furthermore, certain transition metal carbides are known to become superconducting, with transition temperatures ranging from 1.15 °K for TiC_{1-x} to 14 °K for NbC. They are also able to withstand high temperatures and are chemically stable. Initial synthesis of metal carbide nanorods was demonstrated using the carbon nanotube (CNT) confined reaction mechanism by Lieber and co-workers [MRS Symp. Proc. 410, 103 (1996)] and subsequent superconducting behavior was shown by Fukunaga et al. [J. Mater. Res. 13, 2465 (1998)]. Vapor-liquid-solid growth was employed by Johnsson et al. [M. Johnsson and M. Nygren, J. Mater. Res. 12, 2419 (1997)] to synthesize micron-sized carbide whiskers. Here, we have successfully synthesized Mo_2C nanorods and ribbons on Si substrates using a two-step catalytic approach. In the first step we utilize a catalytic vapor phase process to grow Mo and/or molybdenum oxide nanostructures, which are subsequently carburized in situ to form the desired Mo_2C nanostructures. Unlike true VLS growth of carbides, in which high temperature (1100-1300 °C) is required to adequately dissolve carbon into the catalyst particles, our strategy is to react the nanostructures along their entire length with a carbon vapor source after creating the oxide/metal nanostructures, which for Mo_2C can be achieved at relatively low temperatures. ($\leq$ 1000 °C). The nanorods and ribbons are polycrystalline, with a mean grain size of 20-50 nm and 50-150 nm, respectively. We hypothesize that the growth mechanism is a complex mixture of VLS, VSS, and auto-catalytic growth, in which molten catalyst nanoparticles enter a three phase region once the metal precursor is supplied. The growth then presumably continues via a vapor-solid-solid process and is possibly assisted by the presence of various molybdenum oxide species on the surface. Initial single nanowire electrical measurements yield a higher resistivity than in the bulk, which is attributed to the fine grain sizes and/or the presence of an oxide layer. A discussion of the growth mechanism will be presented along with a study of the nanorod/ribbon structure and properties.

3:45 PM FF8.6
Solution Phase Synthesis of Straight and Branched CdSe Nanowires. Katherine Leigh Hull[1,2], James W. Grebinski[1,2], Jing Zhang[3], Tom H. Kosel[3] and Masaru Kuno[1,2]; [1]Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana; [2]Notre Dame Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana; [3]Department of Electrical Engineering, University of Notre Dame, Notre Dame, Indiana.

Long-standing interest in understanding and ultimately controlling crystal growth has recently materialized as studies into new routes for making high quality metal and semiconductor nanocrystals (NCs), nanorods (NRs), nanowires (NWs), as well as other higher order nanostructures. The discovery that metal NCs have catalytic properties for promoting asymmetric crystal growth has motivated studies into making 1D semiconductor NWs. Recent investigations have led to the development of synthetic techniques that include variations of traditional vapor-liquid-solid (VLS) growth, wherein chemically synthesized or laser ablated metal NCs are used as catalyst particles. Such routes take advantage of advances in NC syntheses to overcome intrinsic droplet size limitations, ultimately allowing one to create previously unattainable, narrow diameter NWs. Other approaches include complete solution phase analogues of VLS growth such as solution-liquid-solid (SLS) growth, pioneered by Buhro; and supercritical-fluid-liquid-solid (SFLS) synthesis, developed by Korgel. In all cases, new routes have been established for preparing semiconductor NWs with tunable diameters, lengths, compositions, core/cladding geometries and axial composition gradients. Here the solution phase synthesis of narrow diameter ($<$ 10 nm) straight and branched CdSe NWs is described. Crystalline NWs with lengths between 1-10 microns are obtained using a seeded solution approach, whereby NW growth is initiated using Au/Bi core/shell NCs. A gold biphasic reduction step results in the formation of small 1.5 nm diameter Au NCs followed by the thermolysis of trialkylbismuthines to yield low melting, bimetallic, core/shell particles. The resulting Au/Bi NCs have diameters less than 5 nm and are catalytically active towards the growth of similar diameter (7 nm) CdSe NWs. Such wires may exhibit unique quantum confinement effects given that the bulk exciton Bohr radius of CdSe is 5.6 nm. Manipulating the reaction conditions allows one to transition from straight to branched nanowires yielding tripod, v-shaped, and y-shaped NWs. Further variations in the preparation lead to higher order NWs that exhibit multiple branching points. In all cases, the presence of surface binding surfactants yields soluble straight and branched NWs opening up intriguing opportunities for future surface modification and/or surface functionalization chemistries. Such branched wires also provide the distinct possibility of studying not only the size dependent optical and electrical properties of NWs but their shape dependent properties as well.

4:00 PM FF8.7
Synthesis and property of VO2(M) nanorods. Wen Chen and Liqiang Mai; Wuhan University of Technolgy, Wuhan, Hubei, China.

Vanadium dioxides have found a wide range of applications in temperature sensing devices, optical switching devices, energy-conserving coating for windows and so on, because they undergo a phase transition at approximately 341 K from a semiconductor to a metal [1, 2]. Recently, one-dimensional nanostructure materials, such as nanotubes, nanowires and nanorods, have attracted much attention due to their unique properties originated from their high surface area and low dimensionality [3]. In the present work, VO2(M) nanorods have been synthesized, for the first time. Morphology and structure of the sample were characterized by XRD, SEM, HRTEM and TG-DTA. The results show that for VO2(M) nanorods, the transition temperature is 338 K and the hysteresis loop width is 8 cent degree. The active energy of low temperature semiconducting phase is 0.2eV, which indicates that its Fermi energy level situates on the middle energy level of the forbidden-band. After Mo doping, Tc decreases to 332 K. Mo doping reduces forbidden band width of VO2(M) nanorods as the donor and change its electrical property.

4:15 PM FF8.8
Large-Scale Synthesis of Single-Crystalline BaTiO3 and SrTiO3 Nanostructures. Stanislaus S. Wong[1,2], Yuanbing Mao[1] and Sarbajit Banerjee[1]; [1]Department of Chemistry, SUNY at Stony Brook, Stony Brook, New York; [2]Materials Science Department, Brookhaven National Laboratory, Upton, New York.

Nanoscale structures, such as nanoparticles, nanorods, nanowires, nanocubes, and nanotubes, have attracted extensive synthetic attention as a result of their novel size-dependent properties. However, part of the challenge of developing practical nanoscale devices for a variety of applications is the ability to synthesize and characterize these nanostructures to rationally exploit their nanoscale optical, electronic, thermal, and mechanical properties. Ternary transition metal oxides, including BaTiO3 and SrTiO3, with a perovskite structure, are noteworthy for their exceptional dielectric, piezoelectric, electrostrictive, and electrooptic properties with corresponding electronics applications, including as electromechanical devices, transducers, capacitors, actuators, high-k dielectrics, dynamic random access memory, field-effect transistors, and logic circuitry. In present work, single-crystalline perovskite nanostructures with reproducible shape have been prepared using a simple, readily scaleable solid-state reaction in the presence of NaCl and a nonionic surfactant. Pristine BaTiO3 nanowires have diameters ranging from 50 to 80 nm with an aspect ratio larger than 25. Single-crystalline SrTiO3 nanocubes with a mean edge length of 80 nm have been produced using a similar procedure.

4:30 PM FF8.9
Self-Assembly of ZnO/C Multilayers on Zn Nanowire Surface. Quan Li[1], Kwan-wai Kwong[1] and David Cockyne[2]; [1]Physics, The Chinese University of Hong Kong, Hong Kong, Hong Kong; [2]Materials, University of Oxford, Oxford, United Kingdom.

Zn nanowires with an epitaxial thin surface layer of zinc oxide were dispersed onto amorphous carbon films and stored at room temperature. After 1500 hrs, it was found that a self-organized equal-spaced zinc oxide/carbon multilayer structure had formed outside the Zn nanowire, taking the place of the original ZnO surface layer. We carried a systematic study in order to clarify the self-formation mechanism of the periodical multilayers outside the Zn nanowire, and found out that such configuration originated from chemical reaction between Zn and carbon dioxide, and were formed via a gas phase diffusion-interfacial chemical reaction-phase separation process. This observation also suggests the possibility of decorating nanowire surfaces with multilayer coatings. The coatings could largely modify the surface properties of the nanowires, including improved mechanical behavior and chemical inertness and stability of the nanowire, which may have importance in nanotechnology applications using these nanowires as various nanoprobes, nanosensors, even as field emitters.

4:45 PM FF8.10
Synthesis and Characterization of Electrospun Ferroelectric Nanofibers. Junhan Yuh, Juan C. Nino and Wolfgang M. Sigmund; Materials Science & Engineering, University of Florida, Gainesville, Florida.

Over the past few years the synthesis of nanosized ferroelectrics has received considerable attention due to their potential for realizing nanoscale electronic, optical and mechanical devices. In particular, ferroelectric nanofibers offer the potential for self-assembled nanostructures and therefore are of particular interest. However, the controlled synthesis of long ferroelectric nanofibers is a challenge and future use in nanodevices will depend on the achievable sizes and properties. We report a breakthrough in the synthesis of endless ferroelectric nanofibers by electrospinning. Electrospinning is a common technique for drawing polymeric fibers but is novel to ceramic nanofibers and especially novel for ferroelectric nanowires. We report the electrospinning of barium titanate ($BaTiO_3$) and lead zirconate titanate ($Pb(Zr,Ti)O_3$ - PZT) nanofibers. Fiber diameter can be controlled and less than 100 nm are easily achieved. We report the influence of processing conditions on the diameter, crystallinity and electrical properties of the electrospun ferroelectric nanofibers. The morphology and crystallography of the fibers was characterized by SEM, HR-TEM, and XRD. Bonding arrangement was investigated by Infrared and Raman spectroscopy and ferroelectric properties were analyzed using scanning probe microscopy (SPM).

SESSION FF9: Poster Session: Solid State Posters III
Wednesday Evening, December 1, 2004
8:00 PM
Exhibition Hall D (Hynes)

FF9.1
Structural Behavior and Dielectric Properties in (1-x)LaMg0.5Ti0.5O3-xLa2/3TiO3 Perovskites. Igor Levin and Terrell A. Vanderah; NIST, Gaithersburg, Maryland.

