

SYMPOSIUM D
Perovskite Materials

April 1 – 5, 2002

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* Invited paper

SESSION D1:
COMPOSITION—STRUCTURE-PROPERTIES
RELATIONS I

Chair: Alexandra Navrotsky
Monday Afternoon, April 1, 2002
Golden Gate A2 (Marriott)

1:30 PM *D1.1

HOW THE "A" CATIONS CONTROL PEROVSKITE
STRUCTURES AND PROPERTIES. J. Paul Attfield, University of
Cambridge, Cambridge, UNITED KINGDOM.

The properties of many ABO₃ perovskite materials result primarily from the B cations, but are tuned by the cation(s) at the A sites. Notable examples are ferroelectric titanates, magnetoresistive manganites, and layered superconducting cuprates. The A cation control of these properties can be described through a simple ionic approach by considering the sizes and charges of the A cations. The size control is approximated well by the mean A cation radius, equivalent to the traditional perovskite tolerance factor, and the size variance which describes the mismatch in ionic radii. Studies in recent years have shown that the latter term is extremely significant; ferroelectric, ferromagnetic, superconducting and structural transition temperatures all vary linearly with the size variance. A variance vs. size plot defines the "chemical window" which enables property variations to be displayed usefully. The control of phase separation phenomena in manganite perovskites and 1/8 doped La₂CuO₄ type materials has also been investigated.

2:00 PM D1.2

CHARGE TRANSFER, LATTICE INSTABILITIES AND
PRECURSOR EFFECTS IN PEROVSKITE OXIDES.
Annette Bussmann-Holder, Max-Planck-Institute for Solid State
Research, Stuttgart, GERMANY.

Perovskite oxides are known to undergo various instabilities which are related to metal-insulator transitions, polar instabilities, magnetic ordering and superconductivity. Common to all perovskite oxides is the covalent transition metal d - oxygen ion p bonding, which originates from the local instability of the oxygen ion 2p₆ configuration. This instability can be best accounted for by introducing a local double well potential in the electron-phonon interaction at the oxygen ion lattice site, which corresponds to density - density - multiphonon interactions. Consequences of this modelling are that small charge transfers from the oxygen ion to the transition metal site induce enormous softenings of polar transverse optic lattice modes, which e.g. trigger the ferroelectric instabilities observed in some perovskite oxides. The coupling of these modes to acoustic modes induces giant anomalies in the elastic constants, which appear well above a structural instability and are related to precursor effects. Very specifically it is observed that charge ordering may take place which results in an incommensurate dynamical charge density wave formation. Applications to various perovskite systems are presented together with discussions on the isotope effects on the corresponding phase transitions.

2:15 PM D1.3

SYNTHESIS AND CHARACTERIZATION OF THE FIRST 1:2
ORDERED PEROVSKITE RUTHENATE. Job T. Rijssenbeek,
Kenneth R. Poeppelmeier, Northwestern University, Dept. of
Chemistry, Evanston, IL; Sylvie Malo, Vincent Caignaert, Université
de Caen, Laboratoire CRISMAT-ISMRA, Caen, FRANCE; Takashi
Saito, Masaki Azuma, Mikio Takano, University of Kyoto, Institute
for Chemical Research, Uji, JAPAN.

Perovskite-like mixed metal ruthenates are of interest owing to their varied magnetic properties which are heavily dependent on the ordering of the transition metals. We report the synthesis and structural characterization of Sr₃CaRu₂O₉. The structure is characterized by a 1:2 ordering of Ca²⁺ and Ru⁵⁺ over the six-coordinate B-sites of the perovskite lattice akin to the well known dielectric Ba₃ZnTa₂O₉ (BZT). The serious bond length mismatch between Ca-O and Ru-O leads to significant tilting, twisting and deformation of the metal-oxygen octahedra. Sr₃CaRu₂O₉ is the first example of this structure-type to include a majority metal with d electrons (Ru(V), d³). The relationship of this material to the n=1 Ruddlesden-Popper type Sr_{1.5}Ca_{0.5}RuO₄ (i.e., Sr₃CaRu₂O₈) highlights the dramatic effects of the ruthenium valence on the resultant structure. Remarkably, each of these structures can be quantitatively converted to the other by the appropriate choice of reaction temperature and atmosphere. Preliminary electronic and magnetic data reveal that this material, with two non-equivalent sites for ruthenium, is an insulator and a weak ferromagnet. X-ray, electron, and neutron diffraction; and magnetic and resistivity results will be presented.

2:30 PM D1.4

INFLUENCE OF TI-DOPING ON STRUCTURE AND PHYSICAL
PROPERTIES OF Sr₂RuO₄. Stefan G. Ebbinghaus, Anke
Weidenkaff, Armin Reller, University of Augsburg, Solid State
Chemistry, Augsburg, GERMANY; Robert J. Cava, Princeton
University, Department of Chemistry, Princeton, NJ.

Since the discovery of superconductivity in Sr₂RuO₄ this compound has been studied extensively. Although its low critical temperature of T_c = 1.5 K makes Sr₂RuO₄ uninteresting for technical applications, the academic interest in this material is high because to date it is still the only non-cuprate superconductor with the same crystallographic structure as (La,Sr)₂CuO₄. This analogy offers the opportunity to gain a more detailed understanding of the mechanism of superconductivity in oxides. Unfortunately, Sr₂RuO₄ is very sensitive to impurities and its superconductivity is easily suppressed upon doping. This sensitivity, on the other hand, opens the possibility to study the effect of dopants on the electronic and magnetic structure of the ruthenium-ions. We present a systematic study on the influence of the Ti-content on the crystallographic structure and physical properties of Sr₂Ru_{1-x}Ti_xO₄. Polycrystalline samples covering the entire composition range 0 ≤ x ≤ 1 were prepared by conventional solid state reactions. Their structure was solved by XRD Rietveld refinements. With increasing Ti-content, a localized magnetic moment evolves, showing a pronounced zfc/fc-splitting at low temperatures. At the same time the resistivity increases by several orders of magnitude and changes from a metallic to a semi-conductor type behavior. Additionally, we managed to grow single crystals with x = 0, 0.1, and 0.2 by the floating zone technique. X-ray structure analysis as well as magnetic and resistivity measurements for these crystals are also presented. As expected from the layered crystal structure, a strong anisotropy of the physical properties is observed.

3:15 PM *D1.5

STRUCTURE-PROPERTY RELATIONSHIPS IN PEROVSKITES.
Peter D. Battle, Inorganic Chemistry Laboratory, Oxford University,
Oxford, UNITED KINGDOM.

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

3:45 PM D1.6

SYNTHESIS, CRYSTAL CHEMISTRY AND ENERGETICS OF
NaTi_xNb_{1-x}O_{3-0.5x} PEROVSKITES. Hongwu Xu, Alexandra
Navrotsky, Dept. of Chemical Engineering & Materials Science,
University of California, Davis, CA; M. Lou Balmer, Yali Su,
Environmental Molecular Sciences Laboratory, Pacific Northwest
National Laboratory, Richland, WA; Tina M. Nenoff, May D. Nyman,
Catalysis & Chemical Technologies, Sandia National Laboratories,
Albuquerque, NM.

NaNbO₃-based perovskites are of considerable interest because of their unique combination of superior electrical and mechanical properties. Using the sol-gel method, we have synthesized a series of Ti-substituted niobates, NaTi_xNb_{1-x}O_{3-0.5x} (0 ≤ x ≤ 0.3), in which a portion of Nb⁵⁺ cations are replaced by Ti⁴⁺ and the charge is balanced by the creation of O²⁻ vacancies. Rietveld analysis of X-ray/neutron diffraction data reveals that the structure becomes more cubic-like with increasing Ti content, thereby inducing a series of compositionally driven transitions that are analogous to those for NaNbO₃ at elevated temperatures. Drop-solution calorimetric measurements with the sodium molybdate solvent at 974 K show a

destabilizing effect of the Ti→Nb substitution on the structure. On the other hand, the enthalpies of the transitions across the series appear to be rather small and are within the uncertainties of our data.

4:00 PM D1.7

SYSTEMATICS IN THE PHASE CHEMISTRY AND THERMO-CHEMISTRY OF LEAD OXIDE-BASED PEROVSKITES.

W.T. Petuskey, R. Mangham, Arizona State University, Dept of Chemistry & Biochemistry; P. Majhi, C. Wang, S.K. Dey, Dept of Chemical & Materials Engineering and the Science and Engineering of Materials Program, Tempe, AZ.

Systematic trends are presented on the phase chemistry of lead oxide-bearing chemical systems important to dielectric perovskite compositions. Experimentally, we have been evaluating the PbO-MgO-Nb₂O₅-TiO₂, PbO-BaO-ZrO₂ and PbO-SrO-TiO₂ systems. Moreover, we have been measuring the thermodynamic activities of lead oxide for selected compositions. These results are combined with those of other investigations to examine the thermodynamic stability of the perovskite phases in context of the phases in the immediate, surrounding composition space. The crystal chemistry and composition range of the pyrochlore phase is discussed as it affects the stability of the perovskite. Thermochemical stability with respect to oxygen partial pressure and lead oxide vapor pressure and correlations with measured electrical properties are also presented.

SESSION D2: EARTH'S PEROVSKITES I - EXPERIMENTS

Chair: Raymond Jeanloz
Tuesday Morning, April 2, 2002
Golden Gate A2 (Marriott)

8:00 AM *D2.1

PROPERTIES OF SILICATE PEROVSKITES RELEVANT TO EARTH'S INTERIOR. Raymond Jeanloz, Kanani Lee, and

Sang-Heon Shim, Dept. Earth and Planetary Science, University of California, Berkeley, CA; Wendy Panero, Dept. Geological Sciences, University of Michigan, Ann Arbor, MI.

The geophysical importance of silicate perovskites is highlighted by 1) the observation from high-pressure experiments that at the condition of the Earth's lower mantle all of the primary minerals of the outer mantle, individually as well as in combination, transform to an assemblage dominated by (Mg, Fe)SiO₃ orthorhombic perovskite; and 2) the recognition that seismologically observed density and elastic-wave velocities of the lower mantle match those of the perovskite-dominated assemblage to within ~2-5%. As the lower mantle (670-2900 km depth, spanning pressures of 24-136 GPa) represents more than 60 percent (atomic) of the Earth's interior, orthorhombic-perovskite (Mg, Fe)SiO₃ is inferred to make up nearly half of the entire planet. Experiments of the past 20 years reveal the following properties for orthorhombic-perovskite (Mg, Fe)SiO₃: $K_{0T} = 263.0 (\pm 3.0)$ GPa, $K'_{0T} = 3.9 (\pm 0.5)$, $\mu_0 = 177.0 (\pm 2.0)$ GPa, $\alpha_0 = 2.4 (\pm 0.4) \times 10^{-5}$ K⁻¹, $\alpha_{0HT} = 4.9 (\pm 0.9) \times 10^{-5}$ K⁻¹, $\alpha_{HTP} = 3.0 (\pm 0.6) \times 10^{-5}$ K⁻¹, $\gamma_0 = 2.0 (\pm 0.5)$, $q_0 = 3.0 (\pm 1.0)$ where K, μ , α , γ and q are the bulk modulus, shear modulus, volumetric thermal expansion coefficient, Grüneisen parameter and its logarithmic volume derivative; prime indicates pressure differentiation, and subscripts 0, T, 0HT and HTP indicate ambient, isothermal, zero-pressure high-temperature (1000 ± 200 K), and high-pressure high-temperature (25 ± 5 GPa, 1500 ± 300 K) conditions, respectively. The properties of impure phases are of crucial importance for geophysical applications. Thus, it is significant that the above results are supported by studies on natural rock samples characterized at lower-mantle conditions. We find that Fe-, Al- and Ca-substitution into MgSiO₃ increases the unit-cell volume but otherwise does not significantly change the 300 K equation of state of orthorhombic perovskites created from natural samples. The combined results imply that the dynamics, hence long-term evolution, of the Earth's mantle are more complex than has been assumed by much of the geophysical community.

