SYMPOSIUM FF
Solid-State Chemistry of Inorganic Materials V

November 29 - December 2, 2004

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* Invited paper
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 amenable to 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 damage 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. 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 alkaline and alkaline earth 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 and its growth is preferable. We will present full details of our 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.

SESSION FF1: Synthesis of Novel Materials
Chairs: Nathaniel Brese and Cora Lind
Monday Morning, 8:30 AM - 12:00 PM
Room 200 (Hynes)

8:30 AM *FF1.1
Hydrothermal Synthesis of Alkali and Alkaline Earth Borates for Deep UV Optical Applications by Joseph William Rolls, Colin McMullen, and Tana Francou. The solvothermal chemistry of metal fluorides is in its infancy, in contrast to the corresponding vast metal halides. More recently, the groups of Hare, Albrecht-Schmitt and Weller have developed the corresponding extended-connectivity lattices produced, and no 3-D connected metal fluorides have been discovered. We have extended this work by exploring, inter alia, scandium and yttrium borates. They have very wide bandgaps and exceptionally high damage 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. Amphoteric 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 alkaline and alkaline earth 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 and its growth is preferable. We will present full details of our 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, University of St Andrews, St Andrews, United Kingdom.

The solvothermal chemistry of metal fluorides is relatively unexplored. In particular, the development of organically-templated metal fluoride chemistry is in its infancy, in contrast to the corresponding vast metal halide chemistry. We have extended this work to 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 structures. More recently, the groups of O'Hare, Albrecht-Schmitt and Weller have developed the corresponding uranium, zirconium and beryllium fluoride 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 Steenou, Thibaud Coradin, Jocelyne Maquet and Jacques Livage, Chimie de la Matiere Condensee, University Paris 6, 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 act as structure-directing agents through cooperative interactions within the organic 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 V2O5.nH2O gel whose structure and properties were extensively studied. At first, we typically used some chlorine compounds (ClO4-, ClO3-, ClO2-) in a concentrated solution to generate the cations of the organo-vanadyl complexes. This approach was extended to organic (amines, carboxylic acids) and biorganic molecules (dipeptides, gelatin) that may complex and reduce vanadium. The vanadium oxides incorporating organic molecules were characterized by X-ray diffraction, Transmission electron microscopy and 51V solid-state NMR. In addition, identification of the molecular precursors by 27Al NMR spectroscopy in solution allows us to suggest some chemical mechanisms describing the formation of the different vanadium oxide nanorods at room temperature and below pH 7. These mechanisms are of interest in order 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 Ying Hung, 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 size-dependent 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 auxiliary surface ligand, the material aggregates to the bulk size. An attractive alternative to this approach is the use of surfactants such as cationic and anionic molecular species key 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 offers 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 semiconductor nanomaterials, but expansion of this approach to ternary MME [E = Si, Ge, Sn] nanomaterials remains relatively unexplored. Our approach to the synthesis of MME materials [M, M' = Zn, Cd, Hg; E = Si, Ge, Sn] 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(SiMe3)2 yields silylated zinc-chalcogenolate moieties within MCM-41. The pendant trimethylsilyl groups can readily react with a second solubilized metal acetate [M(OC2H5)2, M = Cd, Hg] whereby there is generation and elimination of ACO3SiMe3 and the formation of Zn-Ge-S 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 MME materials are characterized by PXRD, nitrogen adsorption TGA, CP MAS NMR, 13C, 29Si, 113Cd, IR and Raman spectroscopies, UV-Vis spectroscopy and TEM and EDX analyses.

9:45 AM FF1.5
Silicon cluster formation in mesoporous silica obtained by the Sol-Gel method. Lidia Arnedo1, Gregorio Bottaro2, Renzo Campostrini2, Stefano Gialanella2, Marco Inciso2, Fabrizia Poli3, Cinzia Sada4 and Eugenio Tondello5, 1Chemistry, CNR-ISTM-University of Padova, Padova, Italy; 2Materials Engineering, University, Trento, Italy; 3Chemistry, University, Padova, Italy; 4Physics, University, Padova, Italy.

In recent years, mesoporous 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 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 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 and controllable arrangement of pores have gained increasing interest, owing to their potential applications in catalysis and optical devices.
X-ray Photoelectron Spectroscopy (XPS). Moreover, the optical properties of the nanocomposite materials were studied by means of UV-Visible spectroscopy. This study was performed with the aim to obtain information on both particle size and particle location in the ordered mesoporous matrix. Relevant results concerning the interactions 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 Nanocrystalline Metal Borides, Richard B. Kaner1,2, Robert Cumberland1, Michelle Weinberger1, Sarah Tolbert1, John Gilman2 and Simon Clark2; 1Chemistry & Biochemistry, University of California, Los Angeles, Los Angeles, California; 2Materials Science & Engineering, University of California, Los Angeles, Los Angeles, California; 3Lawrence 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-Murnaghan 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, 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. Pawlak1, Jacki Sierakowiak2, Shane R. Groven2, and Robert 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 composites. This method is very suitable for the formation of nonstoichiometric compounds, solid solutions, and refractory composites. Many reaction 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 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 of the same composition. 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 temperature 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: 1) submicron size of starting powders and 2) low sintering temperature. It was already demonstrated that many metals or ceramic powders may sinter at nanometers. In this research, two nanoreactant energetic systems, TiO2-Al2O3 and Al-Ni-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 pressure 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 aluminate composite 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 initial composition, average particle size of reactants and diluent, temperature-pressure history, and densification force on combustion synthesized product microstructure and its residual porosity.

11:15 AM **FF1.8**

The new organodecaborane polymer, poly(norborenyldecacarbaborane) (PND), was readily prepared via the ruthenium catalyzed ring opening metathesis polymerization (ROMP) of n-boronyldecacarbaborane. The polymer was isolated as an air-stable white powder with a molecular weight in excess of 32 K. 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 100°C and is essentially complete by 500°C, 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 1300°C, while crystalline materials were obtained at higher temperatures. Polymer blends of allylhydridopolycarbosilane (AHCPS)/PND and polynvinilsiloxane (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, Sanjay Mathur1,2, Jared V. R. Palkar1; 1Dept. of Mechanical Engineering, Mahalingam College of Engineering and Technology, Pollachi, Tamil Nadu, India; 2Condensed Matter Physics, Materials Science Group, Tata Institute of Fundamental Research, Mumbai, Maharashtra, India.

High purity alumina is usually prepared using various intermediate aluminum compounds such as aluminum nitrate, aluminum 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 aluminum compounds themselves are produced from aluminum metal. The present investigation is concerned with examining the feasibility of using aluminum hydroxides prepared by hydrolyzing aluminum 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 aluminum metal in large quantities economically. During the present investigation sols were prepared by using various hydroxides, i.e., 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 by controlled gelation method but the presence of a thin layer of bayerite often resulted in translucency. Crack free Xerogels could be prepared by changing the drying conditions ( Xerogel 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 Nanostructured Materials, Sanjay Mathur1, 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 the extensive research in the synthesis 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 chemist—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-property relationships. The transformation of molecular compounds (precursors) or gaseous 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
molecular-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 considering the experimental facts. 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 FP2: Non-oxide Systems

Chair: Mercouri Kanatzidis and Glen Kovach
Monday Afternoon, November 29, 2004
Room 200 (Hynes)

1:30 PM *FP2.1
Synthetic Approaches, Structure Properties Correlations, and Applications of Novel Advanced Nitride 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, Si3N4, or P3N3 exhibit promising properties for the development of novel high-performance materials [1]. In combination with further electronegative elements, ternary and multinary compounds with a wide range of condensation degrees are accessible. For the nitridosilicates [2] anionic substructures of SiN4 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 SiN4 units. From a synthetic pathway are carefully controlled. Hence reports to date of stable, useful emulsion is produced, unless both environment and sols produced by the ammonolysis of silicon amides. With transition metals, the ammono based analogue of the well established alkoxy chemistry is the most developed part of the field 1-3 and we report experiment. Therefore, we are developing chemical concepts for a customized assembly of molecular building blocks with further electronegative elements and the expectation would be that others, e.g. Ti3N4 should be accessible. In fact many of these phases 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 develop precursors to 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(NMe2)4 in solution decomposes to amorphous Ti3N4 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 transformation to TiN, in which the transition metal nitrides to produce the potential to be used in sol-gel processing of metal nitrides. We will also present work on the characterisation of amorphous Ti3N4, using a combination of XPS, EXAFS, IR/Raman spectroscopy and thermogravimetric analysis. The structure is basically a defect form of Rocks salt 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. 


2:00 PM FP2.2
Sol-Gel Deposition of Transition Metal and Silicon Nitride Films. Andrew William Jackson and Andrew Lee Hector, School of Chemistry, University of Southampton, Southampton, 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 Silicon nitride is a popular insulator and encapsulating material in electronics and also useful as a low density ceramic. 6 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 4 and we report the deposition of silicon nitride films by dip-coating, using coating compositions of silicon amides. With transition metals, the ammono based analogue of the well established alkoy route to oxide precursor gels is inherently difficult to control. The basicity of the system and the overwhelming tendency of the starting materials to favor the growth of silicon metal 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. 5 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 thin coatings, multilayer structures, and film deposition onto complex 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. Kuikel, K. Schlicke and B. Zherebko, 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. Helle, P. E. Schmid, R. Bedau and Mi. Wiener, Surf. Coat. Tech. 120 201 284 (1999). 5. P. Baldus, M. Jansen and D. Sporn, Energiek., 285 699 (1999). 6. C. W. Winter, Aldrichchem. Acta 33 5 (2000). 7. U. Schubert and N. Hoering, Spectroscopy/InorganicMaterial, Wiley-VCH, Weinheim 2000. 8. G. M. Brown, L. Maya, J. Am. Ceram. Soc. 71 78 (1988). 8. B. V. Baxter, M. H. Chisholm, V. F. DiStasi, G. J. Gama, A. L. Hector and I. P. Parkin, Chem. Mater. 8 1222 (1996).
interrelated characteristics distinguish these phases from other layered materials: i) the metallic-like nature of the bonding; ii) basal slip, and only basal slip down to 200 K; and iii) the deformation 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-free deformation. We showed that polycrystalline Ti35Sc2 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 bands 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 nonoxidize grains of Ti5Sc2 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 incipient delaminated materials will be described in detail at a later date.

The crystal chemistry and electronic and ionic transport properties of the members of the homologous series Sr2Mn02Cu2n_oSn+l, with n = 1-3, are copper deficient A4Mn30B_xCU2E2 (A = Sr, Ba; E = S, Se) which contain a Co oxidation state of around +2.15. The nature of the large gap and glass formation property. When we attempted to make TI2SnSb2Se6, we made a new compound TI8Sn10Sb16Se48, which is antiferromagnetic 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 incipient delaminated materials will be described in detail at a later date.

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 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 Sr3Sb ions in Sr3Sb, which is a perovskite 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.
The temperature range from 5 to 3000 K. Both EuCuSF and EuCuFSe showed paramagnetic behaviors.

4:45 PM FF2A.10 New Magnetic Zintl Phases in the Eu-In-P System. 
Jiang', Marilyn A., and Z.A.
A.
The structural growth from the melt in the optical floating zone furnace at constant oxygen partial pressure is an open framework with orthorhombic space group with a = 12.6517(15) Å, b = 4.2683(5) Å, c = 13.5639(14) Å, and Z = 4 while EuIn3P3 belongs to Pnma with a = 6.0659(4) Å, b = 16.1016(13) Å, c = 4.2726(4) Å, and Z = 2. These two isostructural compounds EuIn3P3 and SrIn3P3 are both semiconductors.