Complex oxides with perovskite-like structures are attractive candidates for use as dielectric resonators in microwave wireless communication systems. These applications require a combination of high-permittivity, near-zero temperature coefficient of the resonance frequency and low dielectric loss. Complex A(B'0.5B'0.5)O3 perovskites typically exhibit ordering of the cations mixed on the B-sites, and in many compounds the ordering is superimposed onto octahedral tilting; both these effects are known to strongly affect dielectric properties of perovskites. In the present work crystal structures and phase transitions in the (1-x)LaMg0.5Ti0.5O3-xLa2/3TiO3 system were analyzed using combined X-ray and neutron powder diffraction, transmission electron microscopy and Raman spectroscopy. The structural data were related to the dielectric properties measured at microwave frequencies.

FF9.2
Formation Mechanisms of Perovskite Pb(Ni1/2Nb2/3)O3 in Reaction-Sintering Process. Yi-Cheng Liou, Yi-Chen Huang and Chi-Ting Wu; Department of Electronic Engineering, Kun-Shan University of Technology, Tainan Hsien, Taiwan.

Formation mechanisms of perovskite Pb(Ni1/3Nb2/3)O3 (PNN) in reaction-sintering process were investigated. The mixture of PbO, Ni(NO3)2 and Nb2O5 was pressed into pellets and heated to various temperatures then cooled immediately without any soaking period. After heated to 700oC and 800oC, reflections of PbO were still detected in the pellets. Pb3Nb4O13 pyrochlore phase is the only phase formed in the pellets. As the pellets were heated to 900oC, reflections of PbO were still observed and the peak of NiNb2O6 columbite phase at about 30.4o appeared. Another pyrochlore phase Pb2Nb2O7 was also observed. The amount of Pb2Nb2O7 pyrochlore phase increased as the pellets were heated to 950oC and the perovskite phase PNN was observed. This proves the perovskite PNN phase formed after the formation of Pb2Nb2O7 pyrochlore phase and the further reaction with NiO. The perovskite PNN phase became the major phase in the pellet after heated to 1000oC.

FF9.3
Reductive Intercalation of Vanadyl Layered Perovskites. John B. Wiley[1,2], Doinita Neiner[1], Volodymyr O. Golub[2] and Ray L. Sweany[1]; [1]Chemistry, University of New Orleans, New Orleans, Louisiana; [2]Advanced Materials Research Institute, University of New Orleans, New Orleans, Louisiana.

Ruddlesden-Popper and Dion-Jacobson phases are layered structures consisting of perovskite strata separated by alkali-metal-cations. The alkali-metal ions can be easily replaced while maintaining the basic perovskite structure. In Ruddlesden-Popper compounds of general formula $A_2[A'_{m-1}B_mO_{3m+1}]$, (A is alkali metal, A' is rare earth and B is a transition metal) the A ions are replaced by a $(VO)^{2+}$ unit. This ion exchange opens the layered structure to further chemistry. Alkali metal intercalation reaction is then employed on the empty interlayered sites. This study is concerned with the structural as well as the electronic and magnetic property changes induced in the parent compound after lithium intercalation. New compounds will be presented and their properties discussed.

FF9.4
Large Scale Synthesis of Titanate Nanotubes by Oxidizing Metallic Ti. Haoguo Zhu, Sheng Dai and Steven H. Overbury;

Chemical Sciences Division, Oak Ridge National Laboratry, Oak Ridge, Tennessee.

Titanate nanotubes have received a great deal of attention, in part because of TiO2 can exhibit a wealth of important photovoltaic, photo-catalytic, and gas-sensing properties, especially when prepared as a nanomaterial.1 Titanate nanotubes may often only be synthesized in small quantities by hydrothermal treatment of anatase TiO2 nanoparticles in 10 M NaOH solution. The general procedure involves the dissolution of TiO2 nanoparticles in a strong basic solution, leading to the formation of a layered compound, Na2Ti3O7, which unfolds into sheetlike plates and subsequently folds into nanotubes.2 Such a route inspired us to evaluate whether the direct oxidation of metal can be applied to synthesize titanate nanotubes. Herein, we report the in-situ formation of large quantities of titanate tubes through the direct hydrothermal oxidation of metallic titanium (Ti) particles into Na2Ti3O7 in NaOH with the assistance of H2O2. at 160 °C. The length of the nanotubes ranges from one hundred to several micrometers. When a titanium foil was used as a precursor, a large array of oriented nanotubes as a continuous film on the foil substrate was obtained. Transmission electron microscopy, scanning electron microscopy, and X-ray diffraction techniques have been used to characterize these nanotube materials. 1 G. Patzke, F. Krumeich, R. Nesper Angew. Chem. Int. Ed. 41, 2446 (2002). 2 S. Zhang, L. M. Peng, Q. Chen, G. H. Du, G. Dawson, W. Z. Zhou Phys. Rev. Lett. 91, 256103 (2003).

FF9.5

Sol-Gel La1-x MxCoO3 (M = Ca, Sr) Nanopowders: Synthesis, Characterization and Magnetic Properties.

Gregorio Bottaro[1], Lidia Armelao[1], Davide Barreca[1], Andrea Caneschi[3], Claudio Sangregorio[3], Alberto Gasparotto[2], Stefano Gialanella[4], Cinzia Maragno[2], Elisabetta Pierangelo[2] and Eugenio Tondello[2]; [1]Chemistry, CNR-ISTM - University of Padova, Padova, Italy; [2]Chemistry, University of Padova, Padova, Italy; [3]Chimica, University of Firenze, Firenze, Italy; [4]Materials Engineering, University of Trento, Trento, Italy.

Perovskite-type oxides of rare-earth and transition metals (LMO3, L=La, M=Co, Mn, Fe) are being increasingly investigated due to their potential applications in heterogeneous catalysis, oxygen sensors and solid oxide fuel cells (SOFCs) [1]. Among them, lanthanum cobaltite is particularly promising, thanks to the accessibility for cobalt of the II and III oxidation states. Moreover, the partial substitution of lanthanum by strontium and calcium improves the material performances, i.e., ionic conductivity and thermal characteristics [2]. The growing interest in such mixed oxides relies on a detailed investigation of the possibility to prepare them as nanosystems so that the inherent synergy of large surface area and high defect content is expected to result in improved properties with respect to the conventional ones. The possibility to tailor these features as a function of the synthetic procedure appears thus as a powerful tool in order to optimize the material functional performances. In this fashion, this work is devoted to the sol-gel synthesis and characterization of nanophasic La1-xMxCoO3 (M = Ca, Sr) powders. The samples were prepared starting from solutions of Co(CH3COO)2 4H2O, La(NO3)3 6H2O and M(CH3COO)2 H2O. The nanopowders crystallinity and phase composition was studied by X-ray Diffraction (XRD) and Transmission Electron Microscopy (TEM), while the chemical composition was analyzed by X-ray Photoelectron (XPS) and X-ray Excited Auger Electron (XE-AES) Spectroscopies. Furthermore, they were characterized by magnetic measurements and Electron Paramagnetic Resonance (EPR). The comparison between the magnetic results of this series of compounds and a previous one [1] prepared by combustion synthetic procedure is proposed. Some other relevant results concerning the influence of the synthesis procedure on the chemical and physical properties of the systems are presented and discussed. [1] L. Armelao, G. Bandoli, D. Barreca, M. Bettinelli, G. Bottaro and A. Caneschi, Surf. Int. Anal. 34, 112-115, 2002 and reference therein. [2] N.Q. Minh, T. Takahashi in Science and Technology of Ceramic Fuel Cells, Elsevier, 1995

FF9.6

Hierarchical Evolution of Arrayed Nanowires, Nanorods, and Nanosheets in ZnO.

Jae-Hwan Park, Young-Jin Choi and Jae-Gwan Park; Multifunctional Ceramics, Korea Institute of Science and Technology, Seoul, South Korea.

Various intriguing arrayed nanostructures of ZnO, i.e. arrayed nanowires, arrayed nanorods, arrayed nanosheets, were fabricated in series by controlling the processing temperature and oxygen contents systematically based on a simple thermal evaporation process. These structures are monolithically single crystalline and the examples of spontaneous organization of vapor molecular species into nanoscale structures and their microscale assemblies or superlattices in one step. These kinds of arrayed structures might be useful in arrayed nanoscale optoelectronic and electrochemical applications.

FF9.7

ZnO nanorods grown by a Pulsed Laser Deposition process.

Jae-Hwan Park, Won-Jun Ko, In-Sung Whang, Young-Jin Choi and Jae-Gwan Park; Multifunctional Ceramics, Korea Institute of Science and Technology, Seoul, South Korea.

Semiconductors of one-dimensional (1-D) nanostructures have been extensively studied due to their potentials as building blocks for fabricating nanometer-scaled electronic, optoelectronic, electrochemical and sensor devices. Especially, ZnO, a wide-bandgap (3.37 eV) semiconductor with large exciton binding energy (60 meV), have attracted considerable attention due to the potential applications for the optoelectronics. Thus, various 1-D nanostructures of ZnO including nanowires and nanotubes have been fabricated mainly by carbothermal reduction process and MOCVD. In this work, we fabricated highly aligned ZnO nanorods by Pulsed Laser Deposition process with excimer laser. The effect of processing parameters on the sizes and shapes of the ZnO nanowires will be presented. We also tried to realize p-type ZnO nanorods, homoepitaxially on the n-type ZnO substrate, by using Zn(1-x)(P,As)xO2 target materials. XRD, TEM-EDS, I-V measurement results will presented and discussed.

FF9.8

Non-stoichiometric Tungstate-based Ordered Perovskites.

Hui Wu and Peter K. Davies; Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania.

Although many oxides are known with a 1:1 B-site ordered, double perovskite structure, relatively few systems have been prepared with 1:2 cation order. Furthermore, while their 1:1 counterparts can accommodate extensive non-stoichiometry, the known 1:2 systems (e.g. Ba(Zn1/3Ta2/3)O3) are rigidly stoichiometric and low levels (<5mol%) of a foreign ion with different size/charge destabilize the cation order. This paper will describe the formation of the first family of non-stoichiometric 1:2 ordered perovskites in the (1-x)A2+(Li1/4Nb3/4)O3-x A2+(Li2/5Nb3/5)O3, A2+=Ba, Sr, and Ca, systems. In contrast to all known A(BI1/3BII2/3)O3 perovskites, these 1:2 ordered solid solutions do not include any composition with a 1:2 cation distribution. Structure refinements of the phases (P m1 for A=Ba, P21/c for A=Sr, Ca) support a model for the order where Li and W occupy different positions and Nb is distributed on both sites, i.e. A2+[(Li3/4+y/2Nb1/4-y/2)1/3(Nb1-yWy)2/3]O3 (y = 0.9x). 1:2 ordered phases with a mixture of Nb/Ta and W on the B(II) sites were also obtained for compositions in the [A2+2(1+x)/3La(1-2x)/3][Li1/3(Nb,Ta(1-x)Wx)2/3]O3 systems (A2+ = Sr and Ca). The crystal chemistry, structure, and dielectric properties of these new phases will be presented. The stabilization of non-stoichiometric order in these systems, and the absence of non-stoichiometry in the BZT-type phases, can be interpreted by considering the site size/charge differences, the on-site size mismatches, together with the local formal charge imbalance at the A-site positions.