8:30 AM D2.2

ENERGETICS OF ALUMINUM SUBSTITUTION IN MgSiO₃ PEROVSKITE. Alexandra Navrotsky, Hiroshi Kojitani, Mirko

Schoenitz, University of California, Davis, Department of Chemical Engineering and Materials Science, Davis, CA; Jianzhong Zhang, SUNY-Stony Brook, Mineral Physics Institute, Stony Brook, NY; Raymond Jeanloz, University of California, Berkeley, Department of Earth and Planetary Sciences, Berkeley, CA.

MgSiO₃ - rich perovskite is expected to dominate the Earth's lower mantle (pressures >25 GPa), with iron and aluminum as dopants. The substitution of trivalent ions, M³⁺, may occur by two competing mechanisms where A refers to the control γ - coordinated site and B to the octahedral site: (1) $Mg_A + Si_B = M_A + M_B$ (2) $Si_B = Al_B +$

0.5 (vacancy)_O. The first (stoichiometric or Tschermakitic) substitution is favored along the MgSiO₃ - Al₂O₃ join, or when excess SiO₂ (stishovite) is present. The second (defect or Brownmilleritic) may be favored when the system is saturated in MgO, with magnesiowustite (Mg, Fe) O as a buffering phase, as is the case for the mantle. Phase equilibrium and synthesis studies show that both substitutions can occur, and reaction (2) is more prevalent along the MgSiO₃ - MgAlO_{2.5} join. Lattice parameters associated with the two substitutions differ slightly. Oxide melt solution calorimetry can be used to compare the energetics of both substitutions. The reaction 0.95 MgSiO₃ perovskite + 0.05 Al₂O₃ (corundum) = Mg_{0.95}Al_{0.10}Si_{0.95}O₃ (perovskite) has an enthalpy of essentially zero, while the reaction 0.90 MgSiO₃ (perovskite) + 0.10 MgO (rocksalt) + 0.05 Al₂O₃ (corundum) = MgSi_{0.9}Al_{0.1}O_{2.95} has a small positive enthalpy of about 10 kJ/mol. Configurational TΔS terms play a role in both substitutions. The significance of these energetics for silicate perovskite in the Earth is discussed.

8:45 AM D2.3

OXYGEN VACANCIES IN PEROVSKITE AND RELATED STRUCTURES: IMPLICATIONS FOR THE LOWER MANTLE.

Catherine McCammon, Falko Langenhorst, Ulrich Blass, Friedrich Seifert, Bayerisches Geoinstitut, Univ Bayreuth, GERMANY; Ross Angel, Dept Geological Sciences, Virginia Tech, Blacksburg, VA; Ana Isabel Becerro, ICMSE, Sevilla, SPAIN; Stefan Lauterbach, Peter van Aken, TU Darmstadt, Darmstadt, GERMANY.

The physical and chemical properties of lower mantle silicate perovskites can be influenced by the substitution of trivalent cations in the crystal structure through a mechanism involving the creation of oxygen vacancies. We have performed a detailed study of the model system calcium titanate perovskite-brownmillerite and examined the role of oxygen vacancies in determining physical properties, including the influence of short and long range ordering on transport properties. Results suggest that oxygen vacancies are isolated and randomly distributed when the concentration of vacancies is low. With increasing vacancy concentration or decreasing temperature, vacancies cluster into chains of increasing length, eventually becoming infinitely long and arranged in planes with ordered sequences of octahedral and tetrahedral layers. Conductivity measurements show a dramatic decrease in ionic conductivity at the transition from disordered to ordered oxygen vacancies. A similar substitution mechanism has been inferred for trivalent iron and aluminium in lower mantle magnesium silicate perovskite. Our data show evidence for substitution of a brownmillerite-type component. Previous studies have already shown significant changes in the elastic and transport properties upon substitution of minor amounts of aluminium, which has potential implications for the interpretation of geophysical data. We have also focused attention on the substitution of iron in calcium silicate perovskite, and initial results show an intermediate phase where trivalent iron is incorporated into the structure through a defect mechanism. Our experiments have evolved to include multiphase assemblages to model the lower mantle, where major element compositions, including the valence state of iron, can be determined for all phases with a spatial resolution on the scale of nanometres. Results provide insight into the significant effects that substitution of minor amounts of trivalent elements can have on lower mantle physics and chemistry.

9:00 AM *D2.4

SILICATE PEROVSKITES AT HIGH PRESSURES AND TEMPERATURES. Russell J. Hemley, Jie Li, Viktor V. Struzhkin, James A. Van Orman, Yingwei Fei, and Ho-kwang Mao, Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC.

The Earth's lower mantle constitutes more than half of the Earth's interior and consists predominantly of (Mg,Fe,Al)SiO₃ perovskite. We review recent studies of the transformations, structure, defects, oxidation state, and electronic properties of magnesium-rich silicate perovskites at high pressures and temperatures. Recently, the $P - T$ boundaries associated with the transition from upper mantle phases to perovskite have been the subject of debate. We examine the extent to which $P - T$ calibration in laser-heated diamond cell experiments and multi-anvil presses (e.g., thermocouples) can explain these discrepancies. There is now increasing evidence that silicate perovskites may be non-stoichiometric, with significant cation and/or oxygen vacancies similar to perovskite-based ceramics. We have examined the question of stoichiometry, beginning with the MgSiO₃ end-member using powder x-ray and neutron diffraction. The oxidation state, site occupancy, and spin state of iron in the silicate perovskite have significant effects on physical properties of the material. A number of methods can be used to study the behavior of the iron in the structure; we review recent studies using Mössbauer spectroscopy, nuclear resonance forward scattering, x-ray emission spectroscopy, and electrical conductivity. The results are important for understanding the state of the lower mantle and shed light on the behavior of the perovskite family of materials in general.

9:30 AM D2.5

ELASTIC PROPERTIES OF OXIDE PEROVSKITES. Nancy Ross, Dept of Geological Sciences, Virginia Tech, Blacksburg, VA; Tracey D. Chaplin, Dept of Chemistry, University College London, London, UNITED KINGDOM.

Perovskite materials have a flexible structural framework capable of accommodating an extremely wide range of chemical compositions. Substitution of different components may have large effects on the elastic properties of perovskites as shown by Zhang and Weidner (Science, 1999), who found that silicate perovskite containing 5 mol% Al_2O_3 is 10% more compressible than pure MgSiO_3 . These large physical effects for relatively small amounts of cation substitution not only raise questions as to the mechanism of cation substitution in MgSiO_3 perovskite, but also raise questions about the effect of cation substitutions on elastic properties in perovskites in general. We have measured the elastic properties of number of oxide perovskites and related phases using high-pressure single-crystal X-ray diffraction. All perovskites studied have orthorhombic $Pbnm$ symmetry and do not display any phase transitions between room pressure and 10 GPa. End-member perovskites studied include Ca-perovskites and Gd-perovskites that show the effect of substituting cations (such as Ge, Ti, Sn, Zr, Al, Fe^{3+}) in the octahedral framework. High-pressure studies of aluminate perovskites show the effect of substituting extra-framework cations (such as Sc, Y, Gd) in the dodecahedral sites. The trends in elasticity are presented and discussed in terms of the distortion of the framework, the bonding of the cation in the dodecahedral site, and the possible compression mechanisms at high pressure. We compare these results with recent studies of phases related to perovskites, including protonated octahedral framework structures and defect perovskites.

10:15 AM *D2.6

ELASTIC AND PLASTIC PROPERTIES OF EARTH PEROVSKITES. Donald J. Weidner, Baosheng Li, Jihua Chen, Jianzhong Zhang, Mineral Physics Institute, State University of New York at Stony Brook, Stony Brook, NY.

Silicate perovskites are the dominant phases of the Earth's lower mantle, making them the most abundant minerals in the Earth. Here we report the polycrystalline elastic properties of the elastic properties as a function of pressure, temperature, and composition for these materials. In addition, we report the rheological properties for temperatures up to 1100K for the (Mg,Fe) silicate perovskites. The elasticity data are obtained on polycrystalline samples for both Ca-silicate perovskite and for Mg-silicate perovskite with and without Al doping. The Ca-silicate perovskite must be synthesized in the same experimental run as the ultrasonic measurements since it cannot be pressure quenched. The experiment was carried out at a synchrotron so that the length and the phase of the created sample could be precisely defined. In general, we find that the elastic moduli for the Mg endmember are highest and that a small amount of Al has a significant effect on the elastic properties. Plastic behavior is defined by the broadening of x-ray diffraction peaks for (Mg,Fe) silicate perovskites. We find that Fe has a small but significant effect on the strength of this material. The most significant finding is that this material remains very strong to temperatures up to 1100K suggesting that thermally activated processes do not dominate the rheology until at least 900K.

10:45 AM D2.7

HIGH PRESSURE AND TEMPERATURE STABILITY OF PEROVSKITE. Surendra Saxena, Zongwu Wang, Peter Liermann, Florida International University, Center for the Study of Matter at Extreme Conditions, Miami, FL.

Experimental studies of magnesiowüstite (Mg,Fe)O using x-ray in multi-anvil cell to pressures of 30 GPa [1] and in diamond-anvil cells to high pressures [2,5] show a wide range of pressure-temperature stability for this phase. However, perovskite may break down to its component oxides. We studied the stability of perovskite with several new experiments, designed to cover a range of cell designs, sample preparation methods and heating techniques. Our results show that the following important reactions take place in the lower mantle starting at a depth between 1600 to 2000 Km: $(\text{Mg,Fe})\text{SiO}_3 = (\text{Mg,Fe})\text{O} + \text{SiO}_2$ and $(\text{Mg,Fe})\text{O} = (\text{Mg,Fe})\text{O} + (\text{Fe,Mg})\text{O}$ (formation of two solid solutions, one rich in magnesium and the other in iron). The oxide rich domains may form in the lower mantle explaining the seismic tomographic observations of heterogeneity. The FeO component may react with the iron in the outer core and act as a source of oxygen. Some serious difficulties in studying solids at these extreme conditions result in contradictions [4]. A major problem is heating a solid homogeneously for long durations for kinetically slow reactions to occur at high pressures. A second problem is the poor x-ray data, which renders the data analysis very difficult [5]. Both these problems have been addressed in our new experiments. 1.

Funamori et al., J. Geophys. Res., 101, 8257(1995). 2. Saxena, S.K. et al., Amer. Mineral., 84, 226 (1999). 3. Meade, C., H.K. Mao, and J. Hu, Science 268, 1743 (1995). 4. Boehler, R., Earth Planet. Sci. Lett., 185 (1992); Kesson, S.E., J.D. Fitz Gerald, J.M. Shelley, Nature 393,252 (1998); Serghiou, G., A. Zerr and R. Boehler, Science, 280,2093 (1998). 5. Shim SH, Duffy TS, Shen GY, Science, 293 (5539): 2437-2440, 2001.