In this poster, we present results from the successful growth of a large single crystal of hematite of this three-dimensional size and purity has been synthesized at oxygen pressures of less than 35 atmospheres. 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 were metal oxide octahedra 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 titanophosphates that can be divided into three types. The first type consists of phases obtained by substitution of CuO4 squares for the separated TiO5 pyramids of Eu3In2P4. Phase 1 has the space group symmetry C2/m with a = 14.352 Å, b = 13.954 Å, 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 TiO5 pyramids are randomly replaced by CuO4 squares. Phase 2 has the space group symmetry Ccmm with a = 46.402 Å, b = 14.419 Å, c = 13.970 Å. Structural refinements indicate that 2 also has the ETS-4 structure but all the TiO5 pyramids are replaced by CuO4 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 Na2Cu3Ti5Si13O40 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 TiO4 octahedra which are partially substituted by CuO5 pyramids in 3. Phase 4 with the composition K4Cu2Ti6Si13O40 contains separated CuO4 squares and TiO5 tetrahedral pyramids that crosslink a type of silicate double layers to form an open framework. 1. S. M. Kuznicki et al., Nature, 412 (2001) 729-724; US Patent 6289039, 1990. 2. W. Wang, L. Liu, A. J. Jacobson: Angew. Chem. Int. Ed., 42 (2003) 2044-2047.

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


In this poster, we present results from the successful growth of a large single crystal of α-Fe2O3 using a hemicaclic ferrite (CaFe4O7)-based solvent in the optical floating zone furnace in the traveling solvent zone configuration. The as-grown crystal measures 33 mm long by 5 mm 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 of the growing crystal) pressures approaching 35 atm are needed. Considering this observation, and the fact that the furnace as thermally decomposing an incongruently melting material to grow a magnetite at the temperatures and pressures used in single crystal melt and solidify hematite directly, and avoid the magnetite+hematite partitioning step. Barium strontium titanate (Ba0.7Sr0.3TiO3, BST) ceramics prepared by a reaction-sintering process were investigated. The mixture of raw materials of stoichiometric Ba0.7Sr0.3Ti03 was pressed and sintered into ceramics without any calcination stage conducted. Perovskite BST ceramics were obtained after sintered at 1300-1370°C for 2-6 h. For 6 h sintering at 1350°C, density value 5.08 g/cm3 (99.8% of the theoretical value) was obtained. A diffused ferroelectric-paraelectric transition was observed in Ba0.7Sr0.3TiO3 ceramics sintered at 1300°C for 2 h and disappeared at a longer soak time or a higher sintering temperature.

FF3A.2 Preparation of (Pb,Ca)(Fe0.5Nb0.5)O3-δ and Y2TiO5 Perovskite Ceramics by a Reaction-Sintering Process. Yi-Cheng Liu, Jen-Hsien Chen and Chao-Yang Shiu; Department of Electronic Engineering, Kun-Shan University of Technology, Tainan, Taiwan.

Preparation of NiNb2O6 Columbite Ceramics by a Reaction-Sintering Process. Yi-Cheng Liu, Jen-Hsien Chen and Hsu-Hung Lu; Department of Electronic Engineering, Kun-Shan University of Technology, Tainan, Taiwan.

Preparation of NiNb2O6 Columbite Ceramics by a Reaction-Sintering Process. Yi-Cheng Liu, Jen-Hsien Chen and Hsu-Hung Lu; Department of Electronic Engineering, Kun-Shan University of Technology, Tainan, 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(100)-50%NiO (NN1) after sintered at 1250-1450°C for 2 h and 4 h. In pellets using NiO (NN2), Columbite NiNb2O6 ceramics were obtained after sintered at 1150-1350°C for 2 h and 4 h. A density of 4.7 g/cm3 was obtained in NN1 for 2 h sintering at 1400°C. For NN2, a higher density 5.62 g/cm3 (99.8% of the theoretical value) was obtained for 2 h sintering at 1300°C. The
A new ternary compound, CePdGa10, has been synthesized using Ga flux and characterized by single-crystal X-ray diffraction. CePdGa10 adopts a tetragonal structure in the $I4/mmm$ space group and is isomorphous to CeNiGa10. Lattice parameters are $a = 4.3230(3)$ Å and $c = 25.536(3)$ Å, $V = 455.91(7)$ Å$^3$ and $Z = 2$. The compound is metallic ($\rho_{300K} > 0$)$^1$ with the resistance decreasing roughly linearly with temperature from 300 K down to 17 K. The magnetic susceptibility of CePdGa10 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 CePdGa10 and compare them to a structurally related ternary compound, CePdGa6.

**F3.8**
Preparation of Textured Bismuth Titanate Ceramics by Templated Grain Growth Method Application for Spark Plasma Sintering Method, Keishi Nishiyama$^1$, Renn Maeda$^1$, Ysuo Kogo$^1$, Toshio Kenjirou$^1$, and Atsuo Yasumori$^1$, 1Chemistry, Ehime University, Matsuyama, Ehime, Japan.

Textured bismuth titanate ($Bi_2Ti_3O_7$) is the simplest and best-known compound among the bismuth-layer-structure ferroelectrics and is interesting because of its peculiar switching behavior resulting from a small-caxis component of the spontaneous polarization and a small coercive force. $Bi_2Ti_3O_7$ ceramics were prepared by templated grain growth (TGG) method combined with spark plasma sintering (SPS) method. TGG method has been developed to provide a simpler 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 $Bi_2Ti_3O_7$ was synthesized from precursor powder by flux method using Na2O and KCl. The obtained plitelet $Bi_2Ti_3O_7$ has high aspect ratio. The ceramics was prepared by treatment using SPS the mixture of the plitelet $TiO_2$ and amorphous precursor powder. As a result, the obtained 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 $Bi_2Ti_3O_7$ ceramics could be obtained. The ceramics shows high orientation, above 40%, for c-axis direction and high density above 80%.

**F3.9**
Preferential Crystallization of $\beta$-FeSi2 from Micro-droplets

Generation of molten micro-droplets is a peculiar feature of laser ablation of solid targets. The droplets have been used as an important 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 deposited species such as atoms, molecules and ions. On the other hand, $\beta$-FeSi2 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 $\beta$-FeSi2 bulk materials was generally required high temperature multi-processes such as film deposition at $\geq 450 ^\circ C$ and following post-annealing at $\geq 800 ^\circ C$ from several hours up to a few days. Moreover, it is difficult to prepare $\beta$-FeSi2 bulk materials since the semiconducting beta-phase undergoes the phase transformation to a high-temperature equilibrium metallic alpha phase above 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 $\beta$-FeSi2 microcrystallization from the active use of droplets. Based on micro-Raman spectra, it was confirmed that the molten droplets crystallized preferentially as the low temperature equilibrium $\beta$-FeSi2, 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 flow 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 the beta phase, not the equilibrium alpha phase. Consequently, this technique is effective for preparing crystalline materials at room temperature as well as preferential crystal growth of low-temperature equilibrium $\beta$-FeSi2.
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 Chabot**, Xavier Becquelin1, David Le Bihan1, Thuy-Huan Whangbo2 and Stephanie Johic1.

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Phosphorescent materials are semiconducting or insulating phosphors, containing in their forbidden band some discrete levels associated with chemical (donpats) and/or for physical imperfections (vacancies, interstitials) 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 phenomena. 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 (de-trapping energy) is not provided to the system. If this energy is thermal energy at ambient temperature, one speaks about phosphorescence. If it is provided gradually, the trapped charge carriers, followed by a damped light emission due to a radiative recombination. A few years ago, the discovery of very efficient phosphorescent materials (SrAl2O4:Eu2+,Dy3+, C3A2Al2O4:Eu2+ + Na2+, Y2O2Si:Eu2+, 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 discussed, is not properly described in chemical terms and, to some aspects, the trapping and de-trapping 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 many seconds) phosphor is still not properly understood. 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**, Joshua Pelleg1, Misha Sinder1, Roni Schneck1 and Vladimir Sokolovsky2.

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The discovery of the new superconductor MgB2 with critical temperature of Tc = 39 K stimulated great activity in search for materials with higher Tc. Theoretical works [2-4] 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 A2B12 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 [5]. 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 microscopy investigations 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 H. Min, cond-mat/0106631 (2001) [2] I. H. 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 Ba4Al12Si30, Peter Klivins2, Cathie Condon1 and Susan Kuzulich1.**

1Chemistry, UC Davis, Davis, California; 2Physics, UC Davis, California.

Single crystals of Ba4Al12Si30 were prepared utilizing the molten flux growth method. Single crystal x-ray diffraction studies confirm that Ba4Al12Si30 adopts the clathrate (I) structure type, space group Pn = 3m, with a = 16.6079(12) Å and Z = 1. The polyedral structure is built of S12 pentagonal dodecahedra occupied by six Ba (2e) atoms, and S12 tetrahedra occupied by two Ba (6d) atoms. The Ba atoms at the S12 vertices 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, microanalysis and solid state NMR studies have been performed, as well as temperature dependent susceptibility and conductivity measurements. The structure and properties of Ba4Al12Si30 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**, Takashi Yokota2, Nagashiro Saito3, Yasuaki Inoue1 and Osamu Takeda1.

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Carbon nitride has attracted great interest 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 as 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 alternating magnetic field. We can change the radial and axial magnetic field mode from plasma excited 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 Langmuir probe. Plasma components are investigated by using the optical emission spectroscopy. The carbon nitride films are investigated 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 Dichacarboxylate Coordination Structures.**

**Long Pan1, Nancy Ching2, Xiongming Huang3, Jing Li, Tan Yien2 and C.L. Liu3.**

1Department of Chemistry and Chemical Biology, Rutgers University, Piscataway, New Jersey; 2Department of Physics, Temple University, Philadelphia, Pennsylvania.

Incorporation of multidentate dichacarboxylic 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 ligand 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. Solvothermal reactions of 4,4-dihydroxydiphenylic acid (H2dpdc) 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 structure while longer 4-benzylpyridine (4-Bzp) 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 Thompson 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. The ability to rapidly assess the properties of large numbers of discrete compounds prepared using small quantities of reagents makes these techniques attractive for both industrial and academic research. Much of the literature focuses on the preparation of thin film arrays by vapour deposition. 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.\textsuperscript{2,3} We report the development of high throughput techniques, which use 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. Lithium titanates prepared on alumina tiles, using a solution combustion method, were characterised by X-ray diffraction and revealed the formation of Li$_2$Ti$_2$O$_5$ and Li$_2$Ti$_2$O$_7$. These two structure types vary in the layer stacking sequence and are related to two-ferro and two antiferromagnetic interactions, all with identical magnetic structures since the B site in one layer is above the centre of a square of the B site in the next layer. We demonstrate that this is due to a magnetic structure in the layer stacking sequence and that it is possible to control this by adjusting the growth conditions. The paper will describe how we have applied these methods to oxide systems and how this has led to new optical properties with film composition and bonding has been investigated. The importance of silicon oxynitride (SiO$_x$Ny) material for optoelectronic device applications is ever increasing owing to its tunable refractive index. In this research, the influence of deposition parameters on optical properties of SiO$_x$Ny films deposited by PECVD technique were investigated. These properties include optical band gap, transmittance, absorbance and refractive index. The optical band gap of the films was determined from transmittance spectra using the Tauc plot. The absorption coefficients of the films were determined by the linear relation between $\alpha$ and $\lambda^{-1}$. The refractive index was calculated using the spectroscopic ellipsometry. The optical band gap of the films was found to be in the range of 3.2-3.5 eV, which is suitable for use in solar cells. The transmittance of the films was found to be in the range of 75-90%, which is suitable for use in optoelectronic devices. The refractive index of the films was found to be in the range of 1.9-2.1, which is suitable for use in optical devices.
silane (SiH4) and nitrous oxide (N2O) as precursor gases. To investigate the influence of deposition conditions on film properties, a three-dimensional 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 400°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 build-up was determined using X-ray techniques. For materials characterization, 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. Parshat Ahmad1, Shinjiro Yagyu1, Michiko Yoshitake1 and Toyohiro Chikyow2,3. 1National Institute for Materials Science, Tsukuba, Japan; 2CREST-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 materials in a single deposition. We have developed a deposition system to rapidly 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. Jinchun Xie1,2,3, Jia-Wei Zhang1,2,3. 1School of Materials Science and Engineering, Tsinghua University, Beijing, China; 2State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, The Key Laboratory of Material Processing and Manufacture, Ministry of Education, College of Material Science, Jilin University, Changchun, Jilin, China; 3Jilin University, Changchun, Jilin, China.