FF9.9

New synthesis method of nanophased metal oxide catalyst in supercritical water for biomass conversion.

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Biomass conversion for H_2 production in supercritical water (SCW) with heterogeneous acid-base catalyst will be the ecologically benign process because the catalyst does not go out from the process and does not act on the reactor wall. In addition, the catalytic organic reaction with the metal oxide in SCW can be applied to a chemical synthesis that is being operated at the conventional strong acid-base condition. Up to now, little attention has been given to the catalytic property about the metal oxides synthesized in SCW. Some metal oxides (CeO_2, ZrO_2...) are stable and have acidity and basicity on the surface in supercritical water. The catalytic properties (surface area, acidity and basicity, redox character...) of these oxides can be controlled by adding a solute and supporting. Thus, one of the present researches is to control the catalytic properties by making solid solution and support catalyst. Another present research is to find more stable and stronger acid-base catalyst in SCW. In addition, SCW synthesis provides a fine and small particles, that normally have a wide surface area. The key point of the study is to synthesize a novel metal oxide catalyst in supercritical water to compare with conventional method as hydrothermal synthesis and sol-gel process and use it for the biomass conversion in SCW too. At first, we propose to study pure zinc oxide and solid solutions, as CuO-ZnO-Al_2O_3-ZrO_2 systems, synthesized in supercritical water with both a flow and batch apparatus. In flow apparatus, influence of flow rate, precursors concentration and reactor size on structural and textural properties is studied. In Batch, influence of precursors,

additives and concentration on structural and textural properties is studied too. Hydrothermal synthesis and sol-gel route is also employed, in order to compare the method most adapted to obtain nanoparticules and high specific surface area. Then, the catalytic properties (acidity and basicity) are elucidated by TPD. In a second part, the activity test for a reaction is conducted through the reaction such as biomass conversion in sub- and supercritical water. For application of the catalytic reaction by the metal oxide catalysts, biomass conversion is studied to produce a valuable chemicals (H_2, alcohols, aldehydes, furans, and so on) at high selectivity and high yield. The biomass that is being used in the study are glucose (also cellulose) and vegetable oil. Through the new metal oxide catalyst synthesis, the conventional catalyst will be overcome because the metal oxide from supercritical water synthesis has fine particles. This novel metal oxide can be used as an industrial material as well as the catalyst. Thus the expected outcome through the novel metal oxide catalyst synthesis will be spread to not only the catalytic reaction but also the industrial materials, and a greener acid-base organic reaction, that assists to develop a greener industry and society.

FF9.10
synthesis and optical property of vanadium oxide nanotubes.
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In recent years, nanoscale one-dimensional materials have attracted much attention due to their remarkable optic properties and their great potential for nanodevices. The recently discovered vanadium oxide nanotubes (VONTs) are especially interesting since vanadium oxides are widely applied due to their outstanding structural versatility. So it must be a challenging work to study the vanadium oxide nanotubes. Recently, we synthesized the vanadium oxide nanotubes from V2O5 precursors and primary amines in a rheological phase reaction followed by self-assembling process. The products are examined by XRD, SEM and HRTEM. The results show that the nanotube walls consist of two alternative layers of VOx polyhedron layers and protoned HDA layers. The polyhedron layers are composed of paralled [VO5] pyramid which are connected with the tetrahedron of [VO4] in the tube. The average valence of V is 4.31. The optical properties of vanadium oxide nanaotubes are investigated. The results show that there are abundant defects on the nanotube surface and the surface states are easily formed, and VONTs exhibit stronger optical limiting property based on TPA and better infrared radiation property based on two phonon combination radiation mechanism. Moreover, optical limiting property of products is better than carbon nanotubes. The well-resolved photoluminescence band at 450 550 nm is discovered in VONTs, which is attributed to the transitions from the lowest vibrational level of excited triplet T1(V4+-O-) to the various vibrational levels of the ground state S0(V5+=O2-) and belongs to the mechanism of charge transition. In the optical absorption spectra of VONTs, there is an absorption band at 400nm which can lead to calculating the 2.7eV forbidding band. Optical transmittance increases with the increase of incident wavelength. At the 532nm the transmittance is up to 50%.

FF9.11
A General Fabrication Method for Free-Standing as well as Arrays of Single-Crystalline ABO4-Type Nanorods at Room Temperature.
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One-dimensional (1-D) nanomaterials can be used for efficient transport of electrons and optical excitations and are applicable as building blocks to assemble the next generation of molecular electronic and computational devices. Considerable research efforts have been undertaken to synthesize single-crystalline 1-D nanomaterials with high purity in large quantities. However, there are still no generalizable guidelines for their straightforward synthesis with predeterminated chemical and morphological composition, as well as tailor-made sizes and aspect ratios. Single-crystalline BaWO4 and BaCrO4 nanorods of reproducible shape and of varying sizes have been controllably prepared using a simple, room temperature approach, based on the use of porous alumina template membranes. Aligned BaWO4 and BaCrO4 nanorod arrays can be obtained by dissolving the template. Also, the thermal stability of the as-prepared nanorods has been investigated. Our facile technique offers a promising and generalized methodology to prepare other types of free-standing ABO4 nanorods and their corresponding nanorod arrays. Extensive characterization of these samples has been performed using scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), energy-dispersive X-ray spectroscopy (EDS), selected area electron diffraction (SAED), Raman spectroscopy, FT-infrared spectroscopy (FT-IR), and X-ray diffraction (XRD). Since the BaWO4 and BaCrO4 nanorods and their arrays are now available, it could become a valuable starting point for investigating new properties for practical applications, such as lasers and photocatalysis.

FF9.12
Abstract Withdrawn

FF9.13
Fabrication of 1D Nanostructure Materials with Controlled Shapes Using Anodic Porous Alumina as Templates.
Takashi Yanagishita[1], Futoshi Matsumoto[1], Kazuyuki Nishio[2,1] and Hideki Masuda[2,1]; [1]Kanagawa Academy of Science and Technology, Kanagawa, Japan; [2]Tokyo Metropolitan University, Tokyo, Japan.

One-dimensional (1D) materials with nanometer dimensions, such as nanotubes or nanocylinders, are attracting considerable interest because of their unique properties. Control of the geometrical structures of 1D materials is important for the application to several types of functional nanodevice. One method for the fabrication of 1D materials with controlled shapes is template process. In the present report, we describe the fabrication of 1D materials with controlled shapes using anodic porous alumina. Anodic porous alumina, which is a typical self-ordered nanochannel material formed by anodization of Al in an appropriate acidic solution, has recently attracted increasing interest as a starting material for fabrication of nanometer-scale structures [1]. Anodic porous alumina with controlled pore shapes can be also obtained based on the pretexturing process of Al [2]. In the experiment, carbon nanotubes [3] and TiO2 nanocylinders with controlled cross-sections using anodic porous alumina were fabricated. The present process is simple and easy to prepare 1D materials with controlled shapes. The obtained 1D materials with controlled shapes will be applied to several kinds of functional devices. [1] H. Masuda et al. Science, 268, 1466 (1995). [2] H. Masuda et al. Adv. Mater., 13, 189 (2001). [3] T. Yanagishita et al., Adv. Mater., 16, 429 (2004).

FF9.14
Electrochemical Synthesis and Characterization of Tin Oxide Nano Wire.
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Tin oxides is one of useful ceramic materials due to its superior properties; transparency, electrical conductivity and oxidation catalyst in the transparent conducting coating of glass, electrochemical modifiers on electrodes, solar cells and gas-sensing devices. The characteristics were dominated by several factors such as surface morphology, grain size and chemical composition. Recently, those characteristics are expected to be controlled by fabricating novel nano structures. These nano structures could lead to excellent characteristics such as high gas sensitivity and short response time. The nano structural fabrication via electrodeposition has a benefit in large area and mass production. However, there is no report on electrochemically fabrication of tin oxide nanostructure. In this study, we aim to fabricate and control the nano structure of thin film using electrodeposition technique. Tin oxide was electrochemically deposited on ITO substrates from the solutions containing tin dichloride, sodium nitrate, nitric acid, and redistilled water. The electrodeposition was performed at 303 K, 323 K and 353 K using conventional three-electrode cell. The properties of tin oxide were investigated using different techniques. The morphology was observed by scanning electron microscopy (SEM). The qualitative elemental analysis was characterized by energy dispersive X-ray spectroscopy (EDS). The crystal structure was examined by X-ray diffraction (XRD). We confirmed nano structure, nano wire, on the substrate based on a SEM image of sample surface prepared from the solutions containing 20mM tin dichloride, 100mM sodium nitrate, 75mM nitric acid. On the contrary, such a structure was not observed on the sample surface prepared from the solution without sodium nitrate. Thus, the sodium nitrate has a great influence on forming the nano structure of tin oxide using electrochemical deposition.

FF9.15
Study of synthesis variables in the nanocrystal growth behavior of tin oxide processed by controlled hydrolysis.
Caue Ribeiro[1], Eduardo Jia Hua Lee[1], Tania Regina Giraldi[1], Jose Arana Varela[2], Elson Longo[1] and Edson Roberto Leite[1]; [1]Chemistry, Universidade Federal de Sao Carlos, Sao Carlos, SP, Brazil; [2]Chemistry, UNESP, Araraquara, SP, Brazil.

Tin dioxide nanoparticle suspensions were synthesized at room temperature by the hydrolysis reaction of tin chloride (II) dissolved in ethanol. The effect of the initial tin (II) ion concentration, in an ethanolic solution, on the mean particle size of the nanoparticles was studied. The Sn2+ concentration was varied from 0.0025 M to 0.1 M, while all other synthesis parameters were kept fixed. Moreover, an

investigation of the effect of agglomeration on the nanoparticle characteristics (i.e. size and morphology) was also done, by modifying the pH of SnO2 suspensions. The different samples were characterized by transmission electron microscopy, optical absorption spectroscopy in the ultraviolet range and photoluminescence measurements. The results show that higher initial ion concentrations and agglomeration lead to bigger nanoparticles. The concentration effect is explained by an enhanced growth due to a higher supersaturation of the liquid medium. On the other hand, it was observed that agglomeration of the nanoparticles in suspension induce coarsening by the oriented attachment mechanism.