11:00 AM D2.8

SILICATE PEROVSKITES (MgSiO_3 , CaSiO_3) IN EARTH'S LOWER MANTLE - THEIR STABILITY, CRYSTAL STRUCTURE, AND EQUATION OF STATE. Sang-Heon Shim, Univ of California, Dept of Earth and Planetary Science, Berkeley, CA; Thomas S. Duffy, Princeton Univ, Dept of Geosciences, Princeton, NJ; Guoyin Shen, Univ of Chicago, CARS, Chicago, IL.

The perovskite phases of MgSiO_3 and CaSiO_3 are dominant constituents of Earth's lower mantle (25–120 GPa, 1800–2600 K). Thus, their physical properties and equations of state are crucial not only to interpret the seismic observations of the lower mantle but also to understand the material transport, chemistry, and evolution of the lower mantle. The recent availability of a brilliant micro X-ray beam at third generation synchrotron radiation sources and the development of high P–T experimental techniques enable us to study the silicate perovskite phases at in situ lower mantle conditions. We performed energy dispersive X-ray diffraction measurements for MgSiO_3 and CaSiO_3 perovskites using double sided laser heated diamond anvil cell at the GSECARS sector of the Advanced Photon Source at Argonne National Laboratory. Samples were compressed in diamond anvil cells together with a chemically inert pressure transmitting medium, Ar, and a pressure calibrant, Pt. Stability of these materials was confirmed to 2300-km depth of Earth's interior. While major diffraction features of perovskite structure were observed to 108 GPa for MgSiO_3 , an additional new diffraction feature was found above 88 GPa. Among other possibilities, we showed that this new feature can be caused by a phase transition from an orthorhombic phase ($Pbnm$) to monoclinic ($P2_1/m$), orthorhombic ($Pmnm$), or tetragonal ($P4_2/nmc$) phase. Although further investigation is desirable, if the feature is indeed from a phase transition, this has an important implication in the lower mantle dynamics. A recent first principles calculation proposed the stability of a tetragonal structure of CaSiO_3 perovskite. However, we confirmed a cubic structure ($Pm3m$) to 98 GPa and 2400 K with a resolution of 0.7% in unit-cell parameter. Phase boundaries in MgO– SiO_2 system are also important to understand the seismically observed discontinuities in Earth's mantle. We showed that the Mg_2SiO_4 spinel = MgSiO_3 perovskite + MgO phase transition occurs at 660-km depth condition where 5–7% seismic velocity jump is observed. This provides a strong constrain on the chemistry of the transition zone in the mantle (410–660-km depth). P–V–T equation of state for CaSiO_3 perovskite is determined at 11–68 GPa and 1300–2380 K. The accuracy of the static compression curve is confirmed by monitoring differential stresses in the diamond cell. Thermal properties at high pressures are also determined by inverting P–V–T measurement result. A full set of parameters for the Birch-Murnaghan-Debye EOS were obtained for CaSiO_3 perovskite: $K_{0T} = 236(4)$ GPa, $K'_{0T} = 3.9(2)$, $\gamma_0 = 1.92(5)$, $q = 0.6(3)$.

11:15 AM *D2.9

ELECTRONIC, MAGNETIC AND STRUCTURAL PROPERTIES OF THE RFeO_3 ANTIFERROMAGNETIC PEROVSKITES AT VERY HIGH PRESSURES. Moshe P. Pasternak, W. Xu, G. Kh. Rozenberg, School of Physics and Astronomy, Tel Aviv University, Tel Aviv, ISRAEL; R.D. Taylor, Los Alamos National Laboratory, Los Alamos, NM.

At ambient pressure the orthorhombic perovskites R - orthoferrites ($R = \text{La, Pr, Eu, Y, and Lu}$) exhibit very large optical gaps. These large-gap Mott insulators in which the $3d^5$ high-spin Fe^{3+} ions carry large local magnetic moments and orders antiferromagnetically at $T_N > 900$ K, undergo a structural, magnetic and electronic first-order phase transition in the 30-50 GPa range. As a result of the quasi-isostuctural volume reduction (3-5%) the HP phase T_N 's is reduced to 150K, the magnetic super-exchange interactions are drastically weakened, the charge-transfer gap is substantially reduced, and the magnetic sublattices are composed of high- and low-spin Fe^{3+} , the abundance of the latter increasing with pressure. A consequence of the P-dependent *spin crossover*, the HP phase bulk-modulus becomes inelastic. In the case of La and Pr, a "metal with moments" is formed at $P > 120$ GPa. The LuFeO_3 case is an exception, with a spin-crossover transition occurring as a result of a second order phase transition. Finally, based on the magnetic and electrical data a Mott diagram is established.

SESSION D3:
COMPOSITION—STRUCTURE-PROPERTIES
RELATIONS II

Chair: Bernard Raveau
Tuesday Afternoon, April 2, 2002
Golden Gate A2 (Marriott)

1:30 PM *D3.1

EXPLORING COMPOSITION-STRUCTURE-PROPERTY RELATIONSHIPS IN TRANSITION METAL OXIDE PEROVSKITES. Patrick Woodward, Michael Lufaso, Josh Goldberger, Hank Eng, Dept. of Chemistry, Ohio State University, Columbus, OH; and Ram Seshadri, Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore, INDIA.

Transition metal oxides which adopt the perovskite structure display a wide variety of interesting physical properties, including colossal magnetoresistance, superconductivity, mixed electronic-ionic conductivity, among others. These properties are very sensitive to changes in both the crystal structure and the fundamental properties of the constituent ions (electronegativity, ionic radius, etc.). I will describe our efforts to understand the composition-structure-property relationships in these materials in the following areas: (1) Development of the software package SPuDS to predict complete crystal structures of cubic and distorted perovskites from their composition, (2) Use of LMTO tight binding band structure calculations to predict the magnetic and electronic behavior of AMO_3 and A_2MMO_6 perovskites from the structures predicted by SPuDS, (3) The electronic, magnetic and structural properties of ASrMMO_6 perovskites (A = Sr, La; M = V, Mn, Fe; M = Mo, Ru), (4) Studies of the interrelationship between octahedral tilting distortions, cation-ordering and Jahn-Teller distortions about Mn^{3+} ions.

2:00 PM *D3.2

STRUCTURE-PROPERTY RELATIONSHIPS IN PEROVSKITE MATERIALS: FROM SUPERCONDUCTORS TO CERAMIC MEMBRANES. James D. Jorgensen, Materials Science Division, Argonne National Laboratory, Argonne, IL.

A remarkable variety of properties can be achieved in perovskite materials by varying the chemical composition and structure. In broad terms, the properties achieved are a result of competition between orbital ordering, charge ordering, and magnetic ordering. For example, in the superconductors based on chemically-substituted variants of the insulator BaBiO_3 , charge ordering can destroy metallic behavior (and superconductivity); the highest T_c is achieved by adding carriers in a way that avoids charge ordering (often described as a charge density wave in these systems). In colossal magnetoresistive (CMR) materials, charge ordering competes with magnetic ordering. In ceramic membrane materials, where the goal is to simultaneously achieve electronic and oxygen-ion conduction, one seeks to add carriers while avoiding charge ordering that would compete with both forms of conduction and maintaining a structure that has open paths for oxygen diffusion. The subtle competition between these three ordering phenomena can lead to very complex structural, and magnetic, phase diagrams, sometimes involving phase separation. When this complication is added to the fact that distortions of the perovskite structure can be very subtle, researchers are challenged with some perplexing problems in unraveling the behavior. Furthermore, recent work has emphasized that one must also understand the short-range structure, as well as the long-range ordered structure, in order to understand the underlying physics. This work is supported by the US Dept. of Energy, Basic Energy Sciences, contract No. W-38-109-ENG-38.

2:30 PM D3.3

AMORPHIZABILITY OF PEROVSKITE-STRUCTURE COMPOUNDS. Linn W. Hobbs, Bernhardt J. Wuensch, Department of Materials Science & Engineering, Massachusetts Institute of Technology, Cambridge, MA.

Irradiation-induced amorphization of ceramic compounds is a concern for high-level nuclear waste, actinide storage and transmutation, and ion implantation of electronic devices. The relative amorphizability of various compounds can be understood from an application of constraint theory to polytope connectivity in which the progressive destruction of connectivity constraints restores three degrees of translational freedom to polytope vertices and renders previously rigid structures topologically floppy. Perovskite structures are intriguing in that they comprise vertex-sharing octahedral units (e.g. $[\text{TiO}_6]$) arranged in the cubic ReO_3 structure, into the central interstice of which is stuffed a large cation (e.g. Ca). The vertex-sharing octahedra contribute only a small constraint (excess of one constraint over freedom per vertex). The problem is how to assess the additional contribution of the central cation to the connectivity constraints (face-sharing cube-octahedra, e.g. $[\text{CaO}_{12}]$), which is less than geometrical and depends on the chemistry. For example, isostructural

CaTiO_3 and KNbO_3 exhibit more than a factor of two difference in amorphizability under ion irradiation. The deviation from constraint theory predictions actually provides some useful insight into the role of chemistry in the structural stability of these compounds.

3:15 PM D3.4

TEMPLATED ASSEMBLY OF METAL-ANION ARRAYS WITHIN LAYERED HOSTS - SYNTHESIS AND CHARACTERIZATION OF NEW TRANSITION-METAL OXYHALIDE PEROVSKITES. Gabriel Caruntu, Liliana Viciu, Katina B. Theriot, Leonard Spinu, Weilie L. Zhou, and John B. Wiley, Department of Chemistry and the Advanced Materials Research Institute, University of New Orleans, New Orleans, LA.

Topotactic methods were used to prepare a series of new transition-metal-oxyhalide layered perovskites. Exchange reactions with metal halides and Dion-Jacobson-type perovskites allow for the formation of metal-anion arrays within a number of perovskite hosts. Structural and magnetic properties of these compounds will be presented and structure-property relationships will be discussed. Also, recent studies on new mixed oxyhalide systems will also be addressed.

3:30 PM *D3.5

SINGLE CRYSTAL GROWTH OF PEROVSKITES AND RELATED COMPOUNDS AT SEVERAL GPa. Masaki Azuma, Takashi Saito, Shintaro Ishiwata, Ikuya Yamada, Mikio Takano, Inst for Chemical Research, Kyoto Univ, Uji, Kyoto, JAPAN.

High-pressure (HP) synthesis is a powerful technique to search for new materials. A large number of perovskites and related materials such as high- T_c superconductors have been discovered with this technique. Generally speaking, however, it used to be almost impossible to obtain single crystals of these phases because of the lack of the information about the HP-HT (high temperature) reactions. Synchrotron X-ray powder diffraction enabled us to observe such reactions in a HP cell even when the samples are wrapped in gold or platinum capsules. Based on the *in-situ* observations of the formations, melting and the crystallizations of the target compounds, we are growing single crystals of the following oxides by means of flux methods using an in-house cubic anvil type HP apparatus. Details of the crystal growths and their physical properties will be reported.