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 substrate process which has repeatedly heat-treatment at temperature range 450 600°C requires that the glass substrate have 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-H2O(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 TiO2-SiO2 Mixed Oxide. Juang Chien Peng1,2,3, Chia-Ling Hsu1,2, Chien-Hua Wu1,2,3, Chia-Chin Hsu1,2,3. 1Chemical Science and Engineering, National Taiwan University, Taipei, Taiwan; 2Institute of Materials Science, National Taiwan University, Taipei, Taiwan; 3Graduate Institute of Materials Science and Engineering, National Taiwan University, Taipei, Taiwan.

A study on the comparison of porous TiO2-SiO2 mixed oxide synthesized via an amine directed method is reported. The amine capping groups used are octylamine, dodecylamine, decyldimethyl, 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 analyses give the surface area. Because the electronic contribution is needed for the photocatalysis, the chemical bonding of both oxides. The BET results suggested that high surface area can be obtained by the mixed oxide prepared in this manner.


Ti3SiC2 is the most studied ternary of the MAX phase family of compounds (viz. MAxAXn, 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 Ti3SiC2 compounds in various fields are currently 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 Ti3SiC2 considerably improving purity when starting with 2Ti/3Si/3TiC powders. However, the processing window remained narrow and most importantly, the sintering temperature was still high. In order to enhance both, the effect of adding a ternary element, Al, was considered. To that effect, compositions of Ti1-xSic-xC-C-xAl powders with mole fractions of x ranging from 0 to 0.2 were mixed and sintered with PDS, at temperatures ranging from 1200°C to 1500°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 Ti3SiC2 content was 85 vol. %, with TiC as the main phase secondary. With increasing x content the Ti3SiC2 content increased to a maximum of 90% at x=0.15; at x=0.2, the Ti3SiC2 content was reduced slightly. Furthermore, at x=0.15 single-phase samples of Ti3SiC2 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 LaFe4Sb12. Kazimierz J. Plucinski1,2, K. Nouneh3,4, R. Viennois3,5,6, Ivan V. Kityk2,4, F. Terki5, S. Charra5, S. Beast3, J. Eboth5, D. Rovot5 and J. C. Tedana5,6. 1Electronics, University of Military Technology, Warsaw, Poland; 2Inst. of Physics, Ped. University, Czestochowa, Poland; 3Univ. Montpellier, Montpellier; 4Univ. d'Perpignan, Perpignan, France; 5Univ. de Reims, Reims, France; 6Max-Planck Institut, Dresden, Germany.

Thermoelectric materials have recently attracted a considerable amount of interest. Among these, a new group called “filled” skutterudite compounds of unit-formula RMX12 (where R is the rare-earth or alkaline-earth or actinide element; M = Fe, Ru or Os; X = P, As or Sb) should be a subject of high interest because of their extremely large figure of merit Z = (S2 a / k), that is the main requirement for thermoelectric applications. S is the Seebeck coefficient, a the electrical conductivity and k is 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 of Z = (S2 a / k), it is necessary to enhance the power-factor S2 a and to reduce the phonon thermal conductivity. The study of electron-phonon anharmonic interactions existing in these compounds will be useful in reducing the thermal conductivity. In the present paper, the PISHG is used as a main tool for studying very weak electron-phonon anharmonic interactions enhanced by low-temperature ordering including spin alignment. A correlation between the temperature dependence of the resistivity, Seebeck coefficient and photinduced second harmonic generation (PISHG) were found in a specific skutterudite compound, LaFe4Sb12. 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. At the same temperature, a non-Fourier type heat transport behaviour developed in the resistivity. Pump-probe time dependence of the LaFe4Sb12, 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 magnetic interactions, whilst maintaining the insulating and high resistive 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**

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The layered transition metal hydroxide based compound $\text{Co}_2(\text{OH})_x\text{A}_y(\text{A}^{2-})_z\text{H}_2\text{O}$ 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 by biological means 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 $\mu$m thick at a water/air interface. The resulting material was characterized by TOF-mass spectrometry, XRD, UPS, 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 photovoltaic has been observed upon radiation along with the generation of a small photovoltaic. The effects of synthesis surface tension on the morphological and electrooptical 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$^3$ and Christian M. Julien$^3$.

1LMDH, University P et M Curie, Paris, France; 2Faculty of Physics, University of Technology, Warsaw, Poland.

A tremendous resurgence of interest has been displayed in lithium metal polyphosphates because they contain both mobile Li+ ions and redox-active metal sites shrouded within a rigid phosphate framework. Lithium 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 $\text{Me}_2\text{P}_3\text{O}_18$ “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 Li$_3$Fe$_2$(PO$_4$)$_3$ phases using SQUID and ESR measurements. Li$_3$Fe$_2$(PO$_4$)$_3$ compounds were synthesized using wet-chemical techniques 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 atmosphere), the resulting nasicon-like material crystallizes in the orthorhombic system (Pcm 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**


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Recently, transition metal-based compound containing compact tetrahedral polyphosphonic structural units have been investigated intensively as potential positive electrode materials for lithium-ion batteries. Among the lithium metal polyphosphate family, Li$_5$(PO$_4$)$_3$(Me=Fe, V, Mo) compounds crystallize with the nasicon-like structure. They are considered as stable, non toxic and green materials whose structural properties are very different from the corresponding metal oxides. Li$_5$(PO$_4$)$_3$(preheated at 400 C for 4 h and final synthesis at 700 C for 12 h in Ar atmosphere) were synthesized using the rapid quenching technique. Their magnetic properties were measured using a SQUID apparatus in the temperature range 2-800 K. Vibrational features of
vitreous nasicon materials show similarity with those of the Li/Co-V2O5/P2O5 glass system. The spectrum of Li3M2e2(P04)3 is dominated by broad bands located in the mid-infrared and 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 modified 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 B4C 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.

B4C 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. B4C of a grain size of 50 nm to 100 nm was successfully synthesized in the carbothermal reaction route 2 B2O3 + 7 C → B4C + 6 CO. Amorphous B2O3 was filled into a graphite crucible and covered with a graphite foil. Carbon black (grade 9330, Ashby Carbon), characterized as amorphous carbon with a small particle size, was put onto this graphite foil leading to an 100% excess of B2O3 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 °C 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 B4C will be shown.

**FF3.34**

**The Synthesis of III-V Semiconductor InSb Quantum Dots by Solvothermal Reduction Reactions.** Shiria Black, Monica De Lenczets, Margaret Lams, Baoche 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 μm) which makes it a candidate material for applications as a quantum dot material for infrared (IR) detectors. In this study InSb films 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 (XRD), x-ray diffraction (XRD), and transmission electron microscopy (TEM). It was found that InSb with small amounts of Sb precipitated. The particle 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.** Soon-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 doped 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 because most of them are noble metal. The nano powder could be used to multiply 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 206 (Hynes)

8:30 AM **FF4.1**

**Hydrazinolysis 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 (FET) fabrication has accelerated in recent years, as a result of new applications potentially enabled by the alternative technologies (e.g., flexible displays, electronic newspapers, and touch cards this research is aimed 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 hydrazogen (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 - 300 °C). The resulting metal chalcogenide films are only a few unit cell thick, with remarkably large mobilities (>10 cm²/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 (NH3H4)2SnS6, (NH3H4)2InS6 and (NH3H4)2GeS6 and each is shown to consist of dimers of edge-sharing MX6 (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.** Pingyong Feng; Nanfeng Zheng and Xiantian Bu; Chemistry, University of California at Riverside, Riverside, 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. Tetradedral 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; Abderrahim Yassar and Omar Yaghi; 1Department of Chemistry, the University of Michigan, Ann Arbor, Michigan; 2TODYS, Universite Paris 7, Paris, France.

A series of 3-dimensional Metal-Organic Frameworks (MOFs) and 0-dimensional Metal-Organic Polyhedra 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 (XRD), 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.** Jeena Pius; Siu-Wai Chan; Feng Zhang; Jonathan C. Hanson and Xianqin Su; Chemistry and Biochemistry, California State University of Long Beach, Long Beach, California.

CuO is widely used as a catalyst in many reactions, and the CO oxidation activity of CuO and its suboxide Cu2O 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 to Cu nanoparticles. The in-situ experiments show that under a normal supply of CO, monoclinic CuO nanoparticles form a stable intermediate cubic phase, Cu$_2$O, rather than a direct transformation to metallic, cubic Cu, as has been observed for bulk Cu particles. Copper oxide nanoparticles are prepared by mixing aqueous solutions of copper nitrate and hexamethylenetetramine (HMT) at 50°C.

Transmission electron microscope (TEM) results show that the shape and size of the CuO nanoparticles are controlled by varying the HMT concentration. The size of CuO nanoparticles that crystallize in the cubic form as opposed to the tetragonal modification in HMT is the decreased nanoparticle aspect ratio. In addition, the less acicular CuO particles reduce more quickly to Cu$_2$O. These results indicate the relationship among morphology, particle size, and reduction behavior which may have significant consequences for the use of CuO nanoparticles in catalytic applications.

10:30 AM **FF4.4** Crystal Growth and Physical Properties of Ln$_3$Co$_4$Sn$_{13}$ (Ln = La, Ce) and Tb$_4$MGa$_{12}$ (M = Pd, Pt). Julia Y. Chan, Evan L. Thomas, Wills 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$_3$Co$_4$Sn$_{13}$ (Ln = La, Ce) and Tb$_4$MGa$_{12}$ (M = Pd, Pt). Ln$_3$Co$_4$Sn$_{13}$ (Ln = La, Ce) are cubic with space group Pm$n$m with a 9.64(10)Å and 9.60(10)Å, respectively. Ln$_3$Co$_4$Sn$_{13}$ exhibits superconductivity in addition to La and Ce. Cu$_2$octahedra and Sn$_2$icosahedra. The Sn compounds will also be compared to Tb$_4$MGa$_{12}$ (M = Pd, Pt). The Tb compounds crystallize in the cubic space group $I$m $3$m with $Z = 2$ and lattice parameters $a = 8.84(11)$Å, $b = 9.04(11)$Å, $c = 9.12(11)$Å, and $T = 12$ 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 Schaudenbauer$^{1,2}$, John Budding$^1$, Jorge Sofo$^1$,3, Gerald Mahan$^{1}$, Francis DiSalvo$^4$, Jinfang Meng$^{2,3}$, Jorge Sofo$^3$, Gerald Mahan$^{1}$, Francis DiSalvo$^4$, Jinfang Meng$^{2,3}$, 1Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania; 2Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania; 3Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania; 4Department of Chemisty 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 material parameters, such as preparation conditions and doping levels. Each compound then represents a 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 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 to perform additional X-ray measurements of the structure 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, 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, band structure was calculated 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. Rasbud$^1$ and Gavin Lawes$^2$; Materials Department, University of California, Santa Barbara, California; 2Los Alamos National Laboratoryos, Los Alamos, New Mexico.

We have used precursor routes to prepare magnetic transition metal ion (M) substituted wurzite ZnO powders with up to 15% M substitution (M = Cu$^{2+}$ 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 ferromagnetism in wide band gap spinel hosts with two cations sites. This approach has been more successful: dilute magnets based on M substitution in spinel ZnGa$_2$O$_4$ seem promising, displaying magnetic hysteresis in nearly transparent samples.

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

Solid state NMR may be used to correlate local structure with the dynamics that occur in ionic conductors. For example, in studies of α-Bi2O3, we have shown that 17O MAS NMR may be used to distinguish between oxygen ions in the [Bi2O5]2+ and vanadium oxide (perovskite) layers. 17O/18O 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 was used to detect much slower motion, allowing a wider range of oxide-ion conductors to be studied with 17O NMR. Applications of this approach to study motion in Nb3+/4+ doped Bi2O3 and Ca2+/4+ doped Y2O3 will be shown. In more recent work, we are investigating the effect that sample size has on local structure and conductivity of doped fluorides.