FF9.16
Tin oxide nanoribbons with different oxidation states obtained by a carbothermal evaporation method.
Marcelo Ornaghi Orlandi[1], Rosiana Aguiar[1], Edson Roberto Leite[2], Jose Arana Varela[3] and Elson Longo[2]; [1]Materials Engineering, Universidade Federal de Sao Carlos, Sao Carlos, Brazil; [2]Chemistry, Universidade Federal de Sao Carlos, Sao Carlos, SP, Brazil; [3]Chemistry, Universidade Estadual Paulista, Araraquara, SP, Brazil.

A carbothermal evaporation-condensation method was employed to obtain tin oxide nanoribbons. Different configurations of the experimental procedure enabled the preparation of nanoribbons with different oxidation states (i.e. SnO2, Sn2O3 and SnO), due to variations in the oxygen partial pressure of the furnace. The samples were characterized by transmission electron microscopy, scanning electron microscopy and X-ray diffraction. The results indicate that tin oxide nanoribbons with different oxidation state may be grown by different mechanisms. The vapor-solid mechanism is the most probable for the obtention of SnO2 and Sn2O3 nanoribbons, while there is evidence that a self-catalytic vapor-liquid-solid (VLS) mechanism should occur in the formation of SnO nanoribbons. Hartree-Fock Roothoen ab initio calculations were done in order to elucidate some of the possible reactions that occur during the synthesis of the nanoribbons.

FF9.17
Multi-step Redox Synthesis of New Layered Perovskite Materials. John Wiley and Xiao Zhang; Department of Chemistry, University of New Orleans, New Orleans, Louisiana.

The intercalation chemistry of the layered Dion-Jacobson (DJ) perovskite phases, both double layered ALaNb2O7 and triple layered ACa2Nb3O10 (A = alkali metal) were examined. Reductive intercalation of ALaNb2O7 and ACa2Nb3O10 was carried out to produce the mixed-valent compounds A2LaNb2O7 (A = Li, Na, K, Rb, Cs) and A2Ca2Nb3O10 (A=Na, K, Rb, Cs). Then oxidative-intercalation methods were examined in an effort to assembly alkali-metal halide layers within the perovskite host. These methods have so far resulted in the new layered perovskite (AxCl)LaNb2O7 and (AxCl)Ca2Nb3O10 (A = Rb, Cs). Here the synthesis and characterization of this new series will be presented and the importance of this work to the rational synthesis of new layered perovskites will be discussed.

FF9.18
New Magnetic and Magnetoresistant Perovskite Ruthenates. F. Huang and I-W. Chen; Materials Science and Engineering, University of Pennsylvania, Philaelphia, Pennsylvania.

We report two novel observations in perovskite ruthenates which have broad implications. First, by progressively disrupting the conducting pathway in the ferromagnetic SrRuO3, we found it first undergoes Anderson localization, then exhibits very large magnetoresistance. The implication is that any ferromagnetic metal should acquire a large magnetoresistance when it is rendered insulating by way of disorder. This pathway is especially feasible in strongly correlated metals such as SrRuO3. Second, by substitution at the A-site of perovskite ruthenates, we are able to obtain a large family of ferromagnetic metal, with the novel Ru4+/Ru5+ mixed valency. These ferromagnetic metals have unexpectedly high and nearly constant Curie temperature, challenging the current Stoner theory of magnetism for SrRuO3 and related compounds.

FF9.19
Ferroelectricity in $SrTiO_3$ Ceramics Induced by Pr Doping. Alejandro Duran, Eduardo Martinez, Jorge Mata, Jesus Heiras and Jesus Siqueiros; Prop. Opticas, Centro de Ciencias de la Materia Condensada-UNAM, Ensenada, Baja California, Mexico.

SrTiO3 (STO) is considered to be an incipient ferroelectric material. In this study we have investigated the influence of Pr doping of STO on the structural and dielectric properties of the $Sr_{1-x}Pr_xTiO_3$solid solution for values of x = 0, 0.025, 0.050, 0.075, 0.10, 0.15 and 0.20. X-ray diffraction patterns show single phase crystalline structure for all compositions. Rietveld refinement shows that the introduction of Pr in the unit cell produces a decrease of the unit cell volume which gives rise to a compression due to the small radius of the praseodymium ion. This deformation of the unit cell induces a measurable polar behavior of the compound. Dielectric permittivity vs T (ϵ vs T) measurements display a well defined peak at about 238 °C. The position of this peak depends on Pr-concentration. This peak strongly suggests a paraelectric-ferroelectric transition. At low Pr concentrations the solid solution display well defined hysteresis loops at 30 °C with a remnant polarization that tends to decrease with increasing Pr concentration. The polar behavior is probably due to the distortion of the oxygen octahedron of the perovskite structure which produces and off-center site. This work has been partially supported by CONACyT through Project No. 40604-F and by DGAPA-UNAM through Projects IN116703-3 and IN100903

FF9.20
Raman Spectroscopy as a Probe of Local Order in $CaZr_{1-x}Ti_xO_3$ Eric Cockayne, Ceramics Division, NIST, Gaithersburg, Maryland.

Many materials of technological interest are solid solutions where the degree of chemical ordering affects the physical properties. Raman spectra are sensitive to short-range and long-range order, but little is known quantitatively about these relationships. To better understand the connection between chemical order and Raman spectra, a model has been developed for simulating the Raman spectra of solids. The parameters in the model are fit to first-principles results on forces, effective ionic charges, and indices of refraction. Both long-range electrostatics and short-range covalent bonding contribute to the Raman spectra, but not to an equal degree for all peaks. This provides a natural explanation for the experimental observation that different Raman peaks have different sensitivities to the amount of long-range order. Experimentally, $CaZr_{1-x}Ti_xO_3$ (CZT) does not exhibit long-range ordering of Zr and Ti, yet Raman peaks are observed that may be associated with short-range order. The Raman spectra of CZT is simulated as a function of composition and short-range Zr-Ti order, and the results are compared with experiment.

FF9.21
Ordering Transformations in $Ba(Ni_{1/3}Nb_{2/3})O_3$ Perovskites. Meganathan Thirumal[1], Tyke Negas[2] and Peter K. Davies[1]; [1]Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania; [2]TCI Ceramics, Hagerstown, Maryland.

Ordered $A(B^{II}{}_{1/3}B^{V}{}_{2/3})O_3$ (A = Ba, B^{II} = Mg, Zn, Ni; B^{V} = Ta, Nb) perovskites have been widely investigated as a result of their superior dielectric properties in the microwave range. In their stable low temperature form these systems adopt an ordered structure with a "1:2" layering of the B-site cations. While the tantalate systems retain this ordered arrangement to temperatures well in excess of those required for their densification (1550 C), niobates such as $Ba(Ni_{1/3}Nb_{2/3})O_3$(BNN) and $Ba(Zn_{1/3}$—$Nb_{2/3})O_3$(BZN) undergo a transition to a disordered B-site arrangement below their sintering temperature. Therefore, to optimize the dielectric properties of the niobates the order must be induced by annealing the dense, disordered pellets at lower temperature in the region of stability of the order. Previous studies report quite different ordering transition temperatures for BNN, and inconsistencies exist regarding the ordering of free powders and dense ceramic pellets. We find that at high temperature the phase behavior is affected by the volatilization of NiO and the formation of minor impurity phases. However, by carefully controlling the loss of NiO, we observe the small alterations in the stoichiometry of the perovskite induce large variations in the ordering transition (1465 to 1520 C). Possible models for these reactions will be presented. We will also present measurements of the thermal expansion of ordered and disorder variants of this system, which were undertaken to understand if the reactions in dense pellets are affected by changes in their relative molar volumes at high temperature.

FF9.22
Study of the percolative nature of thermoelectric power and resistivity in Pr_0.66R_0.04Sr_0.3MnO_3 (R = Tb, Y, Ho and Er) manganites. N. Rama[1,2], V. Sankaranarayanan[1] and S. R. Rao Mamidanna[1,2,3]; [1]Department of Physics, Indian Institute of Technology Madras, Chennai, Tamil Nadu, India; [2]Materials Science Research Centre, Indian Institute of Technology Madras, Chennai, Tamil Nadu, India; [3]Department of Physics, University of Maryland, College Park, MD 20742, Maryland.

The magnetic and transport properties of Ln1-xAxMnO3 manganite crucially depend on the variance of ionic radii at the A-site. It is seen that as the variance in A-site disorder ($<\sigma>^2$)increases, the Curie temperature decreases even if the average ionic radius <r_> is kept constant. This suggests that local Mn-O-Mn bond bending is more important than the average ionic radius criterion in determining the

physical properties and that disorder plays a major role. Experimental evidence suggests the coexistence of metallic and polaronic regions near the metal to insulator transition temperature and the transition itself can be due to the percolation of these metallic regions. We have studied the resistivity and thermoelectric power of Pr_0.66R_0.04Sr_0.3MnO_3 where R = Tb, Y, Ho and Er and have analyzed it within a percolative framework. Both the resistivity and the thermoelectric power was found to show a strong dependence on ($<\sigma>\hat{2}$) with the high temperature activation energy in both increasing with increase in ($<\sigma>\hat{2}$) implying that as the disorder increases, carriers get more localized. The percolative nature of the thermopower was analyzed assuming that the lattice has coexisting metallic (S_met) and insulating (S_ins) components above and below TC which are independent of each other. Hence total S(T) = pS_met(T) + (1-p)S_ins with volume metallic fraction p=1/(1+exp(-Uo(1-T/T_C)/k_BT) [1]. A similar analysis was done using the resistivity data. It was seen that the TC from both thermopower and resistivity fits were nearly the same indicating that they have a common origin. This analysis clearly proves that the metal insulator transition in manganites is percolative in nature and the transport properties show a strong percolation-tendency. [1] Yuan et al Appl,Phys, Lett 77, 4398(2000) * also, at the Center for Superconductivity Research, Department of Physics, University of Maryland, College Park, MD 20740, USA

FF9.23

The ordered phase of the perovskite methylammonium lead chloride. Lisheng Chi, Ian Swainson, Lachlan Cranswick, Peter Stephens and Jae-Hyuk Her; Neutron Program for Materials Research, National Research Council Canada, Chalk River, Ontario, Canada.