1. HP phase of $(\text{VO})_2\text{P}_2\text{O}_7$: $S = 1/2$ one dimensional alternating exchange antiferromagnet with a spin gap.
2. PrNiO_3 : exhibits a metal-insulator transition at 135 K.
3. BiMnO_3 : known as quite rare ferromagnetic ferroelectric compound.
4. CaFeO_3 : with unusual Fe^{4+} ion which shows charge disproportionation to Fe^{3+} and Fe^{5+} below room temperature.
5. $(\text{Ca}, \text{Na})_2\text{CuO}_2\text{Cl}_2$: a high- T_c superconductor with chlorine instead of apical oxygen. It is an ideal compound for photoemission and STM measurements because a) easy to cleave (fresh CuO_2 plane is available), b) samples from the parent insulator to doped superconductors are available, c) there is no orthorhombic distortion at low temperature, d) it has no modulation.

4:00 PM D3.6

LOCAL ATOMIC STRUCTURE OF $(\text{BiSr})\text{FeO}_3$ FERROELECTRIC AND MAGNETIC OXIDES. Wojtek Dmowski, Alexander Mamchik, I-Wei Chen, Takeshi Egami, Univ. Pennsylvania, Philadelphia, PA.

We have examined structure of the $(\text{Bi}_x\text{Sr}_{1-x})\text{FeO}_3$ system, which shows unique combination of ferroelectric and magnetic properties¹. SrFeO_3 shows metallic conductivity $\sim 10^{-3} \text{ } \omega\text{cm}$ which suppresses Jahn-Teller distortion expected from formal $4+$ iron oxidation state. BiFeO_3 is ferroelectric with $T_c = 1110 \text{ K}$ and an antiferromagnet below 670 K^2 . This system provides unique opportunity to vary its ferroelectric and magnetic response by changing Bi/Sr content and oxygen stoichiometry. We have performed neutron TOF diffraction experiments for samples with $x = 0.9-0.1$. Data have been analysed using Rietveld refinement and the atomic pair distribution function method. Significant local displacements of Bi along 3 fold axis up to 0.65 \AA from the ideal crystallographic position are observed for all compositions. Fe atoms are displaced from the center of the oxygen octahedra even for Sr rich samples suggesting local polarization. We will discuss the implication of the structural effects on the ferroelectric/magnetic properties. 1. J.B. MacChesney, R.C. Sherwood and J.F. Potter, J. Chem. Phys. 41 (1965) 1907. 2. I. Sosnowska, T. Peterlin-Neumaier and E. Steichele, J. Phys. C 15 (1982) 4835.

SESSION D4: POSTER SESSION
PEROVSKITES - GENERAL

Chair: John Paul Attfield
Tuesday Evening, April 2, 2002
8:00 PM
Salon 1-7 (Marriott)

D4.1

STRUCTURE-PROPERTY RELATIONSHIPS IN HEXAGONAL PEROVSKITES. N.A. Jordan, P.D. Battle, J. Sloan, Inorganic Chemistry Laboratory, University of Oxford, Oxford, UNITED KINGDOM; S.H. Kilcoyne, P. Manuel, Department of Physics and Astronomy, University of Leeds, Leeds, UNITED KINGDOM; S. van Smaalen, M. Wunschel, Laboratory of Crystallography, University of Bayreuth, Bayreuth, GERMANY.

A wide range of structures based on mixed cubic and hexagonal stacking of AO_3 layers have been reported. We have now investigated the system $\text{BaIr}_x\text{Fe}_{1-x}\text{O}_3$. A rare 15R phase has been isolated for the $x = 0.3$, though, remarkably, compositions on either side of this exhibit the more common 6H modification. The compounds prepared ($x=0.2, 0.3, 0.6$) have been structurally characterised by Rietveld analysis of powder data, high resolution lattice imaging and Mössbauer spectroscopy. The evolution of the complex magnetic behaviour across the series has been followed by magnetometry (both dc and ac) and the complex factors determining the structural and electronic properties of this series of compounds will be discussed. Related to the hexagonal perovskites is the family of compounds $\text{A}_{1+x}\text{A}'_x\text{B}_{1-x}\text{O}_3$ with chains of polyhedra (octahedra and trigonal prisms) running along [001]. Conventionally these structures have been rationalised in terms of the stacking of A_3O_9 and $\text{A}_3\text{A}'\text{O}_6$ layers (where 1/3 of the oxide ions have been systematically removed and replaced by an alternative A' cation). A number of the compositions show an incommensurate modulation along z and thus cannot be modelled using the conventional 3D approach. Recently a new approach, treating the structures of this family as modulated composites and invoking the $(3+d)$ formalism, has been successfully applied by others to X-ray diffraction data obtained from single crystals. With the release of the refinement package JANA2000 (Petricek et al.), this approach can now be extended to a consideration of data obtained from powder samples. To investigate this, high quality powder samples of $\text{Sr}_{1+x}\text{Co}_x\text{Mn}_{1-x}\text{O}_3$ ($x = 0.27, 0.28$, close to ideal compositions $\text{Sr}_{14}\text{Co}_3\text{Mn}_8\text{O}_{33}$ and $\text{Sr}_9\text{Co}_2\text{Mn}_5\text{O}_{21}$) have been prepared and analysed; details of the Rietveld refinements for these compounds will be presented together with magnetisation data which suggest these compounds to be weakly ferromagnetic.

D4.2

EVALUATION AND PREDICTION OF THE CRYSTAL STRUCTURES OF SINGLE/ORDERED/DISORDERED OCTAHEDRAL CATION PEROVSKITES USING THE SOFTWARE PROGRAM SPUDS. Michael W. Lufaso, Patrick Woodward, Department of Chemistry, Ohio State University, Columbus, OH.

The software program SPuDS has been developed to predict the crystal structures of perovskites, as well as those containing octahedral tilting distortions. The user inputs the atoms and oxidation states and SPuDS calculates an optimized structure of the perovskite. The structure prediction algorithm calculates the size of the BX_6 octahedron by assigning a B-X bond length that adjusts the bond valence sum of the B-cation equal to the oxidation state. Rigid octahedra are maintained and tilting is performed to optimize the bond valence sum of each ion in the structure. Combinations of tilting of neighboring octahedra lead to different tilt systems and space group symmetry. SPuDS calculates for 10 tilt systems with a single or disordered B-site cation. The introduction of a second B-site cation leads to the possibility of an ordered B-site cation arrangement. In its current form SPuDS calculates 6 tilt systems for ordered 2 B-site cation perovskites. Perovskites containing trivalent Mn undergo a Jahn-Teller distortion of the MnO_6 octahedra. SPuDS modeling and synthesis of multiple B-cation perovskites containing Mn(III) comparing experimental and predicted results is presented. A comparison of the predicted and experimental structures illustrates the accuracy of the method. SPuDS has the following applications. 1. Predicted structures can be used to estimate physical (magnetic, dielectric and other) properties of both hypothetical compositions and materials without accurate structural data. 2. SPuDS can be used as a guide for exploratory synthetic efforts including compounds with multiple cations as well as high-pressure synthesis. 3. Predicted structures can serve as the starting point for Rietveld refinements. 4. Structures generated can be compared with experimentally determined structures in order to extract the effects of octahedral tilting distortions from other structural distortion mechanisms.

D4.3

RELAXOR AND GLASSY BEHAVIOR OF $\text{Cd}_2\text{Nb}_2\text{O}_7$ PYROCHLORE. N.N. Kolpakova, P.P. Syrnikov, M.P. Shcheglov, A.F. Ioffe Physico-Technical Inst RAS, St-Petersburg, RUSSIA; P. Czarnecki, W. Nawrocki, Inst of Physics, A. Mickiewicz Univ, Poznan, POLAND.

Relaxor behavior of mixed perovskites like PMN is of current interest in the past decades both from the basic physics viewpoint and possible applications of the materials. We report the recent

developments in investigation of the relaxor and glassy behavior of $\text{Cd}_2\text{Nb}_2\text{O}_7$ (CNO) pyrochlore. The fact that pyrochlores can also exhibit the unusual dielectric properties so far observed mainly in perovskites attracts special attention since (i) both perovskites ($\text{O}_h^1\text{-Pm3m}$) and pyrochlores ($\text{O}_h^2\text{-Fd3m}$) belong to the high-symmetry condensed matters, and (ii) the latter can appear as a second phase during formation of the perovskite structure. The dielectric spectroscopy (100 Hz-13 MHz) and thermal polarizability evidence for the evolution of polar microregions both in pure and modified with Ni or Cu or Zn on the Cd-site CNO over the temperature range of 80-300 K is presented. A polydisperse dielectric response of CNO-type pyrochlores is modelled with the Vogel-Fulcher and Chamberlin relations. Structural modelling the relaxor and glassy behaviour of pyrochlores is also discussed.

D4.4

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF BARIUM ZIRCONIUM TITANATE THIN FILMS FOR MICRO-ELECTROMECHANICAL SENSOR DEVICES. A. Dixit, S.B. Majumder, R.S. Katiyar, Department of Physics, University of Puerto Rico, San Juan, PR.

High piezoelectric coefficients of zirconium doped barium titanate solid solutions are considered attractive for a variety of micro-electromechanical systems (MEMs). In the present work $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ ($x = 0.0, 0.05, 0.08, 0.12, 0.15, 0.30, 0.70$) thin films were deposited on single crystalline lanthanum aluminate substrates by sol-gel technique. X-ray diffraction measurements were performed to analyze the phase formation behavior and growth characteristics. The structural properties of these films were also characterized by micro-Raman scattering measurements using an ISA T64000 triple monochromator. The Raman characteristics of BZT thin films are compared with the corresponding single crystal and ceramic data. Interdigital transducer (IDT) electrodes were deposited on the surface of the films and the dielectric properties were measured. Details of the electrical and optical properties will be presented. This work is supported in part by NASA-MURC and NSF-ID grants.

D4.5

PROCESSING - PROPERTY RELATIONS IN BISMUTH TITANATE. S. Mallick, A. King, K.J. Bowman, E.B. Slamovich, Purdue University, West Lafayette, IN; W. Shelley II, Keramos LLC, Indianapolis, IN.

Bismuth Titanate has an Aurivillius type structure consisting of perovskite like blocks of Bi, Ti and O interleaved with layers of $\text{Bi}_2\text{O}_2^{2+}$. Depending on the number of these perovskite like blocks, stoichiometries like $\text{Bi}_3\text{Ti}_2\text{O}_9$, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $\text{Bi}_5\text{Ti}_4\text{O}_{15}$ etc. are possible. The microstructure evolution of these materials has been observed to be strongly dependent on the sintering atmosphere, with plate like grains for those sintered in air or oxygen and cuboidal for those sintered in nitrogen. Doping with an alkali metal has been found to promote the formation of $\text{Bi}_5\text{Ti}_4\text{O}_{15}$ phase from the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ phase and influences the piezoelectric and dielectric constants.

D4.6

STRUCTURAL AND ELECTRONIC MODIFICATIONS ACROSS THE METAL-INSULATOR TRANSITION IN RNiO_3 (R = Pr, Nd, Eu) PEROVSKITES. C. Piamonteze, H.C.N. Tolentino, A.Y. Ramos, Laboratório Nacional de Luz Síncrotron, Campinas, BRAZIL; N.E. Massa, Universidad Nacional de La Plata - CEQUINOR, La Plata, ARGENTINA; J.A. Alonso, Instituto de Ciencias de Materiales de Madrid, CSIC, Cantoblanco, Madrid, SPAIN.