2:00 PM **FF5.2/K5.2
Structure Specificity of Nanocrystalline Praseodymium Doped Ceria, Vladislav A. Sadovykh1, Vladimir I. Voronin2, Alexander N. Petrov2, Yuliya V. Frolova1, Vladimir I. Zaikoski1, Holger Borchert1 and Stilianos Neophytides2.

Praseodymium doped ceria possessing a high mixed conductivity is of great interest for such applications as fuel cell electrodes, oxygen separation membranes, sensors etc. However, up to day neutron diffraction studies of this system have not been available. In this work, nanocrystalline samples of praseodymium doped ceria (x Pr = 0-0.5) prepared by Pechini route and calcined under air at 500-1300 °C were studied using TEM and neutron diffraction methods. The neutron diffraction study was 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 change state of oxygen was characterised by XPS. TEM revealed a good crystallinity of nanodommains (typical sizes 50-100 Å) 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 non-elastic thermal neutron scattering. The high Pr content Pr4+/3+ ratio increases which explains decreasing of the lattice constant due to smaller size of Pr4+ cation.

The second part highlights the modifications in charge carrier transport mechanisms 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-ions is of similar size to a coherent electronic wave. Solid state NMR may be used to correlate local structure with the mobility of the ions in the perovskite layers. 0/ 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 was used to detect much slower motion, allowing a wider range of oxide-ion conductors to be studied with 17O NMR. Applications of this approach to study motion in Nb3+/4+ doped Bi2O3 and Ca2+/4+ doped Y2O3 will be shown. In more recent work, we are investigating the effect that sample size has on local structure and conductivity of doped fluorides.

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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 transport mechanisms 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-ions is of similar size to a coherent electronic wave. Solid state NMR may be used to correlate local structure with the mobility of the ions in the perovskite layers. 0/ 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 was used to detect much slower motion, allowing a wider range of oxide-ion conductors to be studied with 17O NMR. Applications of this approach to study motion in Nb3+/4+ doped Bi2O3 and Ca2+/4+ doped Y2O3 will be shown. In more recent work, we are investigating the effect that sample size has on local structure and conductivity of doped fluorides.

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 p02-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 = 0.4, 0.6) [1]. Additionally, the samples quenched from the T- p02-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 = 0.4, 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 La0.6Sr0.4CoO3-δ. High resolution transmission electron microscopy revealed a structure within the oxygen sublattice in domains of about 100 nm in size. References 1. E. Bucher, A. Benisick, W. Sitte, Solid State Ionics 137 (2000) 39-44. 2. E. Bucher, W. Sitte, I. Ronn, I. Papas, W. Grogger, F. Hofer, Solid State Ionics 152-153 (2002) 417-421.

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


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Defect Chemical Role of Mn in Gd-Doped CeO2, (GDC), Sang-Hyun Park and Han-Hill 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 CeO2, 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 can 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 MnO, CeO2+ MnO) on increasing oxygen activity. In order to elucidate the defect chemical role of Mn in GDC, we examined the electrical conductivity on 5 mol 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 mol and the sintering enhancement is likely due to a liquid phase at grain boundaries due to the enriched Mn.


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 (OPO-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 that of the ion conductivities of the ceria films. Inter-diffusion of elements at the CeO2/ZrO2 interface has been substantial differences between the lattice parameters of Al2O3(0001) and ceria which is believed to be corrected 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 that of the ion conductivities of the 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 comparison of the results of these and Rutherford backscattering spectrometry results will be presented.

The inorganic compounds of copper oxides with Cu2+ are found that their structural features are well defined towards 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 compounds 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 MmCu2X20n, 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, has been shown 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.

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, scanning electron microscopy (SEM), and transmission electron microscopy (TEM) and electron probe microanalysis (EPMA).
Superconductor films of BSCCO system have been grown by dip coating technique with good success. Chemical method allow us to grow up superconductor thin films of high temperature with a great advantage to get 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 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, specifically Bi1220.5Sr2-xCaxCu20y, also known as 2223 phase with critical temperature around 110 K. The multilayers have been grown up on crystalline substrates of LaAIO3 and orientation (100) after heat treated around 790-900°C in lime time of 1 h 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 layered structure and some films are in 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 of at least two phases, 2212 and 2223, with Tc around 85 K and 110 K, respectively.

**FFG.4 The electronic structure and polaronic conductivity of olivine phosphates.** Thomas Maynich, Fei Zhou, Kusik Kang, Dane Morgan and Gerbrand Ceder, DMSE, MIT, Cambridge, Massachusetts.

Materials with the olivine Li$_{x}$MP0$_4$ (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$_{x}$MP0$_4$ compounds has been determined. The calculated optical band gap value of Li$_2$FePO$_4$ ($E_g = 3.8$ 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-type materials. The local nature of valence electrons in these systems. Additionally, evidence has been found that electronic transport can be explained in terms of nearest-neighbor electron hopping accompanied by a local, short-range correlation forming small polarons in these materials. By evaluating the total 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 behavior and electronic conductivity of Li$_{x}$MP0$_4$ compounds will be discussed.

**FFG.5 Does the Mercury Dope Boron Carbide?** Carolina C. Ilie, Sieranza Balar, Luis G. Rosa, Bernard Daudin 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 organic and metal transportation. Using photomission 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 individual molecule (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. Mercury atoms may form a layer between the Cu substrate and orthocarborane molecular film. Mercury atoms may form a layer between the Cu substrate and orthocarborane molecular film. Mercury atoms may form a layer between the Cu substrate and orthocarborane molecular film. Mercury atoms may form a layer between the Cu substrate and orthocarborane molecular film. Mercury atoms may form a layer between the Cu substrate and orthocarborane molecular film.
by Ba substitution for Sr site. A series samples with starting compositions of \(Co(Sr_{x-y}Ba_y)_{2}YCuO_4\) \((0 \leq x \leq 0.5)\) were prepared also by the solid-state reaction in air. X-ray diffraction measurements revealed that the partial Ba substituted samples have excess oxygen as is in the case of \(CoBa_2YCuO_4\), resulting in remarkably lowered electric resistivity due to hole doping. Furthermore, partially Cu substituted samples \(Co_{0.5}Ba_{0.5}YCu_2O_4\) showed small superconductivity with high \(T_c\). Various attempts for improving superconducting properties of the present system, such as Ba substitution for Y site and high pressure oxygen annealing, are undergoing. [1] J. L. Tallon, et al., *Phys. Rev. B* **51** (1995) 12911.


A novel hollandite-type vanadium oxide \(V_{2}O_2(OH)(CO_3)\) \((\text{H}_2O)_2\) \(_{14}\) was synthesized hydrothermally in the presence of tetraethylammonium 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 under various magnetic fields \((0 \text{ to } 5000 \text{ Oe})\) under field-cooled and zero-field-cooled conditions. The Curie constants were studied from 2 to 30 K with the ac field amplitude 0.1 Oe. ac frequencies varying from 0.05 to 1000 Hz in the absence of dc field and at different dc fields. The temperature dependences 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 and indicates a magnetic phase transition. From the fit of the high-temperature susceptibilities to the Curie-Weiss law, the Curie constant is \((7.71 \pm 0.04)\) emu K/mol, consistent with 3+ vanadium oxidation state, and the Curie-Weiss temperature is \(-5090(2)\) K, indicating a strong antiferromagnetic exchange interaction 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 the temperature dependences of the ac susceptibilities was performed in terms of the spin-glass model. 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 the phase transition temperature \(T_{SF}\). The temperature dependences of the 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 those of other Hollandite-type vanadium oxides containing \(K^+\), \(Ba^{2+}\), \(Bi^{4+}\) 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 \(Ca_3GaBiO_6\) by Large Amount of RE Substitution. Yunoshi Sugimoto1, J. Katana Ngala1, Takachi Okamoto1, Ken D. Otzuchi1, Junichi Shinozuka1,2 and Koji Kishi3; 1Department of Applied Chemistry, School of Engineering, University of Tokyo, Tokyo, Japan; 2PRESTO, Japan Science and Technology Corporation (JST), Kawaguchi, Saitama, Japan.

Among various layered cobaltates, \((Ca_{3-x}La_x)Co_2O_4\) \((0 \leq x \leq 0.6)\) is one of the promising candidates as for new thermoelectric materials up to high temperatures, because its single crystal has high thermoelectric performance with a figure of merit \(ZT > 1\) [1]. The \(Ca_3GaBiO_6\) has an alternate layer stacking structure consisted of \(CdI_2\)-type CoO$_2$ conduction layers and rock salt-type Co$_2$O$_4$ blocking layers along the c-axis. Therefore, \(c\)-axis aligned samples are necessary for reducing resistivity, \(\rho\), of its polycrystalline bulks. Since the \(Ca_3GaBiO_6\) has large anisotropy in its magnetization \((x_{\chi} y < x_{\chi} y)\), strongly \(c\)-axis aligned bulks of \(Ca_3Ga_2O_6\) 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 conduction band gap and suppression of oxygen nonstoichiometry [3]. Similar effects on \(S\) and oxygen nonstoichiometry of the \(Ca_3Ga_2O_6\) have been expected for partial substitution of rare earth elements, RE, for Ca site, however, their substitution level was limited more than 10% in the reports, resulting in slight improvements in thermoelectric properties. In the present study, we have attempted to increase substitution level of RE in the \(Ca_3Ga_2O_6\) polycrystalline bulks and found that higher part of Ca site can be replaced by several RE elements by sintering under flowing oxygen atmosphere. \((Ca_{3-x}RE_{x})Co_2O_4\) \((x = 0, Y, Sm, Eu, Tb, Dy, Ho and Lu)\) bulks showed apparently higher \(S\) than that of undoped \(Ca_3Ga_2O_6\). Thermogravimetric analyses revealed that oxygen nonstoichiometry is strongly suppressed as in the case of high valent metal substituted \(Ca_3Ga_2O_6\). These RE substituted samples showed higher \(\rho\) at low temperatures, however, it decreased with an increase of temperatures and became almost identical to that of undoped \(Ca_3Ga_2O_6\) 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 \(1000 \text{ K}\). Thermoelectric properties of magnetically aligned bulks will be also reported.

**FF6.11** Superconductivity in three layer (3L) sodium cobalt oxyhydrate. Min-Jin Pun1, Tomoe Kineczeko2,3, Lu Li2, Nai-Phuan Choo2,4 and Robert J. Cava5; 1Chemistry, Princeton, New Jersey; 2Physics, Princeton University, Princeton, New Jersey; 3Applied 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 \(Na_2SCO_4\) \(O_2\) \(_{2}\) \(_{2}\) \(_{2}\) \(_{2}\) \(_{2}\) \(_{2}\) has been reported. The new superconductor has three layers of \(CoO_6\) octahedra per crystallographic unit cell, in contrast to the previously reported two-layer superconductor (Takada et al. Nature March 2003, v422, p33). The three-layer cell occurs because the relative orientations of neighboring CoO$_2$ layers are distinctly different from what is seen in the two-layer superconducting phases. 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 \(T_c\) 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 CoO$_2$ layers. The synthesis, stability and physical characterization of the new phase are described.

**FF6.12** Growth of Yb$_2$Y$_2$O$_7$ Single Crystals by the Micro-Pulling-Down Method. Anh-Tuan Le, J. Hup Moon, Akin Yamaoka1, Georges Boulon2 and Tousgu Fakuda2; 1Division of Advanced Crystal Materials, Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan; 2Japan Science and Technology Agency, Sendai, Japan; 3Laboratory of Physical Chemistry of Luminous Materials, Claude Bernard/Lyon I University, Lyon, France.