The ordered structure of perovskite compound methylammonium lead chloride at 80K is refined to be space group Pnma with cell parameters a=11.1747(2)Å, b=11.3552(1)Å, c=11.2810(1)Å, P2=3.574, Rwp=2.57%, Rp=1.79% from combined neutron and synchrotron powder diffraction data. Each of the orthorhombic axes is doubled with respect to the disordered cubic phase. The space group Pnma with this basis cell is not a common perovskite cell. In the structure, two methylammonium ions are ordered in planes with y=0.25 while Pb is in general position. Calculations of octahedral tilting distortion parameters reveal the octahedra are more distorted than those of the ordered phase of methylammonium lead bromide, which itself shows large distortions of the octahedra. Much of the distortion in the chloride is due to displacement of Pb within the octahedra. This suggests that the most rigid unit is actually the methylammonium cation, rather than the $PbCl_6$ octahedra. The methylammonium cation may act as an additional Maxwell constraint in this system.

FF9.24

Effect of Different II-VI Shells on the Photoluminescence of InP Nanoparticles. Madalina Furis[1,3], William David Kirkey[1], Gurinder Singh[1], Alexander N. Cartwright[1], Derrick Lucey[2] and Paras N. Prasad[2]; [1]Electrical Engineering, University at Buffalo (S.U.N.Y.), Buffalo, New York; [2]Chemistry, University at Buffalo (S.U.N.Y.), Buffalo, New York; [3]Los Alamos National Laboratories, Los Alamos, New Mexico.

It is well-known that the quantum efficiency of II-VI semiconductor nanocrystals can be substantially enhanced by encapsulating them in a shell of a second semiconductor with a wider bandgap. Nanocrystals composed of III-V materials, particularly InP, have garnered interest in recent years, but reports of core-shell structures with InP cores are rare. In this work, the colloidal growth and optical and structural characterization of different InP/II-VI core-shell nanoparticle structures will be described. Shell materials used include CdSe, CdS, ZnSe, and ZnS. In each case, samples were extracted from the reaction mixture at various times during shell growth, and the photoluminescence (PL) of each sample was recorded. These studies confirm that, as expected, the characteristics of the emission depend strongly on the degree of confinement of both electrons and holes within the core. For example, bulk CdS has a bandgap of 2.42 eV, while bulk ZnSe has a bandgap of 2.58 eV (the bulk InP bandgap is 1.27 eV). However, most of the bandgap offset between CdS and InP occurs in the valence band, leaving a conduction band offset of only 0.3 eV, and so the electrons are expected to be only weakly confined to the InP core. In contrast, the offset between ZnSe and InP is almost entirely in the conduction band, and the valence band offset is only 0.1 eV. The PL spectra of the InP/CdS and the InP/ZnSe nanoparticles are quite different as a result of this difference in bandstructure. In the former case, the PL is broadened and redshifted substantially relative to that of the original, uncapped InP nanoparticles, with a quantum efficiency that increases during shell growth. The broadening is due to the reduced confinement of electrons, while the increased efficiency is due to surface passivation. In the latter case, the broadening and redshift effects are reduced, but the quantum efficiency of the InP core emission drops during shell growth, while a second, long-wavelength band emerges that we attribute to radiative surface traps. Here, the weak hole confinement allows holes to completely escape the InP core and to reach trap states. Of all the samples, the strongest emission occurs for the case of the ZnS shell, where both electrons and holes are tightly confined to the InP core.

FF9.25

Solution-Phase Synthesis of 1-D Transparent Conducting Oxide (TCO) Nanostructures with Controllable Aspect Ratios. Bin Cheng[1], Joette Russell[1], Wensheng Shi[1], Lei Zhang[2] and Edward T. Samulski[1,2]; [1]Chemistry, University of North Carolina, Chapel Hill, North Carolina; [2]Curriculum in Applied Materials Sciences, University of North Carolina, Chapel Hill, North Carolina.

One-dimensional (1-D), transparent, conducting oxide (e.g. SnO2, ZnO) nanostructures were prepared in solution under low-temperature conditions.1,2 The aspect ratios of the 1-D nanorods are tunable by delicately-selected experimental conditions, allowing for generation of materials ranging in size from nanorods to nanowires. The structures of the as-synthesized nanorods and nanowires were characterized by XRD, TEM, SAED and HRTEM, and the optical properties of these materials are reported. References 1. Bin Cheng, Edward T. Samulski, Chem. Commun. 2004, 986-987; 2. Bin Cheng, Joette M. Russell, Wensheng Shi, Lei Zhang, Edward T. Samulski, J. Am. Chem. Soc. 2004, 126, 5972-5973.

FF9.26

Amorphous Nanowires and Crystalline Thin Films of SiO2-Li2O Compounds obtained by Combustion Chemical Vapor Deposition. Monica Jung de Andrade, Carlos Perez Bergmann and Marcio Dias Lima; Materials Department, Federal University of Rio Grande do Sul, Porto Alegre, Rio Grando do Sul, Brazil.

Amorphous silica films deposited by Combustion Chemical Vapor Deposition (CCVD) were modified by lithium addition in the precursor solution. The modified films were characterized by X-ray diffraction and scanning and transmission electron microscopy. The addition of lithium promoted the crystallization of Li2O-SiO2 compounds, mainly crystalline phases like Li2SiO3, Li2Si2O5, quartz and cristobalite. Besides that, the morphology of the film was modified, leading to the formation of acicular structures and nanowires. The acicular structures were identified through TEM associated with SAED as crystalline phases, mainly constituted by Li2SiO3 and Li2SiO5. TEM and SEM analysis indicated that the nanowires diameter is between 20 and 80nm. In addition to this, SAED and microprobe EDS analysis indicated that these nanowires are constituted by amorphous silica. The probable growth mechanism of these nanowires is the vapor-liquid-solid (VLS) catalyzed by a liquid particulate composed by Li2O-SiO2.

FF9.27

An Experimental and Theoretical Investigation of the Synthesis of CdSe Nanoprecipitates in MgO. S.W.H. Eijt[1], H. Schut[1], M. A. van Huis[2,1] and P. E. Mijnarends[1]; [1]Interfaculty Reactor Institute, Delft University of Technology, Delft, Netherlands; [2]National Centre for HREM, Kavli Institute of Nanoscience, Delft University of Technology, Delft, Netherlands.

Semiconductor nanocrystals have aroused considerable interest because of their strong variation in optical and electronic properties in the size range below ~10 nm. We present a study of the synthesis of CdSe nanocrystals based on the precipitation of Cd and Se supersaturated solid solutions in single crystalline MgO. The precipitation evolves during heat treatments in the temperature range between 700 °C and 1100 °C. Supersaturated solutions were prepared by means of ion implantation in subsurface layers of MgO, reaching maximum Cd and Se concentrations of ~20 at%. The evolution of CdSe precipitation was followed by optical absorption spectroscopy (OAS) and depth-profiling positron beam analysis (PBA), which is a versatile probe to monitor defect chemistry processes in thin films. Here, PBA gave insight into the role of vacancies in the formation process of the embedded CdSe nanocrystals. We have shown in XRD and TEM studies that for sizes below ~20 nm the crystal structure of the nanocrystals prepared at 1100 °C changes from wurzite to zincblende and finally changes to the rocksalt structure below ~5 nm. In order to gain a better understanding of these structural changes and the parameters governing the solid state precipitation process, ab-initio total energy electronic structure calculations were performed on wurtzite, zincblende, and rocksalt CdSe using the VASP plane wave pseudopotential code. The cohesive energy of wurtzite CdSe was found to be larger than for rocksalt CdSe by 0.183 eV/CdSe pair, which stabilizes the wurtzite structure for large precipitates. For small sizes, the rocksalt structure becomes the most stable crystal structure because of the better fit in the MgO crystal lattice and correspondingly lower interface energies. Changes in electronic band

structure between the three crystal structures, which govern the optical properties, are presented. First-principles calculations using a 64 atom supercell yielded an energy gain of 10.82 eV/CdSe pair for isolated Cd and Se impurities at substitutional MgO lattice positions when condensing into the CdSe phase. Lattice relaxation around these impurities is expected to lower this energy gain considerably. Further, the influence of vacancies is discussed on the basis of the calculated migration energies for Cd and Se in MgO via positional exchange with a neighboring Mg or O vacancy, respectively. Finally, a comparison is made with the synthesis of ZnO nanocrystals in MgO using the same preparation methods. Although the ZnO rocksalt crystal structure fits MgO much better than CdSe, the intended phase separation finds competition in the $Mg_{1-x}Zn_xO$ alloying processes.

FF9.28

Preparation of boron carbide nanoparticles by a modified carbothermal reduction method. Baohe Chang[1], Bonnie L. Gersten[1], Steve Szewczyk[2] and Jane W. Adams[2]; [1]Department of Chemistry and Biochemistry, Queens College, CUNY, Flushing, New York; [2]Weapons and Materials Research Directorate, Army Research Laboratory, Aberdeen Proving Grounds, Maryland.

Boron carbide is an attractive material for many applications due to its extreme hardness, low density and high radiation hardness. A main technique for the production of boron carbide powders is by the carbothermal reaction. The powder size usually results in a micrometer size range. In this study, a modified carbothermal reaction process was employed to synthesize nano-sized boron carbide particles. The reactions were carried out by heating a mixture of boric oxide powder and carbon reactant under a flow of argon atmosphere in a rapid heat-up high temperature tube furnace to 1200-1700 C for 1-4 h. In order to obtain stoichiometric powder, additional pure boron powder was added to reacting mixture to compensate for the boron loss in the form of B2O2 gas during the reaction. Different types of carbon reactants were used in the experiment, i.e. amorphous carbon and graphite. The effect of the structure and morphology of the precursor materials on that of the products was also investigated. X-ray diffraction (XRD) studies indicated that the powder product prepared under optimized reaction condition had a pattern matching bulk boron carbide. Transmission electron microscopy observation showed that the sizes of the small boron carbide particle were less than 100 nm. Energy dispersive spectroscopy was also used to determine the stoichiometry of the boron carbide nanoparticle products.

FF9.29

Structural Properties of Amorphous Aluminum and Aluminum-Nitrogen Alloys. Computer Simulations. Alexander Valladares[2], Renela Maria Valladares[2] and Ariel Alberto Valladares[1]; [1]Condensed Matter, IIM-UNAM, Mexico, D. F. , Mexico; [2]Physics Department, Facultad de Ciencias, UNAM, Mexico, D. F. , Mexico.