The rare-earth nickel oxide perovskites (RNiO_3), except for La, present metal-insulator (MI) phase transition as temperature decreases. These systems present antiferromagnetic ordering at low temperature. For PrNiO_3 and NdNiO_3 T_{MI} and T_N are coincident, while for smaller rare earth ions they are far apart, suggesting that the MI transition is not a magnetic governed effect. T_{MI} depends on the R ion size, which also determines the degree of structural distortion. This fact points to a correlation between electronic and structural behaviors. From diffraction measurements it was observed a subtle expansion of the unit cell volume across the MI transition while the Ni-O distances are almost equal. Recently, in compounds with smaller R ion it has been observed a monoclinic distortion at the metallic phase, compatible with the existence of two Ni sites. We have measured EXAFS at Ni K edge in RNiO_3 samples (R = Pr, Nd and Eu). Our results show different Ni-O distances at the insulator phase that could be due to different Ni sites and/or to a unique distorted site. The distortion clearly diminishes at the metallic phase. For the same samples, we have also measured XAS at Ni L edges (transition $2p \rightarrow 3d$), that gives information on the density of Ni 3d empty states, as well as on the degree of hybridization between Ni 3d and O 2p bands. The results show a dramatic difference between the spectra of insulating and metallic samples, which might be due to a decreasing degree of covalence when going from the insulating to the

metallic state. Since this technique is a local atomic probe, such differences would only be induced by modifications on Ni local structure. Therefore, both results are in accordance and show structural and electronic behaviors that are related to modifications at the NiO₆ octahedra.

D4.7

CATION ORDERING IN BROWNMILLERITE-TYPE STRUCTURES: Ca₂LnFe₂GaO₈, Sr₂LnFe₂GaO₈ (Ln = La, Md, Pr, Sm, Eu) AND THEIR SOLID SOLUTIONS. Santhosh P. Nagappan Nair, Peter D. Battle, Oxford University, Inorganic Chemistry Laboratory, Oxford, UNITED KINGDOM; Matthew J. Rosseinsky, University of Liverpool, Department of Chemistry, Liverpool, UNITED KINGDOM.

The brownmillerite-perovskite interlayered phases or the ordered-vacancy perovskite phase, of the formula unit A_nB_nO_{3n-1} (n = 3) were synthesized and characterized in this study. We made compositions with Ca, and Ln (La, Pr, Nd,) ions occupying the A-sites and with Fe and Ga occupying the B-site in a 2:1 ratio. This leads to a OOTOOTOOT... type of layered structures (O-octahedral and T-tetrahedral) perpendicular to the y-axis of the unit cell. From our initial Rietveld refinements of the X-ray diffraction data, with centrosymmetric *Pmma* space group symmetry, we conclude that Fe ions occupy the octahedral sites and Ga ions in tetrahedral site. The A-site cations occupy the cavities between the layers (octahedra/tetrahedral). This series of compounds have the orthorhombic unit cell $\sqrt{2}a_p \times 3a_p \times \sqrt{2}a_p$. Preliminary studies show a partial order among the A site ions (Ca and Ln ions) and the extent of ordering depends on the relative ionic sizes between the A-site ions. The ordering decreases with the decrease in size of the Ln ion. The effect of Ca to Sr ratio in the series Ca_{2-x}Sr_xPrFe₂GaO₈ on the magnetic and structural properties will be presented. A systematic study of these compounds was done with the help of X-ray diffraction Rietveld refinements, TEM and SQUID magnetic measurements. Preliminary results of our investigation into the doping of Fe octahedral sites with Mn or Co ions will also be presented.

D4.8

PLASMA-SYNTHESIZED AlF₃: CHARACTERIZATION OF SURFACE ACTIVITY. E. Hajime, J.L. Delattre, T. Ostomel, A.M. Stacy, Univ of California, Berkeley, Dept of Chemistry, Berkeley, CA.

Metastable aluminum trifluoride phases such as β -AlF₃ are commonly used in industry as halogen exchange catalysts, converting mixed halogen-containing species such as the chlorofluorocarbons (CFCs) into their corresponding higher and lower fluorinated analogues. Until recently, the synthesis of these metastable aluminum trifluoride phases required "soft chemistry" techniques involving the decomposition of fluorometallate (e.g., (NH₄)₃AlF₆) or hydrate (e.g., α -AlF₃·3H₂O) precursors. Recently, our group has shown that fluorine-containing low-temperature plasmas can also be used to synthesize metastable AlF₃ using zeolites as starting material. Preliminary characterization of the zeolite-derived plasma-synthesized AlF₃ (plasma-AlF₃) has revealed an unusually high BET (N₂) surface area (190 m²/g) compared with conventional "soft chemistry" techniques (18 m²/g), as well as unexpected nanoscale morphologies. To probe the metastable nature of plasma-AlF₃, a general-purpose gas-solid flow reactor was designed and built to directly measure the catalytic activity of plasma-AlF₃ toward the dismutation (halogen exchange) reaction of CCl₂F₂. Using the model dismutation reaction, we find that plasma-AlF₃ is catalytically active toward halogen exchange, while also being extremely sensitive toward both hydrolysis in the presence of H₂O and coking in the presence of trace hydrocarbons. Complementary studies on the temperature dependence of dismutation (TPR-CCl₂F₂) reveal unexpected features thought to be linked to structural changes, while temperature-programmed desorption of ammonia (TPD-NH₃) experiments show an enormous amount of NH₃ desorption relative to β -AlF₃, suggesting that a large fraction of the high BET (N₂) surface area consists of acid "sites." Continuing investigations into the reactivity of plasma-AlF₃ include temperature-programmed experiments of bulk and surface structure and possible correlations with the temperature-dependent reactivity data, as well as other potential catalytic reactions. Synthetic studies in the plasma decomposition of modified zeolites and meso/microporous precursors for the production of new metastable, high surface area materials are currently underway.

D4.9

RADIATION DEFECTS IN LiBaF₃. Peter Kulis, Uldis Rogulis, Maris Springis, Ivars Tale, Aris Veispals, Institute of Solid State Physics, University of Latvia, Riga, LATVIA.

LiBaF₃ represents a group of perovskite materials, prospective as scintillators and as radiation memory materials for thermal neutron dosimetry, imaging and tomography. Ce³⁺ and Eu²⁺ luminescence in LiBaF₃ are promising features for thermal -neutron detection [1].

Radiation energy is stored mainly by creating of the color centers [2]. In the present paper we report data on the impurity doped crystal chemistry, origin, accumulation of radiation created defects in LiBaF₃ crystals using the EPR and optical dichroism (OD) studies of radiation created absorption bands. Mechanism of read out processes is discussed owing data of photo- and thermo stimulated bleaching and corresponding recombination luminescence kinetics. X-ray irradiation below 130 K results in creation of the V_K centers (self trapped holes) and several kinds of F-type centers. The X- irradiation up to doses at least of 10² Gy at RT results in non-saturating creation of the F-type centers responsible for composite absorption bands at 270, 320 and 430 nm. Photo-stimulation in these absorption bands results in creation of the aggregate F-centers represented by absorption bands at 650 and 740 nm. Annealing of radiation created F-type centers using advanced glow rate technique [3] occurs in two steps down to 500K and is governed by interaction of F- type centers with mobile anion vacancies. The first stage is limited by dissociation rate of F_A - centers in mobile F- center and anion vacancy – neighbor impurity ion, the second stage – by annihilation of migrating F-centers with complementary interstitial centers (activation energies 0.81 eV and 0.75 eV respectively). 1. C.W.E. van Eijk Nuclear Instr. & Methods Phys Res. A Vol. 460, 1 (2001). 2. I. Tale, P. Kulis, et al. Radiation Measurements. Vol. 29, 279 (1998). 3. I. Tale, G. Rudloff, and V. Tale, Radiat Prot. Dosimetry, Vol. 33 (1996).

D4.10

SYNTHESIS AND ELECTRICAL PROPERTIES OF Ba₂(Nb,M)₅O₉ [M = V AND Zr] AND (Ba,Ca)₂Nb₅O₉. Kouta Iwasaki, Hisanori Yamane, Shunichi Kubota, Junichi Takahashi, Masahiko Shimada, Tohoku Univ, Inst of Multidisciplinary Research for Advanced Materials, Sendai, JAPAN; Hirotugu Takizawa, Kyoto Uheda, Tadashi Endo, Tohoku Univ, Dept of Materials Chemistry, Graduate School of Engineering, Sendai, JAPAN.

Ba₂Nb₅O₉ (m=1, n=2) is one of the A_nNb_{n+3m}O_{3n+3m} [(NbO)_{3m}(ANbO₃)_n] homologous phases, which consist of m-NbO (defect rock-salt type) and n-ANbO₃ (perovskite type) blocks and crystallize in tetragonal structures with a space group *P4/mmm*. There are three Nb sites in the structure of Ba₂Nb₅O₉; Nb atoms in Nb(1) and Nb(2) sites form a Nb₆ octahedron and Nb(3) site is in the center of NbO₆ octahedron.

In the present study, solid solutions of Ba₂(Nb,M)₅O₉ [M = V and Zr] and (Ba,Ca)₂Nb₅O₉ were prepared by solid state reaction at 1373 – 1773 K in flowing Ar. The crystal structures were analyzed by the Rietveld method using X-ray powder diffraction data. In Ba₂Nb_{5-x}V_xO₉, the a and c axis lengths decreased with increasing x (0 ≤ x < 1.9). The Rietveld analysis indicated that V atoms occupied both Nb(1) and Nb(2) sites. On the other hand, Zr atoms occupied the Nb(3) site in Ba₂Nb_{5-y}Zr_yO₉. The a and c axis lengths of Ba₂Nb_{5-y}Zr_yO₉ increased with increasing y (0 ≤ y < 1). The site preferences of V and Zr atoms would be explained in terms of the crystal structures of BaVO₃ and BaZrO₃. Ba₂(Nb,M)₅O₉ [M = V and Zr] showed metallic behavior of electrical resistivity, and the electrical resistivity increased with increasing V and Zr content. In the (Ba,Ca)-Nb-O system, the Ca substitution decreased the lattice parameters of Ba_{2-z}Ca_zNb₅O₉ (0 ≤ z ≤ 0.5). In addition, when the amount of Ca increased (z > 1 in the starting mixture of Ba_{2-z}Ca_zNb₅O₉), (Ba,Ca)Nb₄O₆ (m=1, n=1) was formed with NbO and other minor phases (1573 K for 20 h). The formation of (Ba,Ca)Nb₄O₆ instead of (Ba,Ca)₂Nb₅O₉ was also discussed with the crystal structure of CaNbO₃.

D4.11

FERROELECTRIC TWINNING STRUCTURE AND PHASE TRANSITIONS IN KTa_{1-x}Nb_xO₃ CRYSTALS. Dexun Shen, Qi Luo, Nanjing University, Department of Physics, Nanjing, CHINA; Xian-rong Huang, State University of New York at Stony Brook, Department of MS&E, Stony Brook, NY.