The rare-earth sesquioxides \((RE_2O_3, RE=La-Lu, Y \text{ and Sc})\) 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 \(Y_2Al_5O_{12}\). The existence of \(RE_2O_3\) system 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 \(2400 \text{ °C}\), 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 growth. The crystal growth experiments along with optical properties characterization will be presented and discussed.

Electrostatic spinning is a proven technique, which has been used in the fabrication of electrospun nanofibers. Nanofibers were fabricated via the electrostatic spinning of polycaprolactone (PCL) or poly(l-lactic acid) (PLA). The spun nanofibers were obtained and the obtained nanofibers were used to manufacture nanocomposites. A single-source polymer monomer spray pyrolysis processing and the nanofiber-based methods of the nanofibers were used to obtain a single-source polymer monomer spray pyrolysis processing method based on the nanofiber-based characterizations. The obtained nanofibers were used to fabricate the nanofiber-based monomer spray pyrolysis processing method. This study showed that the nanofiber-based monomer spray pyrolysis processing method is a promising technique for the fabrication of nanofibers.
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 cationic disorder, the Pr atoms occupy both sites.

The dielectric constant has been measured as a function of temperature and experimental results suggest that the position and the shape of the dielectric anomaly strongly depend on the composition. This effect was demonstrated in the Pr substituted Bi-2212. The perovskite blocks of the Bi-2212 structure were systematically studied for (La,Sr)\(_3\)\_27 single crystals. Properties were systematically studied for (La,Sr)\(_3\)\_27 single crystals. Properties were systematically studied for (La,Sr)\(_3\)\_27 single crystals.

We have successfully obtained a solid solution up to \( x = 0.4 \) for RuSr\(_2\)Gd\(_{1-x}\)Sr\(_x\)Cu\(_2\)O\(_8\) systems, where \( Ru = Dy, Ho, Er, Yb \) and \( Lu \). All systems have been synthesized by solid state reaction methods under ambient pressure. These systems are intermetallic compounds and they form a two-dimensional pyrochlore phase in the RuSr\(_2\)Gd\(_{1-x}\)Sr\(_x\)Cu\(_2\)O\(_8\) composition. The single phases have been characterized by X-ray powder diffraction (XRD) and Energy Dispersive X-ray Spectroscopy (EDX) analysis. Studies by Scanning Electron Microscopy give a particle size around 1 to 10 nanometers. We report also the results of the temperature dependence of the electrical resistivity of the samples annealed in oxygen flux during \( 6, 12 \) and \( 48 \) hours. The AC magnetic susceptibility measurements indicate that the RuSr\(_2\)Gd\(_{1-x}\)Sr\(_x\)Cu\(_2\)O\(_8\) systems, with \( 0 < x < 0.4 \) are ferromagnetic, with \( T_C \approx 125-145 \) K. We acknowledge the financial support from the PAPIIT-UNAM-IN102203, IX108104 and CONACyT 53535-E.

**FGF.22**

Effect of Mn Doping on the Structural and Dielectric Properties of (La,Sr)\(_3\)\_27 Single Crystals. Yuui Yokota\(^1\), Jun-ichi Yoneyama\(^2\), Shigeru Rorii\(^3\) and Kohji Kishio\(^3\); \(^1\)Department of Condensed Matter Physics, Chelyabinsk State Univ., Chelyabinsk, Russia; \(^2\)Department of Materials Science, Moscow State University, Moscow, Russian Federation; \(^3\)Department of Chemistry, Moscow State University, Moscow, Russian Federation.

Since the discovery of colossal magnetoresistance (CMR) effect, La\(_{2-x}\)Sr\(_x\)Mn\(_2\)O\(_y\) has 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. 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 by annealing and post-annealing have been tested. We present the results of studies on formation and stability conditions of pyrochlore phase in K-W-Sb-O system.

**FGF.20**

Abstract Withdrawn

**FGF.21**

Internal Oxidation in Solid Solutions Bi\(_2\)\(_{1-x}\)Pb\(_x\)Sr\(_2\)\_yCa\(_{1+y}\)Zr\(_{2+y}\)Cu\(_{2+y}\)O\(_{16}\). Dmitry A. Zakharyevich, Anton Artemyev and Vladimir A. Burmistrov; Condensed Matter Physics, Chelyabinsk State Univ., Chelyabinsk, Russia.

Internal oxidation of Bi\(_2\)\(_{1-x}\)Pb\(_x\)Sr\(_2\)\_yCa\(_{1+y}\)Zr\(_{2+y}\)Cu\(_{2+y}\)O\(_{16}\) solid solutions is a prospective way to create nanocomposites and superconducting nanocomposites. To control the process one can perform simultaneous substitution in different cation sites (e.g., Bi on Pb and Ca on Sr on rare earth elements). Solid solutions were prepared by solid state reaction method using high-temperature post annealing. Structural analysis of the samples has been performed from the XRD X-ray powder diffraction at several temperatures. The particle size of the samples was determined by the Scherrer formula. The results show that the particle size decreases with increasing Pb content and Sr deficiency.

**FGF.19**

Effect of Mn Doping on the Structural and Dielectric Properties of Bi\(_{2-x}\)Ta\(_x\)O\(_6\) (SBT) samples and with Mn(SBT: Mn) doping have been prepared by sol-gel technique. Scanning electron microscope, 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 (\( \varepsilon \)) was found to be very sensitive to excess Bi additions. Highest value of \( \varepsilon = 120 \) 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 Bi\(_{2-x}\)Ta\(_x\)O\(_6\) with substitution of Sr or Ca by Bi was added to the starting composition. This sample also showed the largest area of the hysteresis loop. In the case of Bi\(_{2-x}\)Ta\(_x\)O\(_6\) with substitution of Sr or Ca by Bi was added to the starting composition. This sample also showed the largest area of the hysteresis loop. 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**FGF.10**

Investigation of internal oxidation in phase transitions at higher oxygen uptake and oxygen vacancy concentration. Dmitry A. Zakharyevich, Anton Artemyev and Vladimir A. Burmistrov; Condensed Matter Physics, Chelyabinsk State Univ., Chelyabinsk, Russia.

Investigation of internal oxidation in phase transitions at higher oxygen uptake and oxygen vacancy concentration. Dmitry A. Zakharyevich, Anton Artemyev and Vladimir A. Burmistrov; Condensed Matter Physics, Chelyabinsk State Univ., Chelyabinsk, Russia.
resulting improved CMR effect will be reported. [1] Y. Morimoto et al., 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

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 into account. 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, and the minimal distortion which was originally proposed to classify Mott-Hubbard insulator classification and symmetry measures of the electron density will be plotted in a shape map that provides hints on the type of distortion expected. Recent studies aimed at systematic structural studies in such a map. Recent studies aimed at systematic structural studies in such a map. Recent studies aimed at systematic structural studies in such a map. Recent studies aimed at systematic structural studies in such a map. Recent studies aimed at systematic structural studies in such a map. Recent studies aimed at systematic structural studies in such a map. Recent studies aimed at systematic structural studies in such a map.

9:00 AM *FF7.2
Origin of ferromagnetism in novel spintronic oxides. Nicola A. Spaldin, Priya Gopal and Rebecca Janisch; Materials Science Department, UCSC, 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 TiO2. 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 well-established piezoelectricity of wurtzite-structure ZnO.

9:30 AM FF7.3
Charge Transfer in Mixed 3d/4d Transition Metal Oxides. I.W. Chen1, F. Huang1 and Wojciech Dmowski2; 1Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, USA; 2Materials 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 to the Zan-Baikwary-Zallen scheme, which was originally proposed to classify Mott-Hubbard insulators versus charge transfer insulators. 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 calculations. 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. Many interesting spin states 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. XiQiu Wang and Friedrich Liebau; 1Department of Chemistry, University of Houston, Houston, Texas; 2Institut Geowissenschaften, Universitat 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 found a correlation between the stereo chemical activity of the LEP and bond valence sums (BVS) calculated according to the bond valence model. 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 bond 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 appreciated by the BVS values. BVS values should be related to material properties as shown for the conduction paths in the semiconducting cetonite-type phases. 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 0.5 v.u. higher than its formal valence. 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 effective valence of the lone-pair cations tend to be balanced by low effective valence of alkali cations. For example, in the structure of Na4SnO3 the BVS values for Na+ and Sn(II) or O2- 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-pair electrons and bonding electron pairs.

10:30 AM *FF7.5
Shape Measures, Shape Maps and Polyhedral Interconversion Paths in the Solid State. Santiago Alvarez1, Pere Alemany2, Miguel Llunell1, David Casanovas1 and Jordi Civera1; 1Departament de Quimica Inorganica, Universitat de Barcelona, Barcelona, Spain; 2Departamento 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. The term 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 present in that structure and the stereo distortion interconversion pathway between two polyhedra is univocally defined in such a map. Recent studies aimed at systematic structural studies using these measures have been published [1]. The shape maps can be constructed and discussed, with special emphasis in the field of solid state structures.

A prospective of future developments such as automatic shape classification and symmetry measures of the electron density will be also discussed.


One of the major challenges for over 30 years in the physics and chemistry of the photographic process is 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- and aggregate-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 unsolved. The dynamics of interstitial cations near the surface, and the role of environmental adsorbates such as H₂O, O₂ and H₂O 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 and J. Jacobs P. W. M., J. Phys. C, 12, 3433 (1979). [2] Baetzold R. C., Catlow C. R. A., Corish P., Jacobs P. W. 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).

11:00 AM EF7.6

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11:15 AM EF7.7
Analysis of the Complex Refractive Index of Inorganic Solids and Determination of the Relevant Parameters Governing n and k. Stephane Jobic1, Xavier Rocquefelte1, Fabrice Goubin2 and Myung-Hwan Whangbo2; 1LCS, IMN-CNRS, Nantes, France; 2Department 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, follow the well-known relation n² - k² = ε, where ε is the complex dielectric function, 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 c(λ) of the refractive index (also known as the power of the material) and the imaginary part k(λ) is associated with the electronic absorption of the material. n and k are related to c and k(λ) as follows: c = ε = n² - k² and k(λ) = 2πnλ/k, where c is related to λ via the Kramers-Kronig relation. Consequently, if k(λ) is determined experimentally or theoretically, n and k can be deduced. A relation between the electronic energy band structure and optical constant c(E) exists which takes into account the electric dipolar momentum. Thus, on the basis of first principles electronic structure calculations, the dielectric functions c(λ) and the complex refractive indices of the solid materials may be determined and discussed in terms of ionity, structure, compactness, and the main factors that govern these values can be deduced. Our discussion will lie on new results acquired on borates and oxydes (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- and aggregate-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 unsolved. The dynamics of interstitial cations near the surface, and the role of environmental adsorbates such as H₂O, O₂ and H₂O 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 and J. Jacobs P. W. M., J. Phys. C, 12, 3433 (1979). [2] Baetzold R. C., Catlow C. R. A., Corish P., Jacobs P. W. 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).
Extreme aspect ratio semiconductor nanostructures are currently the subject of considerable scientific and technological interest. High pressure fluids are often selected for the fabrication 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 different types of extremities of nanorods and nanowires. We have characterized both the electronic and photonic properties of these structures, which are expected to have wide ranging application.

3:30 PM FF8.3
Synthesis of InP and InAs Quantum Rods Using Myristic Acid. Itzik Shweky1, Assaf Aharoni1, Eli Rothenberg1, Taleb Mokari1, Inna Popov2, Moshe Nadler1 and Uri Banin1; 1Institute of Chemistry The Farkas Center for Light Induced processes and the Center for NanoScience and Nanotechnology, The Hebrew University of Jerusalem, Jerusalem, Israel; 2The 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 and important challenge especially with relation to shape control to achieve rod growth. To this end, a novel strategy is to react the nanostructures along their entire length with a post-treatment of these spherical nanoparticles in pyridine at 80 °C. This methodology for the development of other shapes and/or 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 different types of extremities of nanorods and nanowires. We have characterized both the electronic and photonic properties of these structures, which are expected to have wide ranging application.