The theoretical/simulational study of amorphous materials has proven to be a very difficult subject which has hindered the development of the field. Computational simulations of metallic systems has relied on models like random packing, the quasi crystalline approach or the tunnel model. For semiconducting random networks the use of clusters or supercells are hopeful approaches to the subject, especially when simulations are based on ab initio molecular dynamics techniques. Nevertheless, the pioneering ab initio work of Car and Parinello, no doubt, has permeated all efforts during the last 17 years, to the point that their annealing processes have been used frequently, almost without questioning. Recently we have developed a new approach to amorphizing semiconducting elements and alloys, and porous silicon (Ref. 1); approach that we have now applied to non-magnetic pure metals, like aluminum and its alloys. We find that our new process generates amorphous metallic atomic structures in good agreement with experiment. Radial Distribution Functions for amorphous supercells of aluminum and aluminum-nitrogen will be reported and compared with previous experimental and theoretical/simulational results; also, the atomic arrangements within given supercells will be presented and analyzed. Agreements and discrepancies with results existing in the literature will be pondered. We hope that our results will further the development of the field. 1. A. A. Valladares, F. Alvarez, Z. Liu, J. Sticht and J. Harris, Eur. Phys. J. 22 (2001) 443. F. Alvarez and A. A. Valladares, Appl. Phys Lett. 80 (2002) 58. F. Alvarez, C. C. Diaz, A. A. Valladares and R. M. Valladares, Phys. Rev. B 65 (2002) 113108-1. F. Alvarez and A. A. Valladares, Solid State Comm. 127 (2003) 483. F. Alvarez and A. A. Valladares, Phys. Rev. B 68 (2003) 205203-1.

FF9.30

Preparation and characterization of (C4H9NH3)2MCl4 (M=Mn, Cu). Liling Guo, Hanxing Liu, Kunyu Shi and Shixi Ouyang; State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan, Hubei Province, China.

In the present study, organic-inorganic layered perovskite-type compounds (C4H9NH3)2MCl4 (M=Mn, Cu) were prepared from solutions in an air atmosphere. X-ray diffraction(XRD), scanning electron microscopy (SEM), and thermal analysis (TG, DSC) were used to characterize the obtained powders including the structure and thermal stability. The heat of water bath at different temperatures was taken to prepare (C4H9NH3)2MCl4, and the results indicated that 70? is advisable. From the SEM pictures, both of (C4H9NH3)2MnCl4 and (C4H9NH3)2CuCl4 took on obvious sheet-like microstructure, it demonstrated that the crystals' growth was also highly oriented. Although both of title compounds had good thermal stability, (C4H9NH3)2CuCl4 was inferior to the former due to distorted [CuCl6].

FF9.31

The Chemical Bonding of Organic-Inorganic in Hybrid Compounds. Liling Guo, Yadong Dai, Kunyu Shi, Hanxing Liu and Shixi Ouyang; State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan, Hubei Province, China.

As most people discussed, the research on the electronic structure between organic and inorganic in hybrid compounds become important. In present study, first principle method was employed to calculate the electronic structure of the hybrid compound. The influence of inorganic part and organic part in perovskite-type structure on the hybrid compound was discussed. The experimental data including XRD, XPS were used to confirm the model for electronic structure calculation. The information including bonding order, fermi energy etc. were obtained basing on quantum mechanism calculation.

FF9.32

Evaluation of Applicability of Borosilicate Glasses Waste Form to Immobilisation of Fluorine Salt Waste from Pyrometallurgical Reprocessing. Agnes Grandjean and Jean Luc Dussossoy; DTCD/SCDV/LEBV, CEA Valrho Marcoule, Bagnols Sur Ceze, France.

Separating the actinides from the fission products through reductive extraction by aluminium in a LiF/AlF3 medium is a process investigated for pyrometallurgical reprocessing of spent fuel. This process will generated a fluorine waste containing alkali-metal, alkaline-earth and rare earth fission products. We have studied ceramic-glasses as an immobilisation matrix for this salt waste. Waste loading, processability and durability are three important factors to be considered in developing optimised glass compositions. In this study the waste loading was fixed to 15% weight. Processability is related to a particular vitrification technique. In our case, the use of cold crucible melter allow high temperature. Nevertheless, because of fluorine volatility the melting temperature was fixed to 1200 C. We have studied the effect of composition on the properties of glasses in the SiO2-B2O3-Na2O-Al2O3-CaO(BaO)-ZrO2 system. At this temperature, only glass without calcium oxide present a significant fluorine emission from the melt. The crystalline phases observed in these glasses are zircone (ZrO2), zircon (ZrSiO2) and fluorite (CaF2). Microstructural observations by SEM showed the presence of only a few ZrO2 crystals (not detectable by XRD) after heat treatment at 1050 C for 17 hours. Substitution of calcium oxide for barium oxide suggests a positive effect on the quantity of fluorite phase in slowly quenched samples. An effect of the number of the non bridging oxygen, attached to a silicon, to durability of the glass ceramic is observed. According to these results, a preliminary glass composition including 15% weight simulated salt-containing waste was chosen. Experiments show that at the processing temperature (1200 C) the glass melt is homogeneous and his conductivity and viscosity are compatible with the technological process. The conclusion is that glass-ceramic is a promising immobilisation matrix for waste fluorine salts generated by pyrometallurgical processing of spent fuel.

FF9.33

Synthesis and Characterization of High Surface Area CdSe Aerogels. Indika Udayakumara Arachchige and Stephanie L. Brock; Department of Chemistry, Wayne State University, Detroit, Michigan.

Aerogels are a unique class of inorganic polymers that have low densities, large open pores and high inner surface area. This results in interesting physical properties as well as a wide variety of potential applications as catalysts, sensors and novel electrochemical device components. So far, a great deal of research has been conducted on aerogels based on single and mixed metal oxides. However, non-oxide aerogels, with the exception of carbon aerogels, are virtually nonexistent. Properties of aerogels can be effectively modified by substitution of the primary gel component to make a chemically unique framework. An extensive range of aerogel chemical and physical properties may be achieved if the framework can be

assembled from components other than oxides. We have recently developed a synthetic route for the production of pure metal chalcogenide based semiconductor aerogels from controlled aggregation of primary particles followed by super-critical fluid extraction. Herein, the application of this methodology to CdSe is presented and the optical, electronic and surface properties of the resultant material will be discussed as a function of the characteristics of individual nanoparticle precursors (hexagonal vs cubic phase, primary particle size) and gelation and processing conditions (chemical vs photo-oxidative initiation, ageing time).

SESSION FF10: Perovskites and Related Materials
Chairs: Martha Greenblatt and Martin Jansen
Thursday Morning, December 2, 2004
Room 200 (Hynes)

8:30 AM FF10.1
Synthesis, crystal and magnetic structures of the Sr2RuREO6 (RE <¿ Rare Earth) double perovskites. Rocio Ruiz-Bustos[1], Myriam H. Aguirre[1], Emilio Moran[1], Regino Saez-Puche[1], Jose Luis Garcia-Munoz[2] and Miguel A. Alario-Franco[1]; [1]Laboratorio de Quimica del estado Solido, Universidad Complutense, Madrid, Spain; [2]Instituto de Materiales de Barcelona, C.S.I.C., Barcelona, Spain.

Double perovskites are among the most studied mixed oxides in view of their interesting magnetic, electric and other properties (1,2) yet there are still some inconsistencies concerning their crystal and magnetic structures. This is often due to the fact that changes in size and oxidation state of either the A or B (B & B‘) cations may produce subtle changes in the symmetry and magnetic properties. The title family has received some attention in the literature (1, 2) and it appears that the structure is monoclinic (S.G. P21/n). This is to be compared to the Ba homologues where very recently (1)it has been shown that the structure it is cubic with a double cell with parameters a 2ap (ap being the basic simple cubic cell perovskite parameter). However, some doubts exist concerning the magnetic structure. In the present work, we have prepared samples of the Y, Tb, Ho and Er materials from RuO2, SrCO3 and TR2O3 or Tb4O7, at room pressure and 1200 C in air during 120 hours with intermediate quenching and grinding processes. X- ray powder diffraction confirmed the monoclinic cell and the presence of a BB‘ ordering. Magnetic susceptibility data as a function of the temperature indicate that the materials are antiferromagnetic with TN < 50 K and that at higher temperatures they show a Curie-Weiss behaviour. Neutron diffraction at decreasing temperatures, confirmed the presence of a magnetic phase transition with substantial changes in the peaks intensity and the appearance of new peaks at the lower range of temperatures due to the magnetic structure, the transition temperature and magnetic structure being dependent of the Rare Earth element. 1. R.H. Mitchel: Perovskites, Almaz Press Ontario, Canada, 2002, Chapter. 4 2. P.D. Battle,C.W. Jones, F. Studer. , J. Solid State Chem 90 (1991) 302

8:45 AM FF10.2
Nonstoichiometry, Structure and Electrical Properties of '$SrPrO_3$'. Sossina M. Haile[1], Camille Y. Jones[2] and Mary A. Thundathil[1]; [1]Materials Science, Chemical Engineering, California Institute of Technology, Pasadena, California; [2]NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland.

Many doped perovskite oxides including $BaCeO_3$, $BaZrO_3$, $SrCeO_3$ and $SrZrO_3$ have received recent attention as proton conductors. Introduction of a trivalent dopant onto the quatravalent site results in the creation of oxygen vacancies. Upon exposure of the material to humid atmospheres OH groups are dissolved onto the formerly vacant oxygen sites and additional protons are incorporated at other oxygen ion sites. Protons, present in the form of hydroxyl ions, can easily jump from one oxygen ion to the next, giving rise to the observed high proton conductivity. To date, few mixed proton and electron conducting oxides, as would be useful in a variety of applications, have been examined. As part of an ongoing program to develop such materials, we have examined the properties of $SrPrO_3$. Based on an analogy to compounds such as $SrCeO_3$ and $BaCeO_3$ acceptor doped $SrPrO_3$ might be anticipated to adsorb atmospheric H_2O and exhibit good proton conductivity, whereas the variable valence of the Pr ion, between 3+ and 4+ oxidation states, might be anticipated to result in high electronic conductivity. In addition, $SrPrO_3$ and the analogous perovskite $BaPrO_3$ are unusual in their ability to host Pr primarily (if not entirely) in the 4+ oxidation state, and have therefore been of interest for their magnetic properties. A careful combinationof chemical analysis, thermal gravimetric analysis and nuetron powder diffraction experiments has revealed that the single phase composition with the perovskite structure type in the Sr-Pr-O system has stoichiometry $(Sr_{0.935}Pr_{0.043 0.022})Pr_{1.0}O_3$. Thus, the compound contains excess Pr relative to the Sr content, but is overall cation deficient. It crystallizes in a $GdFeO_3$-type orthorhombic structure, space group Pbnm, with lattice parameters a = 5.98800(17), b = 6.12136(17), c = 8.54858(24) Å and Z = 4 at 300 K. Thermogravimetric analysis confirms that the compound is not oxygen deficient. The material is electronically conducting, with a bulk (grain interior) conductivity at 36 °C of 5.2 x 10^{-5} S cm^{-1} with an activation energy for charge transport of 0.26 eV. Unlike typical perovskites, it is n-type rather than p-type as a result of the unusual defect chemistry. This feature may have important implications for electrochemical applications.