Ferroelectric twinning configurations and microstructures of perovskite KTa_{1-x}Nb_xO₃ (KTN) crystals in both orthorhombic and tetragonal phases are studied by high-resolution x-ray diffraction (HRXRD), x-ray topography (XRT), and polarizing microscopy (PM). XRT and PM observations show that the twinning patterns in the two ferroelectric phases vary remarkably in KTN plates of different thicknesses, which indicates that for thin plates, the strain relaxation effect has significant influence on the twinning structures. Small-beam HRXRD scanning across the twinning boundaries reveals clearly the strain fields and polarization profiles of the 60°, 90°, and 180° twinning walls in the ferroelectric phases. Numeric simulations based on these profiles show that the walls can be either "Ising-type" or "Bloch-type" walls, depending on whether the plate thickness is above or below a critical thickness $t_c \approx 70 \mu\text{m}$. In-situ observation of the orthorhombic-tetragonal-cubic phase transitions of KTN using XRT and PM shows the transformations of twinning structures between the different phases. In particular, it is found that the 60° walls in the orthorhombic phase can change into either 90° or 180° walls in the

tetragonal phase, while the 90° walls can either disappear or turn into 180° walls in the latter phase. Detailed transformation mechanisms of the twinning structures are discussed.

D4.12

STRUCTURE OF UMo_4O_{14} GROWN BY SOLID PHASE REACTION METHOD. N.D. Zakharov, P. Werner, Max Planck Institute of Microstructure Physics, Halle, GERMANY.

The crystal structure of U-Mo oxide prepared by solid phase reaction method have been determined by High Resolution Transmission Electron Microscopy (HRTEM) and Selected Area Electron Diffraction (SAD). The composition of new phase was investigated by Energy Dispersive X-ray microanalysis (EDX) in transmission mode. It gives U/Mo = 0.25 and chemical formula UMo_4O_{14} . Unit cell is orthorhombic, s.g. Cccm, with dimensions: $a=0.72$, $b=3.2$ and $c=0.82$ nm. The basic structure is formed by corner sharing MoO_6 octahedra. The slabs of ReO_3 -type and two MoO_6 octahedra wide are separated by the blocks of Hexagonal Tungsten Bronze (HTB)-type structure two row of hexagonal tunnels wide. Hexagonal tunnels are filled by -O-U-Mo-O-U-strings. In some crystals incommensurate modulations have been observed.

D4.13

THE HYPERFINE CHARACTERIZATION OF $Ba_xSr_{1-x}HfO_3$ CUBIC STRUCTURES. Roberto E. Alonso and Alberto Lopez Garcia, Departamento de Fisica, Universidad Nacional de La Plata, La Plata, REP. ARGENTINA.

In order to study how the Ba replacement by Sr affects the crystalline and electronic structures of the pure perovskite $BaHfO_3$, the hyperfine characterization of $Ba_xSr_{1-x}HfO_3$ cubic phases for $x = 0.12, 0.25, 0.50, 0.75$ and 0.88 is presented for the first time. The hyperfine electric quadrupole interaction at tantalum probes was determined by Perturbed Angular Correlation spectroscopy. The electric field gradient tensor at probes is produced by the surrounding charges and is deduced from the measurements of the electric quadrupole interaction. The samples were prepared by mixing high purity oxides or carbonates of the selected cations in stoichiometric proportions. Using the high temperature solid state reaction procedure the compounds were produced. The samples were characterized by X-ray diffraction technique. No lines corresponding to the initial pure components were observed. The samples were then irradiated with thermal neutrons to produce the probe $^{181}Hf/^{181}Ta$. The impurity concentration is 1:106 and no radiation damage was detected. In every sample the spin precession curves were measured from room temperature to 1273K, with 50 K steps. To fit the data the conventional perturbation factor describing a static, axially asymmetric and disorder electric field gradient model was used. From this numerical analysis, the quadrupole frequency ω_Q , the asymmetry parameter η and the line width δ were obtained as a function of temperature and composition. This results are analyzed in terms of the same model used to interpret the $Ba_xSr_{1-x}HfO_3$ results.

D4.14

FIRST-PRINCIPLES CALCULATION OF THE ORBITAL MAGNETIC MOMENT OF O AND Cr in HALF-METALLIC CrO_2 . Horng-Tay Jeng, National Center for Theoretical Sciences, Hsinchu, TAIWAN; D.J. Huang, Synchrotron Radiation Research Center, Hsinchu, TAIWAN; G.Y. Guo, Dept of Physics, Natl. Taiwan Univ., Taipei, TAIWAN.

The electronic and magnetic properties of half-metallic magnet CrO_2 have been studied by using the full-potential linearized muffin-tin orbital (FP-LMTO) method within the local spin density approximation (LSDA) and the LSDA+U approach. The orbital magnetic moment and the magnetocrystalline anisotropy energy are investigated by incorporating the spin-orbit interaction in both schemes. The orbital magnetic moment for oxygen atoms in CrO_2 is more significant than that in other oxides. It is found that the spin and orbital magnetic moments of O atom are dramatically enhanced as the onsite Coulomb energy U increases. For Hubbard U of 3 eV, LSDA+U gives the orbital moment of $-0.0023 \mu_B$ for O, being in good agreement with the experimental orbital moment of $-0.003 \mu_B$ from magnetic circular dichroism (MCD) measurements. This is to be compared with the orbital moment of $-0.0012 \mu_B$ for O from LSDA calculations. Interestingly, the calculated spin moment of Cr is also raised substantially by U , whereas the calculated orbital moment of Cr atom turns out to be insensitive to the Hubbard U . For various U considered in this work, the orbital moment of Cr remains at about $-0.03 \mu_B$, being slightly smaller than the experimental orbital moment of $-0.05 \mu_B$.

D4.15

PEROVSKITE d-STATE ELECTRONIC STRUCTURE AND X-RAY ABSORPTION. M. Croft, Rutgers Univ, Physics Dept, Piscataway, NJ; G. Popov, G. Veith, Rutgers Univ, Chemistry Dept, Piscataway,

NJ; P. Ansari, Seton Hall Univ, Physics Dept, S. Orange, NJ; M. Greenblatt, Rutgers Univ, Chemistry Dept, Piscataway, NJ; D. Sills, S-W. Cheong, Rutgers Univ, Physics Dept, Piscataway, NJ; Q. Qain, T. Tyson, New Jersey Institute of Technology, Physics Dept, Newark, NJ.

Perovskite materials have long been a central in optical, ferroelectric and piezoelectric applications. In recent years High T_c superconductivity magnetoresistance, and metal-insulator transition phenomena have stimulated a far broader renaissance in perovskite-based transition metal oxide physics. There has been a symbiosis in this field between the evolving understanding of electronic structure, the materials synthesis routes to tune/control it and the experimental spectroscopies which probe it. X-ray absorption spectroscopy (XAS) has both contributed to and benefited from this symbiosis in substantial ways. Here we discuss XAS results on $4d/5d-L_{1,2,3}$ -edges and the $3d$ -K-edge, and the ways in which each probe the d-orbital electronic structure of such perovskite based systems. A leit-motif in these results is the direct evidence for particularly prominent and well-resolved spectral features related to the crystalline electric field splitting of the empty $t_{2g}-e_g$ d-states in these materials. The systematics of the coupling of these features to the d-state-hole-count will also be addressed. Results for materials with the pure perovskite structure, for layered-materials with perovskite planes, and for ordered double perovskite materials will be presented.

D4.16

CATION ORDERING IN $n=2$ RUDDLESDEN POPPER PHASES. Jennifer A. Rodgers, Peter D. Battle, Inorganic Chemistry Laboratory, University of Oxford, Oxford, UNITED KINGDOM; Chris J. Kiely, Materials Science and Engineering, Department of Engineering, University of Liverpool, Liverpool, UNITED KINGDOM; Clare P. Grey, Department of Chemistry, SUNY Stony Brook, Stony Brook, NY.

There has been renewed interest in manganese-containing $n=2$ Ruddlesden Popper (RP) phases $A_{n+1}B_nO_{3n+1}$ due to the occurrence of the CMR phenomenon. Ruthenium doping has been shown by others to have a marked effect on the properties of the manganates, and we have therefore initiated a more general study of $n=2$ RP ruthenates. The strategy has been to introduce onto the 6 co-ordinate B-site, at a 50% doping level, a second element having a chemistry different from that of ruthenium with the aim of introducing structural ordering. This is predicted to allow a degree of control of the magnetic interactions by reducing the number of significant superexchange pathways. Polycrystalline samples of $Ln_2SrLiRuO_7$ and $LnSr_2MgRuO_7$ ($Ln = La, Pr, Nd$) have been structurally characterised by Rietveld analysis of X-ray powder diffraction data and electron diffraction with subsequent characterisation including magnetometry, magic-angle spinning (MAS) solid state NMR and high resolution lattice imaging to probe the local environment. Results suggest both compounds have an $n=2$ RP structure with a varying degree of B-site ordering. $Ln_2SrLiRuO_7$ shows ordering on a large enough scale to give reflections indicative of a supercell in X-ray diffraction patterns. This type of 1:1 cation ordering leads to an expansion of the unit cell and a lowering of the crystal symmetry from body-centred tetragonal ($I4/mmm$) to primitive monoclinic ($P2_1$). These are believed to be the first $n=2$ RP compounds to show long range 1:1 structural ordering of two elements over the 6 co-ordinate sites. This ordering generates double thickness elpasolite sheets. By comparison $LnSr_2MgRuO_7$ produces diffuse Bragg scattering at high d-spacing, suggestive of ordering on a shorter scale. Due to a lack of structural coherence between the neighbouring ordered blocks, the pattern can be indexed in $I4/mmm$.

D4.17

COMPUTER MODELING OF SINGLE AND INTERACTING Li IMPURITIES IN $KTaO_3$ AND $K_{1-x}Li_xTa_{1-y}Nb_yO_3$ PEROVSKITE SOLID SOLUTIONS. R.I. Eglitis, V.A. Trepakov, S.E. Kapplan, and G. Borstel, Dept. of Physics, University of Osnabrueck, Osnabrueck, GERMANY.

The magnitudes of off-center Li displacements and the relaxation energies related to reorientation of Li are calculated in ABO_3 perovskites using semiempirical Hartree-Fock-based method of the Intermediate Neglect of Differential Overlap (INDO). Results are compared with experimental data and earlier calculations. The spatial extent of a lattice relaxation around Li impurities and contributions from different neighbors to the relaxation energy are discussed. We have applied the INDO method for the study of interaction between Li impurities in $KTaO_3$. The calculations have been done using the supercells containing up to 270 atoms, the possible implications of the limited supercell size are discussed. The Li-Li interaction energy as a function of the Li-Li distance and orientation are calculated, including the lattice relaxation around Li-Li impurities. According to our calculations, the Li-Li interaction energies are smaller and less long-ranged than it was estimated from earlier shell model (SM)

calculations. Lastly, we performed theoretical modeling of KTaO_3 perovskites with a small amount of Li and simultaneously diluted by Nb ($\text{K}_{1-x}\text{Li}_x\text{Ta}_y\text{Nb}_{1-y}\text{O}_3$, KLTN). We compare our theoretical results with recent experimental results for the complex dielectric permittivity and Raman spectroscopy studies.

D4.18
APPLYING CONCEPTS OF BOND VALENCE FOR DESCRIBING STRUCTURAL TRENDS OF PEROVSKITES. William T. Petuskey and George H. Wolf, Arizona State University, Dept of Chemistry & Biochemistry, Tempe, AZ.