2:45 PM FF8.4
Low-Temperature Solution-Phase Conversion of MnP Nanoparticles to Nanowires: Implications for Dimensionality Control in Nanoscale Phosphides. Kanchana Somaskandan1, George M. Tsoi1-4, Lowell Wengeraler-2 and Stephanie Brock2; 1Chemistry, Wayne State University, Detroit, Michigan; 2Physics, Wayne State University, Detroit, Michigan, 3Physics, University of Alabama, Birmingham, Alabama.

The evolution of shape in nanoscale materials remains a poorly understood phenomenon, despite the promise of enhanced or directional properties in materials prepared by the self-assembled, engineered anisotropy. We have developed a methodology for the preparation of discrete ferromagnetic MnP spherical nanoparticles from Mn2(CO)10 and P(SiMe3)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.

3:00 PM FF8.5

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 Mo2C is 70 pW-cm compared to that of Mo (4.85 pW-cm), whereas that of NbC is 50 pW-cm as compared to 15.2 pW-cm for Nb. Indeed, the temperature dependent resistivity of metallic-like conduction. Furthermore, certain transition metal carbides are known to become superconducting, with transition temperatures ranging from 1.15 K for TiC1-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, 163 (1996)] and subsequent superconducting behavior was shown by Fukuyma et al. [J. Mater. Res. 13, 2455 (1998)]. Vapor-liquid-solid growth was employed by Johnson et al. [M. Johnsson and M. Nygren, J. Mater. Res. 12, 2416 (1997)] to synthesize micron-sized carbide whiskers. Herein, we have successfully synthesized Mo2C nanowires 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 nanostuctures, which are subsequently carburized in an environment of carbon monoxide. Unlike true VLS growth of carbides, in which high temperature (1100-1200 °C) is required to adequately dissolve carbon into the catalyst particles, our strategy is to react the nanowires along their entire length with a carbon vapor source after creating the oxide/metal nanostuctures, which for Mo2C can be achieved at relatively low temperatures (< 1000 °C). The nanowires 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 are dissolved into a three phase region of the metal, metallic oxide and a carbon vapor-solid interface. The growth is then continuously sustained via a vapor-solid-growth process and is poised 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 structure of the nanowires and/or the presence of an oxide layer. A discussion of the growth mechanism will be presented along with a study of the nanowire/ribbon structure and properties.

3:45 PM FF8.6
Solution Phase Synthesis of Straight and Branched CdSe Nanowires. Katherine Leigh Hull1,2, James W. Grebinski1,2, Jing Zhang3, Tom H. Koes1 and Masaru Kuno1; 1Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana; 2Notre Dame Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana; 3Department 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), nanowires (NWs), nanowires (NWs), as well as other higher order nanomaterials. 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 mechanisms and/or chemically synthesized or laser sintered metal NCs as used as catalyst particles. Such routes take advantage of advances in AC synthesis to overcome intrinsic droplet size limitations, ultimately allowing one to create narrowly unattainable, narrow diameter NWs. Other approaches include complete solution phase analogues of VLS growth such as solution-liquid-solid (SLS) growth, pioneered by Buhr; 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 nanowires (8-10 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/Al core/shell NCs. These core/shell NWs are then used as catalysts for the subsequent growth of CdSe NWs. The resulting Au/Al 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 wires yielding tripods and y-shaped NWs. The choice of NCs may also influence 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 interesting opportunities for future surface modification and 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.
Vanadium dioxides have found a wide range of applications in temperature sensing devices, optical switching devices, energy-conserving coatings 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 great attention due to 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 0.2 eV, which indicates that its Ferri energy level situates on the middle energy level of the forbidden band. After Mo doping, the transition temperature decreases to 332 K. Mo doping reduces forbidden band width of VO2(M) nanorods as the donor and change its electrical property.

Large-Scale Synthesis of Single-Crystalline BaTiO3 and SrTiO3 Nanostructures. Stanislau S. Wong1,2, Yungsheng Mao1 and Surabjit Banerjee1,2. 1Department of Chemistry, SUNY at Stony Brook, Stony Brook, New York; 2Materials 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 wide range 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 particularly attractive to use as optoelectronic devices. The high dielectric constant and low dielectric loss of perovskite ceramics make them ideal materials for dielectric applications, especially high-frequency applications. These materials are also attractive in the field of electronics due to their high performance in microelectronics. In this present work, single-crystalline perovskite nanostructures with reproducible shape have been prepared using a simple, readily scalable solid-state reaction in the presence of NaCl and a manonic 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.


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 (BaTiO3) and lead zirconate titanate (Pb(Zr,Ti)O3 - PZT) fibers. 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 morphoogy 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).
Titanate nanotubes have received a great deal of attention, in part because of TiO2 can exhibit a wealth of important photo-thermal, photo-catalytic, and gas-sensing properties, especially when prepared as a nanomaterial. Nanotube platforms often only been synthesized in small quantities by hydrothermal treatment of anatase TiO2 nanopowders 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 sheet-like plates and subsequently folds into nanotubes. Such a route inspires our efforts to develop whether the independent dissociation of metal can be applied to synthesize titanate nanotubes. Herein, we report the in situ formation of large quantities of titanate nanotubes 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 thousand micrometers. The titanate nanotubes are easily dispersed in a titanium oxide film 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. 95, 3156103 (2005).

**FF0.5**

**Sol-Gel La1-xMxCo03 (M = Ca, Sr) Nanopowders**

Synthesis, characterization and magnetic properties

Gregorio Bottaro1, Lidia Armeño1, Davide Bareca2, Andrea Caneschi3, Claudio Sangregorio4, Alberto Gasparotto5, Stefano Gialanella4, Cinzia Maragno1, Elisabetta Piazzalunga2 and Eugenio Tondello2

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Perovskite-type oxides of rare-earth and transition metals (LM03, L=Ln, 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 cobaltites is particularly promising thanks to the accessibility for both 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 nanophase La1-xMxCo03 powders (M = Ca, Sr).

The powders were prepared starting from solutions of (CH3CO)2H2O, La(N03)3·3H2O and M(CH3CO)2·2H2O. The powders 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) Spectroscopy. 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 1 on the chemical and physical properties of the systems are presented and discussed. [1] L. Armeño, G. Bandoli, D. Bareca, M. Bettinelli, G. Bottaro and A. Caneschi, Surf. Int. Anal. 34, 112-115, 2002 and reference therein. [2] N.Q. Minh, T. Takahashi; Materials Science and Technology of Ceramic Fuel Cells, Elsevier, 1995.

**FF0.6**

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, and nanosheets, were fabricated in series by controlling the processing temperature and oxygen contents systematics by using a simple thermal evaporation. These structures are monolithically single-crystalline and the examples of spontaneous organization of vapor molecular species into nanostructures and their microscale assemblies or superlticians in one step. These kinds of arrayed structures might be useful in arrayed nanoscale photonic and electrochemical applications.

**FF0.7**

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-sized electronic, optoelectronic, electrochemical and sensor devices. Especially, ZnO, a wide-bandgap (3.37 eV) semiconductor with large exciton binding energy (60 meV), has attracted considerable attention due to the potential applications for the optoelectronics. Thus, various 1-D nanostructures of ZnO including nanowires and nanorods 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 size and shape of the ZnO nanorods will be presented. We also tried to realize p-type ZnO nanorods, homoeptaxially on the n-type ZnO substrate, by using Zn(1-x)(P,As)O2 target materials. XRD, TEM-EDS, I-V measurement results will presented and discussed.

**FF0.8**


Although many oxides are known with a 1:2 B-site ordered, double perovskite structure, relatively few 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. BaZn1/3Ta2/3O3) are rigidly stoichiometric and low (e.g. 0.01) of a foreign ion with different size/charge can disturb the cation order. This paper will describe the formation of the first non-stoichiometric 1:2 ordered perovskites in the (1-x)La2/3Ni3/3O3-x+2 Li2/3Ni3/3O3 system. A mixture of La, Sr and Ca, systems. In contrast to all known A(B1/3B2/3)2/3 perovskites, these 1:2 ordered solid solutions do not include any composition with a 1:2 cation distribution. Structure refinements of the phases (P m) for A=La, 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+[Li2/4Nb3/2]2/3[Ni1/3(1-x)Wx]03 (x = 0.9x) 1:2 ordered phases with a mixture of Nb/Ta on the B(II) sites were also obtained for compositions in the [A2+[Li2/4Nb3/2]2/3[Ba/3(1-x)Ta]03]03 system. 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-stoichiometric 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.

**FF0.9**

New synthesis method of nanophased metal oxide catalyst in supercritical water for biomass conversion. Catherine Veronique Levy1,2, Kenta Murakawa1,2, Masaharu Watanabe1,2, Yuichi Aizawa1,2 and Hiroshi Inomata1,2; Tohoku University, RCSFT, Sendai, Japan; 2Tokoh University, Environmental Chemical Engineering, Sendai, Japan.

Biomass conversion for H2 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 reactions 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 such as CoO, ZrO2 ... 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 research 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 new method for catalysts, 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. As a first step, we propose to study pure zinc oxide and solid solutions, as CoO-ZnO-Al2O3-ZrO2 systems, synthesized in supercritical water with both a flow and batch apparatus. In flow apparatus, influence of flow rate, precursors concentration, reactor size on structural and textural properties is studied. In batch, influence precursors...
additives and concentration on structural and textural properties is studied too. Hydrothermal synthesis and sol-gel route is also employed, in the method most adapted to obtain nanopolymers and high specific surface areas. 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. The application of the catalytic reaction by the metal oxide catalysts, biomass conversion is studied to produce a valuable chemicals (\(H_2\), alcohols, nitrates, furans, and so on) at high selectivity and high yield. The beneficial or harmful effects being used in the study are seen as their unique properties. Control of the geometrical structures of 1D materials is important for the application to several types of functional devices. 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 devices [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 TiO\(_2\) 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).

### F90.10

**synthesis and optical property of vanadium oxide nanotubes.** Ligiang Ma and Wen Chen; wuhan University of Technology, Wuhan, China.

In recent years, nanoscale one-dimensional materials have attracted much attention due to their remarkable optical 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 far no comprehensive studies of VONTs’ properties have been done. In this study, we synthesized the vanadium oxide nanotubes from V2O5 precursors and primary amines in a thermolysis phase reaction followed by self-assembling process. The products are examined by XRD, SAED, cross-section HRTEM. The results show that the nanotube walls consist of two alternative layers of VO\(_x\) polyhedron layers and protoned HDA layers. The polyhedron layers are composed of parallel [VO\(_5\)] units which are connected with the tetrahedron of [V\(_4\)] in the tube. The average valence of V is 4.31. The optical properties of vanadium oxide nanotubes 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 absorption spectra of VONTs, there is an absorption band at 400 nm, which can be assigned to the 2.7 eV forbidden band. Optical transmittance increases with the increase of incident wavelength. At the 532 nm the transmittance is up to 50%.

### F90.11

**A General Fabrication Method for Free-Standing as well as Arrays of Single-Crystalline Nanowires at Room Temperature.** Stanislaus S. Wong,1,2 and Yuanbing Mao1.

1Department of Chemistry, SUNY at Stony Brook, Stony Brook, New York; 2Material Sciences Department, Brookhaven National Laboratory, Upton, New York.

One-dimensional (1D) 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 1D nanomaterials with high purity in large quantities. However, there are still no general guidelines for their straightforward synthesis with predetermined chemical and morphological compositions as well as tailor-made sizes and aspect ratios. Single-crystalline BaW\(_4\)O\(_7\) and BaCrO\(_4\) 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 BaW\(_4\)O\(_7\) and BaCrO\(_4\) 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 robust methodology to prepare other types of free-standing ABO\(_4\) nanorods and their corresponding nanorod arrays. Extensive characterization of these samples has been performed using scanning electron microscopy (SEM), transmission electron microscopy (TEM), angular-resolved ultraviolet photoelectron spectroscopy (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 BaW\(_4\)O\(_7\) and BaCrO\(_4\) 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.