9:00 AM FF10.3
Floating Zone Growth of Bulk Single Crystals of Complex Oxides. Prasenjit Guptasarma, Mark S. Williamsen and Shishir K. Ray; Physics, Univ Wisconsin Milw, Milwaukee, Wisconsin.

Complex oxides are host to a large number of unconventional strongly-correlated phenomena of recent interest including those found in oxide superconductors like Sr2RuO4 (low Tc) or Bi2Sr2CaCu2Oy (high Tc), colossal magneto-resistive materials, novel multi-phase systems such as doped ruthenate oxides, and multi-ferroics or magneto-electrics such as YMnO3 and BiFeO3 with potential importance in information storage and spintronics. Our ability to understand the fundamental mechanisms in these system or to convert them into viable applications are deeply coupled with our understanding of the solid state chemistry of these complex oxides. Of importance is the availability of high-quality single crystals of such phases. Oxide single crystals grown from a floating molten zone generally have among the highest homogeneity, purity and size thanks mainly to controlled growth rates and the lack of the need of a crucible or a substrate to hold or contain the crystal phase as it grows. Among other advantages is the ease of studying both bulk and surface properties in the same single crystal. Here, we review the current understanding of the solid state chemistry of these phases - as applied to the science of floating zone (FZ) crystal growth - and report on our studies of phase formation from the high temperature melt and the dependence on starting chemistry. In an FZ crystal growth process, single crystals are grown from a molten zone held together by forces of surface tension between polycrystalline rods made up of components similar to that of the melt. FZ synthesis of ruthenate and manganate oxides using a focused infrared image is generally difficult because of the high volatility of component oxides. These components tend to deposit on the quartz tube surrounding the growth chamber, obscuring light from the image and interfering with the optics and temperature control. Partly to compete with this process, investigators tend to use a higher speed of growth in order to be able to finish growing the entire crystal before the quartz tube becomes clouded, e.g., with volatile Ru-O. We find that such higher growth speeds compromise quality of the single crystal, inducing the precipitation of foreign microscopic phases within the host crystal. In Sr2RuO4 where we confirm the inclusion of mesoscopic Ru metal precipitates in crystals grown at higher speeds leading to a higher Tc. We shall report our studies of the formation of such phases. We confirm that slower growth rates help eliminate such inclusions. We have successfully used a cold trap and higher gas flow to flush and trap volatile particles away from the quartz tube, helping slow down growth rates. In cuprate oxides, we find that the use of a 'traveling solvent' is detrimental to the homogeneity of the crystal, and that the ability to maintain a stable zone from stoichiometric Bi2Sr2CaCu2Oy yields much higher homogeneity.

9:15 AM FF10.4
Dielectric Constant of Barium Titanate Synthesize by Containerless Processing. Jianding Yu, Paul-Francois Francois Paradis, Takehiko Ishikawa and Shinichi Yoda; Japan Aerospace Exploration Agency, Tsukuba, Japan.

Containerless processing is an attractive synthesis technique as it permits deep undercooling and provides a possibility to solidify the undercooled liquid into a selected phase to synthesize materials with novel properties. Spheroid BaTiO3 samples with a diameter ca. 2mm were solidified with containerless processing by electrostatic and aerodynamic levitation facilities. A single-crystal hexagonal BaTiO3 was grown at an undercooling of about 50 K and a polycrystalline perovskite BaTiO3 was crystallized at an undercooling of about 500 K. Dielectric constants of the single-crystal hexagonal BaTiO3 were affected significantly by oxygen deficient. A stoichiometric hexagonal BaTiO3 showed a permittivity of about 100 at room temperature, whereas the oxygen-deficient hexagonal BaTiO3 exhibited a giant permittivity higher than 100000 with a loss component tan? of about 0.1 at room temperature. The permittivity showed weak temperature dependence in the 70 K to 300 K range and a dramatic drop by 2 orders of magnitude below 70 K. The polycrystalline perovskite BaTiO3 showed a very coast dendrite microstructure and permittivity of 4000 at room temperature.

9:30 AM FF10.5
Charge and Coordination States of Iron Cations in (La,Me)FeO3-y (Me=Ca, Sr, Ba) Prepared by Mechanochemical Route. Lyubov Alexandrovna Isupova[1], Irina Srgeevna Yakovleva[1], Sergei Vasilievich Tsybulya[1], Alexander Chernysh[1], Alexei Rogov[1], Galina Litvak[1], Yurii Pavlyukhin[2] and Vladislav Sadykov[1]; [1]SB RAS, Boreskov Institute of Catalysis, Novosibirsk, Russian Federation; [2]SB RAS, Solid State Chemistry, Novosibirsk, Russian Federation.

La1-xCaxFeO3-y and La1-x(Sr/Ba)xFeO3-y perovskite systems are known to be characterised by different types of charge compensation required to maintain electroneutrality (namely, oxygen vacancies are generated in the former and Fe4+ cations in the latter systems) that may influence the oxygen bond strength. Preparation route (method, T, P, cooling conditions..) may influence the oxide defect structure as well. This studies aimed at elucidation of the effect of the type and content of dopant (Ca,Sr, Ba) on the coordination and charge states of the iron cation as well as on the formation of new oxygen forms in lanthanum ferrite prepared by mechanochemical route. Samples were prepared by preliminary mechanochemical activation in high planetary ball mill of mixture of initial oxides followed by calcination at 900-1100 oC, 4 h. X-ray, Moesbauer spectroscopy, TPR in H2 and TA were used for samples characterisation. According to X-ray analysis homogeneous solid solutions (with Orthorhombic and Cubic structures) were formed in the samples in the case of Sr and Ba substituted perovskites and two-phase samples (composed of LaFeO3 and Ca2Fe2O5) were revealed for all Ca substituted perovskites. Formation of Fe+4 cations in O coordinations was determined by Moessbauer investigation in Sr and Ba substituted perovskites. Formation of Fe+3 in P coordination is not excluded only for samples with x>0.6. No Fe+4 cation was detected in Ca-substituted perovskites, only Fe+3 cations in O1, O2, P and T coordinations were revealed. A formation of new low-bounded oxygen forms was detected by TPR in H2. Fe+4 content calculated from TPR data was higher than that obtained from Moessbauer data, that may be a result of formation not only Fe+4 or oxygen vacancy to maintain the elecroneutrality of substituted with Me perovskites, but of the low charge oxygen anion as well. Probably such low charge oxygen anions are formed during reoxidation of vacancy high-temperature solid solutions under cooling in the air.

9:45 AM FF10.6
Alkoxide Based Sol-Gel Processing of CMR Manganites. Annika Pohl and Gunnar Westin; Department of Materials Chemistry, Uppsala University, Uppsala, Sweden.

In the year 2000 we reported the first soluble manganese alkoxide $[Mn_{19}O_{12}(moe)_{14}(moeH)_{10}]\cdot moeH$. The successful preparation of this compound has opened up new possibilities for sol-gel processing of manganese containing ceramics. Sol-gel processing represent an inexpensive and fast route to industry scale thin film production, and contrary to pulsed laser deposition, sol-gel methods also offer the possibility of large area deposition. It is therefore of great interest to develop and study sol-gel routs to technologically interesting compounds. In sol-gel processing the advantage of alkoxide precursors compared to *e.g.* acetyl-acetonates, acetates or citric acid complexes, is that alkoxides yield more homogeneous and pure gels, thereby allowing for well-controlled low temperature conversion of the gel to oxide. We have used $[Mn_{19}O_{12}(moe)_{14}(moeH)_{10}]\cdot moeH$ in the first all-alkoxide synthesis of Ca, Sr and Ba substituted lanthanum manganites as powders and thin films. These oxides are known to exhibit colossal magneto resistance (CMR) and are of interest for *e.g.* spintronic devices. To gain detailed knowledge about the sol-gel processes the phase development form gel to target oxide was monitored by TGA, DSC, powder-XRD, FT-IR spectroscopy and TEM-EDS. Here we compare the effect of dopant on the phase development. It was found that the dopants influence the temperature of complete oxide formation ($\geq$650°C). The main differences in the phase evolution were seen in the 300-600°C range, where the formation of crystalline trace phases seemed to temporarily reduce the elemental homogeneity. The observed inhomogeneities were on a nanometer scale, and the homogeneity could be restored by just complete oxide formation, *i.e.* without long annealing times. The gels absorbed CO_2 from the air, but contained little or no organic residues and can therefore be described as hydrated oxo-carbonates. The phase development studies indicated that when starting from an amorphous precursor material such as a gel, there can be small amounts of amorphous carbonate impurities even above 600°C. This should be of importance also for other sol-gel and decomposition methods, as combustion of organic components can produce CO_2 that might be absorbed by the material to form unwanted phases -not always detectable by XRD. It is thus of great importance to ensure complete decomposition carbonates, which might otherwise affect the homogeneity and the properties of the material.

10:30 AM FF10.7
Crystal Chemistry and Physical Properties of 2:1 Ordered Perovskites. Michael Wayne Lufaso[1] and Anna Llobet Megias[2]; [1]Ceramics, National Institute of Standards and Technology, Gaithersburg, Maryland; [2]Lujan Neutron Scattering Center, Los Alamos National Laboratory, Los Alamos, New Mexico.