The bond valence method has long been applied by crystallographers and crystal chemists to test the validity of proposed crystal structures and to predict bond lengths in ionic solids. The parameters used are based on empirical compilations of bond lengths for atom pairs in many different environments of known crystal structures. This presentation discusses how the bond valence method can be successfully applied to perovskites for structural systematics involving both ferroelastic and ferroelectric distortions. Other details, such as unit cell volumes can also be predicted with good accuracy.

D4.19
CHARACTERIZATION OF SOL GEL PREPARED KTN THIN FILMS AND POWDERS BY RAMAN, XRD, AND THERMAL ANALYSIS TECHNIQUES. A.A. Savvinov, S.B. Majumder, and R.S. Katiyar, University of Puerto Rico, Department of Physics, San Juan, PR.

The renewed interest in $\text{KTa}_{1-x}\text{Nb}_x\text{O}$ (KTN) mixed perovskite materials is connected with their remarkable dielectric properties in the dilute compositions. KTN thin films with $x=0.35$ have been prepared on different substrates by sol-gel technique as well as a set of powders with $x = 0, 0.05, 0.1, 0.25, 0.48, 0.65, 0.75$, and 1. Properties of the material change drastically with the change of x , because of relaxation of both translational and inversion symmetry due to a static disorder in the Nb distribution and the dynamic effect of a precursor ferroelectric order above T_c . Especial attention was paid to the characteristic feature of coupling of the single-phonon state to a two-acoustic-phonon state through anharmonic terms in the potential function as well as behavior of the TO_3 mode which becomes a narrow peak of the first-order scattering in the tetragonal ferroelectric phase and shows a tendency to split below the transition temperature in the orthorhombic phase. The wide range of x allows better understanding of dynamic processes in the KTN bulk materials which in turn helps in studies of thin films. The abovementioned materials were studied using Raman scattering, XRD, and thermal analysis techniques.

D4.20
X-RAY CHARACTERIZATION OF PEROVSKITES WITH VARIOUS ORDERING IN CATION AND ANION SUBLATTICE. B.N. Kodess, L.A. Butman, I.P. Jouravlev, Dept. Mater. Science, ICS&E at Denver, CO, Department of Crystals Metrology, VNIIMS, Moscow, RUSSIA.

Characterization of oxygen-deficient Perovskites is carried out at various levels of a structure - macro-, microstructural and electronic. The new iterative multistage refinement allowed to determine peaks positions (connected with change of stacking faults, vacancies sub-lattice and short-range order) and FWHM (connected with mosaic block and defects of a various type contribution) with a high accuracy. Single crystals and powder data of SrFeO_3 show that positions of cations are populated completely, and occupation of positions of oxygen is not completely. The presence of vacancies results in stabilization of low-symmetric phase as well as for SrTiO_3 . Lattice parameters of powder of ferrate strontium within a space group P4mm $a=b=3.8558$ and $c=3.8781$; the difference (b-c) is close to a difference (b-c) = 0.0246 for single crystals which correspond to a composition $\text{SrFeO}_{2.78}$. Observation the super-structural reflexes by J.P. Hodges, S. Short, J.D. Jorgensen and these data can be explained by static displacements of atoms, anisotropy of thermal vibration, as well as for some chemical compounds (B. Borie). The outcomes demonstrate considerable (more 20%) anisotropy of a line broadening correlating with a type of indexes. Similar anisotropy of line-width along axes a and c we have obtained for more oxygen-deficient Perovskites in a YBCO-system. The dimensions of a unit cell are determined for these phases by definitely ordering of cations of yttrium and barium, which result in the trebled value c in relation to axes a and b. Deformation density maps and anharmonicity parameters were studied by high-accuracy X-Ray analysis of single crystals using atomic factors calculated from the first-principles calculations.

D4.21
FORMATION OF STRONTIUM ZIRCONATE PEROVSKITE NANOCRYSTALS IN STRONTIUM ION IMPLANTED CUBIC ZIRCONIA. Lu-Min Wang, Sha Zhu and Rodney C. Ewing,

Department of Nuclear Engineering and Radiological Sciences, The University of Michigan, Ann Arbor, MI; Shixin Wang, Micron Technology Inc., Boise, ID.

Strontium ions have been implanted into yttria stabilized cubic zirconia (YSZ) single crystals to study the behavior of the fission product in a potential YSZ based Inert Matrix Fuel (IMF) for burning excess plutonium from the dismantlement of nuclear weapons. The 400 keV strontium ion implantation was conducted at the room temperature and it generated a peak displacement damage level of 330 dpa and a peak strontium concentration of 11.6 at %. Transmission electron microscopy (TEM) was used to investigate the microstructure changes caused by the ion implantation. Cross-sectional TEM has revealed nanocrystalline strontium zirconate rods with the perovskite structure after annealing of the implanted bulk sample at 1000°C for 2 hours. The perovskite nanocrystals are concentrated in a narrow band 80 nm below the surface. The average dimensions of the nanocrystalline rods are 15×30 nm. The specific orientation relationship between the perovskite precipitates and the YSZ matrix has been determined. The lattice mismatch between the two phases has been compensated by interface dislocations as clearly revealed by high resolution TEM. The results from a similar experiment on strontium ion implanted rutile will also be presented.

SESSION D5: MAGNETORESISTIVE PEROVSKITES I
Chair: Peter D. Battle
Wednesday Morning, April 3, 2002
Golden Gate A2 (Marriott)

8:00 AM *D5.1
FERROMAGNETISM AND METALLICITY OF Mn-SITE DOPED MANGANITES: WHAT IS THE ORIGIN? B. Raveau, S. Hébert, A. Maignan, M. Hervieu, C. Martin and R. Frésard, Laboratoire CRISMAT, UMR 6508, CNRS/ISMRA, Caen, FRANCE.

The doping of the manganese sites of the manganites with various cations is shown to induce either ferro- magnetism and metallicity of ferromagnetism only. The substitution of divalent (Ni^{2+} , Co^{2+} , Zn^{2+}) or univalent (Li^+) cations for Mn^{3+} in stoichiometric antiferromagnets (AFM) LaMnO_3 , induces ferromagnetism (FM with T_c up to 150 K, and lowers the resistivity. In contrast, by doping with trivalent cations such as Rh^{3+} or Ga^{3+} , the compound remains AFM or weakly FM insulator. This behavior is explained in terms of valency effect: doping with a cation of smaller valency than Mn^{3+} , introduces Mn^{4+} species in the matrix, so that double exchange (DE) between $\text{Mn}^{3+}/\text{Mn}^{4+}$ can be obtained.

The doping of "charge-orbital" ordered CE-type AFM manganites such as $\text{Ln}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ ($\text{Ln} = \text{Pr}, \text{Sm}$) by various cations destroys charge ordering, but moreover for magnetic cations such as Cr, Co, Ni, Ru it induces an insulator to metal transition and a FM state. For such doping, the magnetic phase diagram is modified in a spectacular way, wide ferromagnetic regions, with T_c up to 240 K in the case of ruthenium, replacing charge ordered regions. Such properties can be explained by DE mechanism on the basis of the local antiferromagnetic coupling between chromium and manganese, or ferromagnetic coupling between ruthenium and manganese, leading to the formation of FM domains which extend under a magnetic field. Moreover, valency fluctuations are also supposed to play an important role in the case of ruthenium doping, implying both Ru^{4+} and Ru^{5+} species. The recent discovery of similar properties by doping $\text{Ln}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ with Rh^{3+} and Ir^{4+} is also explained by valency fluctuations.

8:30 AM D5.2
PHOTOEMISSION AND X-RAY ABSORPTION MEASUREMENTS ON THE CMR MATERIALS $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ AND $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. N. Mannella, Department of Physics, University of California at Davis, Davis, CA and Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA; B.S. Mun, S.-H. Yang, Material Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA; M.W. West, A. Mei, Engineering Division, Lawrence Berkeley National Laboratory, Berkeley, CA; Y. Tomioka, Joint Research Center for Atom Technology, Tsukuba, JAPAN; Y. Tokura, Joint Research Center for Atom Technology, Tsukuba, JAPAN and Department of Applied Physics, University of Tokyo, Tokyo, JAPAN; C.S. Fadley, Department of Physics, University of California at Davis, Davis, CA and Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA.

We report core and valence photoemission results obtained with synchrotron radiation for a set of high quality single-crystal CMR samples, namely $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ with $x = 0, 0.1, 0.2, 0.25, 0.3$ and $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ with $x = 0.3$ and 0.4. The measurements were

performed after cleaving the crystals in situ in UHV, yielding very clean and stoichiometric surfaces, as verified by an analysis of core photoemission spectra. In particular, Mn 3s core level spectra show the expected multiplet splitting in binding energy, a well-known effect in transition metal ions which can sensitively probe the exact spin state of magnetic atoms. To a first approximation, the multiplet splitting is proportional to the net spin on a given site. Our data reveal a strong dependence of the multiplet splitting on the hole concentration x , indicating the sensitivity of this quantity to changes in the relative numbers of Mn species with different valence states. We further find that this dependence is not linear as a function of the hole doping x , as one would expect in the simplest picture according to which hole doping causes a corresponding number of Mn³⁺ ions to become Mn⁴⁺. These results may indicate an inadequacy of the conventional model based on the nominal Mn³⁺ - Mn⁴⁺ valence states that is used to describe the transport properties of the manganites. Additional photoemission results from other core levels and valence levels, as well as x-ray absorption measurements, will also be discussed.

8:45 AM D5.3

INFLUENCE OF OXYGEN ISOTOPE EXCHANGE ON THE GROUND STATE OF MANGANITES. V.N. Smolyaninova^a, Amlan Biswas^a, P. Fournier^b, S. Lofland^c, X. Zhang^a, Guo-meng Zhao^d, and R.L. Greene^a; ^aDepartment of Physics and Center for Superconductivity Research, University of Maryland, College Park, MD; ^bCentre de recherche sur les propriétés électroniques de matériaux avancés et Département de Physique, Université de Sherbrooke, Sherbrooke, Québec, CANADA; ^cDepartment of Chemistry and Physics, Rowan University, Glassboro, NJ; ^dTexas Center for Superconductivity, University of Houston, Houston, TX.

We report a study of the influence of oxygen isotope exchange on the resistivity, magnetization, and specific heat of single phase and phase separated manganites. For the metallic compositions of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ and for charge-ordered $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ no change in the low temperature specific heat has been detected with ^{16}O - ^{18}O exchange, while compounds of $(\text{La}_{1-y}\text{Pr}_y)_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ ($0.4 < y < 0.6$) show a significant change in low temperature properties. The variation of the specific heat with Pr content y in $(\text{La}_{1-y}\text{Pr}_y)_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ samples is consistent with the larger volume fraction of the CO phase for higher y . Oxygen isotope exchange in these materials induced changes similar to the increase of the Pr content y which suggests an increase of the volume fraction of the CO phase in ^{18}O samples. Variation of the specific heat and magnetization in the magnetic field will also be discussed. We suggest that the changes induced by the oxygen isotope exchange are caused by an increase of the charge-ordered phase in ^{18}O samples. We will discuss the role of phase separation in giant oxygen isotope effect on ferromagnetic and charge-ordering transition temperatures.