### F90.12

**Abstract Withdrawn**

### F90.13

**Fabrication of 1D Nanostructure Materials with Controlled Shapes Using Anodic Porous Alumina as Templates.** Takashi Yanagishita1, Futoshi Matsumoto2, Kanzawa Academy of Science and Technology, Kanazawa, Japan; 2Tokyo 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 devices. 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 devices [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 TiO\(_2\) 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).

### F90.14

**Electrochemical Synthesis and Characterization of Tin Oxide Nano Wire.** Saito Nagahiro1, Ishizaki Takahiro2, Uehara Takuya2 and Takai Osamu3,4.

1Department of Molecular Design and Engineering, Nagoya University, Nagoya, Japan; 2Department of Materials, Physics and Energy Engineering, Nagoya University, Nagoya, Japan; 3EcoTopia Science Institute, Nagoya University, Nagoya, Japan.

Tin oxides are 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 nanowire. 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 293 K, 292 K and 288 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 prepared from the solutions containing tin dichloride 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.

### F90.15

**Study of synthesis variables in the nanocrystal growth behavior of tin oxide processed by controlled hydrolysis.** Caue Ribeiro1, Eduardo Jia Hua Lee1, Tania Regina Giraldi2, Jose Arana Varcas3, Elson Longo1 and Edson Roberto Leite1.

1Chemistry, Universidade Federal de Sao Carlos, Sao Carlos, SP, Brazil; 2Chemistry, 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 the solution. The particles were then 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 observed 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 induces coarsening by the oriented attachment mechanism.

**FF9.16**

Tin oxide nanoribbons with different oxidation states obtained by carbothermal evaporation method.

Marcelo Ornaghi Orlandi, Rosana Aguiar, Edson Roberto Leite, Jose Arana Varela and Eleno Longo; 1Materials Engineering, Universidade Federal de Sao Carlos, Sao Carlos, Brazil; 2Chemistry, Universidade Federal de Sao Carlos, Sao Carlos, SP, Brazil; 3Chemistry, Universidade Estadual Paulista, Araruama, 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, Sn3O3 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 Sn3O3 nanoribbons, while there is evidence that a self-catalytic vapor-liquid-solid (VLS) mechanism should occur in the formation of SnO nanoribbons. Hartree-Fock-Roothaan ab initio calculations were done in order to elucidate some of the possible reactions that occur during the synthesis of the nanoribbons.

**FF9.17**


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 ALa2NbO7 (A = Li, Na, K, Rb, Ca) and ACa2Nb3O10 (A = Na, K, Rb, Ca). Then oxidative-intercalation methods were examined in an effort to assemble alkali-metal halide layers within the perovskite host. These methods have so far resulted in the new layered perovskite (ACaCl)La2NbO7 and (ACaCl)Ca2Nb3O10 (A = Rb, Ca). 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**


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 perovskites such as SrRuO3, we are able to obtain a large family of SrRuO3-related compounds.

**FF9.19**

Raman Spectroscopy as a Probe of Local Order in CaZr1-xTixO3.

Eric Cochlaye; Ceramics Division, NIST, Gaithersburg, Maryland.

Many materials of technological interest are solid solutions where the degree of chemical ordering affects the physical properties. Raman spectroscopy, being highly sensitive to short-range and long-range order, is a powerful tool for investigating the effect of composition on the order-disorder behavior. In the present study, we will use Raman spectroscopy to investigate the effect of substitution at the A-site on the order-disorder behavior of the perovskite CaZr1-xTixO3. The results show that higher initial ion concentrations and agglomeration produce and off-center site. This work has been partially supported by CONACyT through Project No. 49064-F and by DGAPA-UNAM through Projects IN16703-3 and IN160903.

**FF9.20**

Ordering Transformations in Ba(Ni0.5(Nb2/3) O3 Perovskites.

Meganathan Thirumal, Tyke Nagas and Peter K. Davies; 1Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania; 2TCI Ceramics, Hagerstown, Maryland.

Ordered A(B1/2/4)O3 (A = Ba, B = Mg, Zn, Ni; B = Tb, Dy) 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 "122" layering. The Raman spectroscopy has different sensitivities to the amount of long-range order. Experimentally, CaZr1-xTixO3 (CZT) does not exhibit long-range ordering of Zr and Ti, yet Raman peaks are observed that match the order-disorder Raman peaks in CZT. The Raman order parameter in CZT is simulated as a function of composition and short-range Zr-Ti order, and the results are compared with experiment.

**FF9.21**

Study of the percolative nature of thermoelectric power and resistivity in Pr0.66R0.34Sr0.33MnO3 (R = Tb, Y, Ho or Er) manganites. N. Rama*, V. Sankaranarayanan* and S. R. Rao Manish; 1Department of Physics, Indian Institute of Technology Madras, Chennai, Tamil Nadu, India; 2Materials Science Research Centre, Indian Institute of Technology Madras, Chennai, Tamil Nadu, India; 3Department of Physics, University of Maryland, College Park, MD 20742, Maryland.

The magnetic and transport properties of Ln1-xA2Mn3O12 manganites depend crucially on the variance of ionic radii at the A-site. It is seen that as the variance in A-site disorder decreases, the Curie temperature decreases and the average ionic radius of A increases. It is seen 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-insulator transition. This behavior, and the transition itself, can be due to the percolation of these metallic regions. We have studied the resistivity and thermoelectric power of Pb_0.6Bi_0.4Sr_2.3MoO_5 where R = Bi, Yb, 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 (c<0.5) with the high temperature activation energy in both increasing with increase in (c<0.5) implying that as the disorder increases, the localization of the charge carriers in the metallic phase can be described. The thermopower was analyzed assuming that the lattice has coexisting metallic (S_metal) and insulating (S_ins) components above and below TC which are independent of each other. Hence total S(T) = pS_metal(T) + (1-p)S_ins with volume metallic fraction. [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.

**FF9.09**
The order of the perovskite methylammonium lead chloride, Liszheng Chi, Ian Swainson, Lachlan Cranwack, 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 Pmna with cell parameters a=11.1747(3)Å, b=11.3552(1)Å, c=11.2810(1)Å, P=3.574, Rp=1.79%. Refined 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 Pmna with this basis cell is not a common perovskite cell. In the structure, two methyl ammonium ions are ordered in planes with y=0.5 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 the presence of Pb within the octahedra. This suggests that the most rigid unit is actually the methylammonium cation, rather than the PbCl_6 octahedra. The methyl ammonium 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 Fursui, William David Kirby.

Gurinder Singh¹, Alexander N. Cartwright², J. Derek Lucey² and Parra N. Frasard³; ¹ Electrical Engineering, University at Buffalo (S.U.N.Y.), Buffalo, New York, ²Chemistry, University at Buffalo (S.U.N.Y.), Buffalo, New York; ³Los 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-V 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 the electron, holes 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 conduction band, leading to 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. On the other hand, the InP core nanoparticles are quite different as a result of this difference in band structure. In the former case, the PL is broadened and redshifted substantially relative to that of the original, unencapsulated InP nanoparticles with a quantum yield of over 95% 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 leave the InP core and travel to the shell 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 Cheng¹, Jian-Chen Hao², Wensheng Shi², Lei Zhang² and Edward T. Samulski¹, ¹Chemistry, University of North Carolina, Chapel Hill, North Carolina; ²Curriculum in Applied Materials Sciences, University of North Carolina, Chapel Hill, North Carolina.

One-dimensional (1-D), transparent, conducting oxide (e.g. SnO_2, ZnO) nanostructures were prepared in solution under low-temperature conditions. The aspect ratios of the 1-D nanorods are tunable by deliberately 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. Comm. 2004, 986-987; 2. Bin Cheng, Jiake 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 SnO_2-Li_2O Compounds obtained by Combustion Chemical Vapor Deposition, Monica Andrade-Arias, Christopher Bergmann and Marcio Dias Lima; Materials Department, Federal University of Rio Grande do Sul, Porto Alegre, Rio Grande do Sul, Brazil.

Amorphous silica films deposited by Combustion Chemical Vapor Deposition (CCVD) were modified with lithium addition in the precursor solution. The modified films were characterized by X-ray diffraction and transmission electron microscopy. The addition of lithium promoted the crystallization of Li_2SnO_3, Li_2SnO_5 and cristobalite. Besides that, the morphology of the film was modified, leading to the formation of thin films of amorphous structures and nanowires. The acicular structures were identified through TEM associated with SAED as crystalline phases, mainly constituted by Li_2SnO_3 and Li_2SnO_5. 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 composed by amorphous silica. The probable growth mechanism of these nanowires is the vapor-liquid-solid (VLS) catalyzed by a liquid particulate composed by Li_2O-SnO_2.
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 precursors, noting that although the structure of the crystallites fits MgO much better than CdSe, the intended phase separation finds competition in the Mg$_x$-Zn$_y$O 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 reduction 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 acid and graphite. The effect of the structure and morphology of the product on the hybrid compound was discussed. The experimental work including bonding order, composition, and structure of the boron carbide nanoparticles products.

FF9.29 Structural Properties of Amorphous Aluminum and Aluminum-Nitrogen Alloys. Computer Simulations. Alexander Valladares$^{1}$, Remyal Maria Valladares$^{2}$ and Ariel Alberto Valladares$^{1}$; $^{1}$Condensed Matter, IMM-UNAM, Mexico, D. F., Mexico; $^{2}$Physics Department, Facultad de Ciencias, UNAM, Mexico, D. F., Mexico.

The theoretical/simulation 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 quasicrystalline 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 performed at high temperatures and in the presence of pressures. Nevertheless, the pioneering ab initio work of Car and Parrinello, no doubt, has permeated all efforts during the last 17 years, to the point of mandating that every new process be compared with the results of that work. In the present study, organic-inorganic layered perovskite-type compounds (C$_4$H$_9$NH$_3$)$_2$MCl$_4$ and (C$_4$H$_9$NH$_3$)$_2$CuCl$_4$ 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 products including the structure and thermal stability of the synthesized compounds. The heat treatment was taken to prepare (C$_4$H$_9$NH$_3$)$_2$MCuCl$_4$, and the results indicated that 70$^\circ$C is advisable. From the SEM pictures, both of (C$_4$H$_9$NH$_3$)$_2$MCuCl$_4$ and (C$_4$H$_9$NH$_3$)$_2$CuCl$_4$ took on obvious sheet-like microstructure. It means that the growth was also highly oriented. Although both of title compounds had good thermal stability, (C$_4$H$_9$NH$_3$)$_2$CuCl$_4$ was inferior to the former due to distorted [CuCl$_6$].

FF9.30 Preparation and characterization of (C$_4$H$_9$NH$_3$)$_2$MCuCl$_4$ (M=Mn, Cu). Liling Guo, Huang 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 (C$_4$H$_9$NH$_3$)$_2$MCl$_4$ (M=Mn, Cu) were obtained 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 of the synthesized compounds. The heat treatment was taken to prepare (C$_4$H$_9$NH$_3$)$_2$MCuCl$_4$, and the results indicated that 70$^\circ$C is advisable. From the SEM pictures, both of (C$_4$H$_9$NH$_3$)$_2$MCuCl$_4$ and (C$_4$H$_9$NH$_3$)$_2$CuCl$_4$ took on obvious sheet-like microstructure. It means that the growth was also highly oriented. Although both of title compounds had good thermal stability, (C$_4$H$_9$NH$_3$)$_2$CuCl$_4$ was inferior to the former due to distorted [CuCl$_6$].
assembled from components other than oxides. We have recently developed a synthetic route for the production of pure metal chalcogenide superconductors and incorporated the 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 materials are discussed. A comparative characterization 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 Martijn Jansen
Thursday Morning, December 2, 2004
Room 200 (Hyne's)

8:30 AM FF10.1
Synthesis, crystal and magnetic structures of the Sr2RuREO6 (RE = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb) family of double perovskites. Rocio Ruiz-Bustos, Jose Luis Garcia-Munoz and Miguel A. Alario-Franco; Laboratorio de Quimica del estado Solido, Universidad Complutense, Madrid, Spain; 2Instituto 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. Part of the reason 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. This talk will focus on some attention to the structure (1,2) and 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 is cubic with a double cell with parameters a = 2ap (ap being the basic 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 Ru02, SrC03 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 B'B ordering. Magnetic susceptibility data as a function of the temperature indicate that the materials are ferromagnetic 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: Materials Science, Chemical Engineering, California Institute of Technology, Pasadena, California; 2NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland.