The perovskite structure class contains compounds which exhibit diverse physical properties and has lead to significant research on the crystal structures and correlation with the properties. For example, exceptional microwave dielectric properties are exhibited by the 2:1 ordered perovskites $Ba_3ZnTa_2O_9$ and $Ba_3MgTa_2O_9$. Substitution of Nb^{5+} for Ta^{5+} results in isostructural compositions with significantly different physical properties, including a higher dielectric constant, more positive temperature coefficient of resonant frequency, and a smaller Q×f value. A-site substitution of Sr for Ba has been shown to significantly change the dielectric properties, most significantly the temperature coefficient of the resonant frequency. The smaller A-site cation induces the onset of an octahedral tilting transition, which has also been reported as the origin of the change in physical properties. The onset of the octahedral tilting transition was investigated by refinement of the crystal structures by the Rietveld method from neutron powder diffraction data.

10:45 AM FF10.8
Oxygen Nonstoichiometry and Related Physical Properties of Various Functional Layered Oxides. Jun-ichi Shimoyama[1,2], Yuui Yokota[1], Masahiro Shiraki[1], Yuhki Sugiura[1], Shigeru Horii[1] and Kohji Kishio[1]; [1]Department of Superconductivity, University of Tokyo, Tokyo, Japan; [2]PRESTO-JST, Kawaguchi, Japan.

In the past two decades, particularly after discovery high-Tc superconductivity in layered cuprates in 1986, various layered oxides have been eagerly developed for new functional materials, such as superconductors, colossal magnetoresistance devices, ferroelectric materials, thermoelectric materials etc. All these functional layered materials are consisted of transition metal oxide layer showing characteristic physical properties and blocking layers which control valence state of the transition metal ions. Therefore, these layered materials include several metal elements and have several cation and anion sites. It is well known that oxygen nonstoichiometry plays crucial role to determine physical properties of transition metal oxides, however, there are few information on the oxygen content as functions of temperature and partial pressure of oxygen for these newly developed layered oxides. Based on the background, nonstoichiometric oxygen phase diagram of various functional layered oxide were precisely investigated and their physical properties were systematically evaluated as a function of oxygen content in the present study. Thermogravimetric measurements were performed using electro-microbalances (CAHN-1000H and SHIMADZU TGA-41S) for sintered bulk samples of various transition metal oxides having layered crystal structures. For a famous CMR material (La,Sr)3Mn2Oy, very small oxygen nonstoichiometry with a y range of 6.980 7.016 was observed. However, both excess oxygen and oxygen deficiency were found to strongly affect the CMR properties. Samples with stoichiometric oxygen composition, y = 7.00, obtained by rapid quenching from 1273K in air, exhibited the sharpest ferromagnetic transition. On the other hand, ferromagnetic transition disappeared in slightly oxygen deficient sample with y = 6.99. In the case of Co-based oxides showing excellent thermoelectric properties up to high temperatures, the CoO2 layer was confirmed to be quite robust in terms of oxygen nonstoichiometry, while the blocking layer shows large change in oxygen content when it contains transition metals, for example, (Ca2CoO3-d)0.62CoO2 with d = 0 0.14. In this compound, thermoelectric properties are degraded by generation of oxygen vacancies at high temperatures above 800K, however, substitution of high valence metals for Ca or Co sites in the blocking layer was discovered to be quite effective for suppression of oxygen nonstoichiometry up to high temperatures, resulting in record-high thermoelectric performance. Similar important results on the oxygen nonstoichiometry and related physical properties of other layered functional oxides will be reported.

11:00 AM FF10.9
Effect of Impressing Rate of Field on Polarization Reversal in Mg Doped Near Stoichiometric Lithium Tantalate Single Crystals. Sarveswaran Ganesamoorthy, Nakamura Masaru, Takekawa Shunji, Somu Kumaragurubaran, Terabe Kazuya and Kitamura Kenji; Opto Single Crystal Group, Advanced Materials Laboratory, National Institute for Materials Science (NIMS), Tsukuba, Japan.

Lithium tantalate (LT) is an important single crystal oxide material in surface acoustic wave, electro-optic and wavequide optical applications. Since the domain inversion field for the congruently melting LT crystal is high (21 kV/mm), it is quite difficult to obtain periodically poled LT (PPLT) structures thicker than 1 mm. The near Stoichiometric LT (SLT) crystals grown from a Li-rich melt by a

double crucible method are showing improved performances as the domain inversion fields has decreased remarkably (1.7 kV/mm). The low coercive field (Ec) value permits PPLT devices thicker than 3mm, which will increase the transverse area for transmission light so that the output power can be increased greatly. However, the domain switching behaviour of SLT crystals is not completely understood. Data on the rate of applied field dependence of Ec in a rate range as wide as possible would be valuable in understanding the mechanism of polarization reversal. Hence in this study, we report the ramp rate dependence of Ec in pure and Mg doped SLT crystals. Hysteresis loop measurements were done using triangular wave with liquid electrolyte. The advantage of the triangular fields instead of sinusoidal ones is that ramp rate is constant during the trace of the loops. Hysteresis studies performed revealed low coercive field value of 0.5 kV/mm in Mg(1mol%)SLT, while pure SLT has 1.7 kV/mm. A small built in internal field is found to exist, which is formed after polarization reversal from the asymmetry of the ferroelectric hysteresis loops. The internal field is considerably reduced in Mg doped SLT. In the case of SLT and Mg(0.5 mol%)SLT there is not much variation in the coercive field value with ramp rate, while Mg(1mol%)SLT shows a strong dependence on the impressing rate of the field. Even at a low frequency of 0.005 Hz coercive field was not found to saturate in case of 1 mol% Mg doped samples. For ramp rates upto 500 V/s there is almost a linear rise in the coercive field value in Mg1SLT samples. Transient current peaks were found to be sharp for pure samples in comparison to Mg:SLT samples. Coercive field get lowered with increased thickness of the sample. A strong correlation is found to exist between Ec value and the Curie temperature, i.e., Ec decreases for samples having higher Curie temperature. SLT crystals grown from Li-rich melt (59 mol%) exhibits a Curie temperature of 685 C, while Mg1SLT has a Curie temperature of 696 C. Dependence of the applied voltage on sample thickness, domain pinning mechanism and switching kinetics and the effect of Mg addition on internal field are explained on the basis of nonstoichiometry in the samples.

11:15 AM FF10.10
Sintering and Electromechanical Behavior of Ba-Zr Codoped Sodium Bismuth Titanate by Wet Chemical Route.
Andrey Soukhojak and Animesh Kundu; Materials Sci & Eng, Lehigh University, Bethlehem, Pennsylvania.

Sodium bismuth titanate (NBT) based ceramics has been shown to be a promising alternative for lead-free piezoelectrics and high capacitance materials. Depending on dopants and dopant level, the properties of NBT can be engineered to predominantly electrostrictive to predominantly ferroelectric. Barium-zirconium co-doped NBT (BNBZT) exhibits very promising electromechanical properties. Predominantly electrostrictive composition in the BNBZT system exhibiting a piezoelectric coefficient d33 approx. 780 pC/N has been reported. Predominantly ferroelectric polycrystalline BNBZT compositions exhibit d33 of 310 pC/N, which makes them competitive with lead zirconate titanate (PZT) ceramics. To date, only conventional solid-state synthesis route has been predominantly used for the preparation of polycrystalline doped NBT. It is well known that this method cannot produce highly homogeneous solid solutions in realistic time due to a long diffusion path. Moreover, the volatilization of bismuth and sodium during high temperature processing can be detrimental to the properties due to non-stoichiometry. The main advantages of solution chemistry approach are (1) the atomic level mixing to produce highly homogeneous powders and (2) low temperature synthesis giving precise control over the composition without significant volatilization losses. We explore the possibility of the preparation of BNBZT by wet chemical route that can be sintered at lower temperatures. A "citrate-gel" technique has been used to prepare the powders. A mixed solution containing the desired ingredients was prepared and allowed to slowly evaporate to get a clear viscous gel. The viscous gel was dried and subsequently calcined to produce the desired NBT composition. The present investigation presents the phase composition and microstructure of the calcined and finally sintered materials, the densification behavior of the calcined materials and the electromechanical behavior of the sintered pellets.

11:30 AM FF10.11
Prediction and Investigation of $PbTiO_3$ based Morphotropic Phase Boundary Systems. Matthew R. Suchomel and Peter K. Davies; Department of Materials Science and Engineering, Univ. of Pennsylvania, Philadelphia, Pennsylvania.

Ceramics based on compositions near the morphotropic phase boundary (MPB) in perovskite $PbTiO_3$ solid solution systems dominate the market of ferroelectric and piezoelectric materials due to their superior response at those compositions. Many $PbTiO_3$ solid solutions containing an MPB have been reported, both in simple (x)$PbTiO_3$ - (1-x)$PbM'O_3$-type (e.g. $PbZr_{1-x}Ti_xO_3$), complex (x)$PbTiO_3$ - (1-x)$Pb(M'M'')O_3$-type, and more recently (x)$PbTiO_3$ - (1-x)$BiM'O_3$ - type systems. Although many systems are known, no relationships exist to pre-predict the composition of the solid solution at the MPB. In this paper a new qualitative correlation is presented which relates the Goldschmidt tolerance factor of the end members to the compositional position of the MPB in $PbTiO_3$ based solid solution systems. This relationship is then successfully used to predict the location of the MPB in new examples of (x) $PbTiO_3$ - (1-x) $Bi(M'M'')O_3$ type systems (M' = Ni^{2+}, Mg^{2+}, Zn^{2+} and M" = Ti^{4+}, Sn^{4+}, Zr^{4+}, Ce^{4+}). The structural properties, including a discussion of perovskite stability and competing impurities, as well as dielectric and piezoelectric properties are reported. This relationship is also used as a guide to identify other new $PbTiO_3$ based MPB systems, and unreported end members for $PbTiO_3$ solid solutions, in particular systems with low tolerance factors based on mixed A-site chemistries such as $(Pb_{1/2}Th_{1/2})M^{3+}O_3$, are also explored.

11:45 AM FF10.12
$Ba_2Ti_5O_{12}$ – A Ternary Compound in Disguise: Crystal Chemistry and Properties of $Ba_{11}FeTi_{27}O_{66.5}$.
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Early phase equilibrium studies of the binary BaO-TiO_2 system revealed the existence of the so-called barium polytitanate phases that form between $BaTiO_3$ and TiO_2. Some of these phases exhibited electrical properties that resulted in their ensuing commercial importance as ceramic dielectric resonators for the earliest cellular base stations. The compound $Ba_2Ti_5O_{12}$ was first reported in 1958; however, several subsequent studies of the BaO-TiO_2 system failed to confirm its formation. Eventually, it was realized that a third component (sometimes unintentionally added) is required to stabilize this crystal structure. A detailed description of the structure and properties of this phase formed by the addition of Fe_2O_3 will be presented.