Many doped perovskite oxides including BaCeO3, BaZrO3, SrCeO3 and SrZrO3 have received recent attention as proton conductors.

Introduction of a trivalent dopant onto the quadrivalent 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 our ongoing program to develop such materials, we have examined the properties of SrPrO3. Based on an analogy to compounds such as SrCeO3 and BaCeO3 acceptor doped SrPrO3 might be anticipated to adsorb atmospheric H2O and exhibit good proton conductivity, whereas the variable valence of the Pr ion, between 3+ and 4+ oxidation states, might be anticipated to be high in electronic conductivity. In addition, SrPrO3 and the analogous perovskite BaPrO3 are unusual in their ability to host Pr primarily (if not entirely) in a +3 oxidation state, and have therefore been of interest for their magnetic properties. A careful combination of chemical analysis, thermal gravimetric analysis and neutron powder diffraction experiments has revealed that the single phase composition with the perovskite structure type in the Sr-Pr-O system has stoichiometry (Sr0.95Pr0.05O2.95±0.02)Pr2O3. Thus, the compound contains excess Pr relative to the Sr content, but is overall cation deficient. It crystallizes in a GdFeO3-type orthorhombic structure, space group Pbnm, with lattice parameters a = 5.98800(17), b = 6.12136(17), c = 8.54888(24) Å and Z = 4 at 300 K.

The magnetic properties confirm the presence of a bulk (granular) conductivity at 36 0C of 5.2 x 10-8 S cm-1 with an activation energy for charge transport of 0.26 eV. Unlike perovskites in general, it is a n-type as well as 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. Praajesh Guptaaram, Mark S. Williamsen and Shishir K. Ray; Physics, Univ Wisconsin Milw, Milwaukee, Wisconsin.

Complex oxides are 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 systems 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 zone melt 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 of the CZ technique is the ease of studying its growth, 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 molten zone. The growth 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 compensate 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 RuO. We find that such high 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 tube 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

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. Spherical BaTiO3 samples with a diameter ca. 2mm were successfully synthesized by containerless processing by electrostatic and aerodynamic levitation facilities. A single-crystral hexagonal BaTiO3 was grown at an undercooling of about 50 K and a polycrystalline perovskite BaTiO3 was crystallized at an undercooling of about 700 K. Dielectric constants of the single-crystal hexagonal BaTiO3 was affected significantly by oxygen deficient. A stoichiometric hexagonal BaTiO3 showed a permittivity of about 100 at room temperature, whereas the oxygen-deficient hexagonal BaTiO3 showed a permittivity higher than 100000 with a low component tantalate 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₋ₓ (Me=Ca, Sr, Ba) Prepared by Mechanochemical Route. Lyubov Alexandrovna Isupova¹, Irina Sergeeva Yakovleva¹, Sergei Vasilevich Tsybulya¹, Alexander Chernysh¹, Alexei Rogov¹, Galina Litvak¹, Yuri Pavlyukhin² and Vladislav Sadykov¹. ¹SB RAS, Borevsk Institute of Catalysis, Novosibirsk, Russian Federation; ²SB RAS, Solid State Chemistry Institute, Novosibirsk, Russian Federation.

La₁₋ₓCaₓFeO₃₋ₓ and La₁₋ₓ(Sr/Ba)ₓFeO₃₋ₓ perovskite systems are known to be characterised by different types of magnetic ordering 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 study 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°C. X-ray, Mössbauer spectroscopy, TPR in H₂ and TA were used for samples characterisation. According to X-ray analysis homogenous 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 structures) were formed in the samples in the case of Sr and Ba substituted perovskites. Formations of Fe³⁺ cations in T0, P, and O coordinations were revealed only for samples with x<0.6. No Fe⁴⁺ cation was detected in Ca-substituted perovskites, only Fe⁴⁺ cations in O1, O2, P and T coordinations were revealed. A formation of new low-bounded oxygen forms was detected by TPR in H₂. The total calculated TPR data was higher than that obtained from Mössbauer data, that may be a result of formation not only of Fe⁴⁺ or oxygen vacancy to maintain the electroneutrality of substituted with Me perovskites, but of the low charge oxygen anions as well. Probably such low charge oxygen anions are formed during recrystallisation of vacancy high-temperature solid solutions under cooling in the air.

9:45 AM FF10.6 Alkoxy 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 [Mn₉O₅(μ₄-O)(μ₄-H),,O]·moleOH. 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 alternative routes to the technologically interesting compounds. In sol-gel processing the advantage of alkoxide precursors compared to e.g. acetyl-acetonates, acetics or acid complexes, is that alkoxides yield more homogeneous and pure gels, thereby allowing for varying gelation and low temperature conversion of the gels to oxide. We have used [Mn₂O₅(μ₄-O)(μ₄-H),,O]·moleOH 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 spintronic devices. To gain detailed knowledge about the sol-gel processes the phase development from sol 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 (≥500°C). The main differences in the phase evolution were seen in the 300-600°C range, where the formation of single-phase phases seems to dependently reduce the elemental homogeneity. The observed inhomogenieties 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 CO₂ from the air, but contained little of it, and can therefore be described as hydrated oxo-carbonates. The phase development studies indicated that when starting from an amorphous precursor material of Mn₉O₅(μ₄-O)(μ₄-H),,O, small amounts of amorphous carbonate impurities even above 600°C. This shows that important role of for other sol-gel and decomposition methods, as combustion of organic components can produce CO₂ that might be absorbed by to form unwanted phases -not always detectable by XRD. It is thus of great importance to ensure complete decomposition compounds, which might affect the homogeneity and the properties of the material.

10:00 AM FF10.7 Crystal Physics and Physical Properties of 2:1 Ordered Perovskites. Michael Lusfate² and Anna Lisonova². ²Institute for Materials Science (NIMS), Tsukuba, Japan.

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 Ba₃Ti₄O₁₂ and Ba₃Zr₄O₁₂. Substitution of Ni⁴⁺ for Ti⁴⁺ results in isomorphic compositions with significantly different physical properties, including a higher dielectric constant, more positive temperature coefficient of resonant frequency, and a smaller Q×f value. S-air is therefore of great interest to study the effect of the type and content of dopant (Ba, Sr) 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°C. X-ray, Mössbauer spectroscopy, TPR in H₂ and TA were used for samples characterisation. According to X-ray analysis homogenous 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 structures) were formed in the samples in the case of Sr and Ba substituted perovskites. Formations of Fe³⁺ cations in T0, P, and O coordinations were revealed only for samples with x<0.6. No Fe⁴⁺ cation was detected in Ca-substituted perovskites, only Fe⁴⁺ cations in O1, O2, P and T coordinations were revealed. A formation of new low-bounded oxygen forms was detected by TPR in H₂. The total calculated TPR data was higher than that obtained from Mössbauer data, that may be a result of formation not only of Fe⁴⁺ or oxygen vacancy to maintain the electroneutrality of substituted with Me perovskites, but of the low charge oxygen anions as well. Probably such low charge oxygen anions are formed during recrystallisation of vacancy high-temperature solid solutions under cooling in the air.

10:45 AM FF10.8 Oxygen Nonstoichiometry and Related Physical Properties of Various Functional Layered Oxides. Jun-ichi Shimoyama¹, Yui Yokota¹, Masahiro Shiraki¹, Yukinori Fujiwara² and Koji Kishio¹. ¹Department of Superconductivity, University of Tokyo, Tokyo, Japan; ²PRESTO-JST, Kawaguchi, Japan.

In the past two decades, particularly after discovery of 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. Various functional layered oxides were investigated their physical properties systematically evaluated as a function of oxygen content in the present study. Thermogravimetric measurements were performed using electro-microbalances (CAHN-1000H and SHIMADZU TGA-418) for sintered bulk samples of various transition metal oxides having layered crystal structures. For a famous CMR material (La,Sr)Mn₂O₄, very small oxygen nonstoichiometry with n ≈ 0.6 at 678°C was observed. However, both excess oxygen and oxygen deficiency were found to strongly affect the CMR properties. Samples with stoichiometric oxygen composition, n = 2, obtained by rapid quenching from 1270°C in air, exhibited the sharpest ferromagnetic transition. On the other hand, ferromagnetic transition disappeared in slightly oxygen deficient sample with y = 0.0.9. In the case of Ca₃Mn₂O₇ oxides showing excellent thermoelectric property 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, (Ca₂CoO₄)ₓ(Fe₂CoO₄)ₓ with y = 0.1. In this compound, thermoelectric properties are degraded by generation of oxygen vacancies at high temperatures above ~600K, 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 Tantulate Single Crystals. Sarveswaran Ganesamoorthy, Nakamura Masaru, Takekawa Shunji, Sonu Kumaragurubaran, Terabe Kazuya and Kitamura Kenji; Opto 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 acoustoelectric, electro-optic and waveguide 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 (SELT) 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 what which will increase the transverse area for transmission light so that the output power can be increased greatly. However, the domain switching behavior of SLT crystals is not completely understood. Data on the rate of applied field dependence of Ec is 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(1 mol%)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(1 mol%)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 up to 500 V/s there is almost a linear rise in the coercive field value in MgSLT samples. Transient current peaks were found to be sharp for pure samples in comparison to MgSLT 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 Lead-rich melt (50 mol%) exhibit 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 non-stoichiometry in the samples.

11:15 AM FF10.10 Sintering and Electromechanical Behavior of Ba-Zr Codoped Sodium Bismuth Titanate by Wet Chemical Route, Andrey Soukhajak 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 or 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.


Ceramics based on compositions near the morphotropic phase boundary (MPB) in perovskite PbTiO3 solid solution systems dominate the market of ferroelectric and piezoelectric materials due to their superior response at those compositions. Many PbTiO3 solid solutions containing an MPB have been reported, both in simple (x)PbTiO3 - (1-x)PbM'O3-type (e.g. PbZr12Ti2O33), complex (x)PbZrO3 - (1-x)Pb(M'M')O3-type, and more recently (x)Pb(Mn1/2Ti,Sn1/2)O3-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 PbTiO3 based solid solution systems. This relationship is then successfully used to predict the location of the MPB in new examples of (x)PbTiO3 - (1-x)Bi(M'M')O3-type systems (M' = Ni2+, Mn2+, Fe3+ and M'' = Y3+, Sn4+, Zr4+, Ce4+). 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 PbTiO3 based MPB systems, and unreported end members for PbTiO3 solid solutions, in particular systems with low tolerance factors based on mixed A-site chemistries such as (Pb1/2Ti1/2)M''O3, are also explored.

11:45 AM FF10.12 Ba2Ti2O5 - A Ternary Compound in Disguise: Crystal Chemistry and Properties of Ba2Ti2O5, A. Pandey, A. Vandersley, T. Siegrist, and R.S. Roth; 1Ceramics Division, NIST, Gaithersburg, Maryland; 2Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey.

Early phase equilibrium studies of the binary BaO-TiO2 system revealed the existence of the so-called barium polytitanate phases that form between BaTiO3 and TiO2. Some of these phases exhibited electrical properties that resulted in their ensuing commercial importance as ceramic dielectric resonators for the earliest cellular base transceivers. The compound Ba2Ti2O5 was first reported in 1998; however, several subsequent studies of the Ba2O2Ti2O5 system failed to confirm its formation. Eventually, it was realized that a third component (sometimes unintentionally added) is required to stabilize the crystal structure. A detailed description of the structure and properties of this phase formed by the addition of Fe2O3 will be presented.