9:00 AM D5.4

STRUCTURAL PHASE TRANSITIONS IN MANGANITES INDUCED BY "PARALLEL" MAGNETIC FIELDS. Michael D. Kaplan, Boston University, Physics Department and Simmons College, Chemistry Department, Boston, MA; George O. Zimmerman, Boston University, Boston, MA.

In low doped colossal magnetoresistance manganites the external magnetic field can induce a phase transition from a ferromagnetic metal to a ferromagnetic insulator state as observed in [1]. The measurements of the magnetostriction anomalies at this phase transition confirmed [1] that the transition is accompanied by drastic structural transformations and can be induced at either of two orientations of the external magnetic field - perpendicular to the (ab)-plane or parallel to it (in-plane orientation). In this crystal (ab)-plane the xy-ordering of the tetragonally elongated octahedrons takes place as a result of the cooperative Jahn-Teller effect. In [2] the microscopic model of structural transitions in manganites induced by the magnetic field perpendicular to the (ab)-plane was developed. Here we report the results of the development of this model for the case of the "parallel" (in-plane) magnetic field. The problem for the Jahn-Teller antiferroelastics is reminiscent of the antiferromagnetic Ising model in a parallel magnetic field. However, the triple degeneracy of the electronic state of the Mn³⁺-cation and its octahedral local symmetry contribute to several important differences. Numerical calculations are performed for the temperature and magnetic field dependence of the sublattice octahedron elongation in all three - x, y, and z - directions. The calculations of the magnetostriction are in qualitative agreement with the experimental results. 1. H. Nojiri, K. Kaneko, M. Motokava, K. Hirota, Y. Endo, K. Takahashi, Phys. Rev., B60, 4142 (1999); 2. M. Kaplan, B. Vekhter, G. Zimmerman, "Vibronic Interactions: Jahn-Teller Effect in Crystals and Molecules", M. Kaplan, G. Zimmerman, Eds., p.157, Kluwer, Dordrecht, (2001)

9:15 AM *D5.5

THE INTERPLAY OF LATTICE, MAGNETIC AND ELECTRONIC DEGREES OF FREEDOM IN MANGANITE AND RUTHEHNATE PEROVSKITES. David J. Singh, Center for Computational Materials Science, Naval Research Laboratory, Washington, DC.

Density functional calculations are used to illustrate the interplay of lattice, electronic and magnetic degrees of freedom in perovskite structure manganites and ruthenates. While both materials classes display strong couplings, the underlying physics is different - local moment double exchange physics dominates in manganites, while itinerant effects are key in the ruthenates. The variety of behaviors in the two systems and the essential similarities and differences are highlighted.

10:15 AM D5.6

OXYGEN DEFECTS IN LAYERED PEROVSKITE MANGANITES: IMPACT ON STRUCTURE, MAGNETISM, AND CHARGE. J.F. Mitchell, H. Zheng, C.D. Ling, D.N. Argyriou, Materials Science Division, Argonne National Laboratory, Argonne, IL.

Study of the delicate balance among charge, lattice, and spin in layered perovskite colossal magnetoresistive (CMR) manganites, $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$, requires a broad picture of the available structural and magnetic states. To date, these states have been tuned by appropriate changes in the La/Sr ratio. We have recently begun to study the impact of oxygen nonstoichiometry on the chemistry and physics of these quasi-2D materials. By varying the oxygen ambient and cooling process (quench vs. slow-cool), we have succeeded in preparing layered manganites in the region $0.4 < x < 1.0$ with disordered or ordered oxygen vacancies. We discuss the crystal chemistry of these phases, including oxygen location and ordering, and the impact of the defect structure on the magnetic and charge states of the layered manganites. Specifically, we show how extremely low concentrations of oxygen defects dramatically impact the transport properties and relate this effect to the oxygen defect structure.

10:30 AM *D5.7

SELF-TRAPPED STATES IN PEROVSKITES WITH CHARGE, SPIN, OR ORBITAL ORDER. Philip B. Allen and Yiing-Rei Chen, Department of Physics and Astronomy, State University of New York, Stony Brook, NY; Vasilii Perebeinos, Department of Physics, Brookhaven National Laboratory, Upton, NY.

Doped perovskite oxides often have insulator-to-metal (ItM) transitions, sometimes at very low doping (as in SrTiO_3) and sometimes at rather high doping (20% in LaMnO_3 and 50% in BaBiO_3). When charge, spin, or orbital order occur, small polarons form easily and cause the delayed ItM transition. The simplest case is BaBiO_3 , a prototype charge-ordered system. Rice and Sneddon introduced a model with nearest neighbor hopping between Bi 6s levels which are coupled energetically to distortions in the Bi-O bond lengths. Doped holes then form bipolarons. For finite hole concentration, bipolarons reorganize into stacking-faults in the charge order. These planar defects are 3d analogs of 2d stripes or 1d topological (fractionally charged) solitons in the closely related Su-Schrieffer-Heeger model of polyacetylene. The next simplest case is CaMnO_3 , a prototype two-sublattice (G-type) antiferromagnet. The relevant orbitals are now the empty Mn 3d orbitals of E_g symmetry ($x^2 - y^2, 3z^2 - r^2$). The large Coulomb interaction is modeled by taking both U and the atomic Hund energy to be ∞ . CaMnO_3 remains insulating when doped with electrons. The host Mn^{4+} ion has 3 electrons filling the T_{2g} subshell with spin $S = 3/2$. The doped electron flips the 3/2 spin to form a spin polaron, gaining delocalization energy. The resulting state retains E_g degeneracy and is Jahn-Teller-unstable. It lowers its energy by oxygen distortion, forming a hybrid which is mostly spin polaron but partly lattice Jahn-Teller polaron. A more complicated example is LaMnO_3 which has orbital order below the cooperative Jahn-Teller transition at $T_{JT} = 750\text{K}$ as well as antiferromagnetic order below $T_N = 140\text{K}$. Lattice effects dominate ($T_{JT} \gg T_N$) and doped holes form polarons which are mostly lattice type. Predictions are made for all three materials of excitation spectra and ground state properties, including Frank-Condon broadening of photoemission and optical spectra.

11:00 AM D5.8

INCREASE OF MAGNETIC TRANSITION TEMPERATURES BY REDUCTION OF LOCAL DISORDER FOR PEROVSKITE MANGANITES. B. Dabrowski, S. Kolesnik, O. Chmaissem, J. Mais, P. Prior, Department of Physics, Northern Illinois University, DeKalb, IL; J.D. Jorgensen, Materials Science Division, Argonne National Laboratory, Argonne, IL.

Thermogravimetric measurements of oxygen vacancy concentration as a function of oxygen partial pressure have established synthesis conditions for a wide range of previously unknown perovskite manganites, $\text{RE}(1-x)\text{A}(x)\text{MnO}_3$ -d (RE = La - Lu, Y; A = Ca, Sr,

Ba). Compositions with tolerance factor $0.9 < t < 1.1$ have been synthesized "in situ" on TG and their structure-properties relations studied by neutron and synchrotron diffraction, magnetic, and resistive measurements as a function of temperature (4 - 1000 K) and magnetic field (0 - 7 T). Results show that crystallographic structure is controlled mostly by t , magnetic structure by t and x , and magnetic transition temperatures by t , x , and local disorder through bond-angle dependent exchange interactions. We have succeeded to reduce local disorder by stabilizing cation and anion ordered structures over a wide range of compositions around $x = 0.5$ resulting in substantial increase of Neel (420 K) and Curie (365 K) temperatures. We show that by using this kind of atomic-scale crafting it is possible to design novel materials with desired magnetic and resistive properties, for example, enhanced low-field CMR effect near room temperature. This work was supported by ONR/ARPA and the State of Illinois under HECA

11:15 AM *D5.9

THERMALLY EXCITED SPIN DISORDER CONTRIBUTION TO THE RESISTIVITY OF LaCoO_3 . Chris Leighton, Suzanne R. English and Jing Wu, Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN.

The compound LaCoO_3 is remarkable amongst the series LaTMO_3 (where TM is a transition metal) in that it undergoes spin-state transitions with increasing temperature. At $T = 0$ the Co ion is in a non-magnetic ground state and the system is diamagnetic. At about 90 K the Co ion undergoes a thermally excited transition to a finite spin state, which is reflected as a steep rise in the magnetic susceptibility. To date it was thought that this unusual transition has no effect on the transport properties of the material. We have shown that the magnetotransport properties of this material are in fact greatly influenced by this spin-state transition. In fact the excitation to a finite spin results in a thermal activation of spin disorder. This spin disorder is suppressed by a magnetic field leading to significant negative magnetoresistance effects, which are in effect thermally excited. The effects of the spin-state transition can also be seen in the activation energy for conduction, which shows a distinct change in the region of 90 K. The data suggest that the transport at low temperature (< 90 K) is intimately related to the "spin gap". To the best of our knowledge this is the first observation of a thermally excited spin disorder contribution to the resistivity of a material with a strong correlation between electronic transport and local magnetism. Moreover, this unique situation provides us with the opportunity to study the conduction in a perovskite-type system where we can turn on the effects of a finite spin simply by increasing temperature.

11:45 AM D5.10

HIDDEN PHASE TRANSITION IN COBALTATES. Despina Louca, University of Virginia, Department of Physics, Charlottesville, VA.

$(\text{La,Sr})\text{CoO}_3$ serves as a prototype for studying crossover characteristics from static to dynamic lattice effects associated with Jahn-Teller excitations. Pair density function analysis provided strong evidence for local lattice distortions associated with a Jahn-Teller active mode that is directly correlated to the change in the magnetic/conductive states of this system. Measurements of $S(Q,\omega)$ as a function of carrier density and temperature show the presence of phonons centered at ~ 10 and 15 meV, and are not seen in an otherwise identical structure, LaAlO_3 . These phonon peaks are quite unusual and are most likely due to soft Jahn-Teller localized modes that are dispersionless. Their collective activation appears around ~ 60 -70 K marking the temperature of a Jahn-Teller gap below which spin fluctuations appear frozen.

SESSION D6: EARTH'S PEROVSKITES II - THEORY

Chair: Graeme J. Ackland
Wednesday Afternoon, April 3, 2002
Golden Gate A2 (Marriott)

1:30 PM *D6.1

THERMOELASTIC PROPERTIES OF $(\text{Mg,Fe})\text{SiO}_3$ -PEROVSKITE. Boris Kiefer and Lars Stixrude, University of Michigan, Department of Geological Sciences, Ann Arbor, MI.

Ferromagnesian silicate perovskite is thought to be the most abundant mineral in the earth's lower mantle between 660 km and 2900 km depth. Most previous theoretical work and laboratory experiments have focused on the magnesium endmember and little is known about the influence of iron on important geophysical parameters such as elastic constants at relevant pressure and temperature conditions. To explore the effects of iron we performed static spin-polarized first-principle calculations with variable cell shape. We employed the planewave pseudopotential method to investigate super cells with up to 80 atoms and iron contents up to 25 at%. We investigated $\text{Mg} \rightarrow \text{Fe}$ substitutions and fixed iron in its high spin state which is thought to

be prevalent throughout the earth's lower mantle. We optimize the cell shape and the internal coordinates simultaneously to investigate the equilibrium structure for a pressure range that covers the earth's lower mantle. The calculated elastic constants can be used directly to determine the effect of iron on aggregate properties such as the shear modulus and the single-crystal elastic wave velocities at high pressures.

Our preliminary results show that the unit cell increases in volume and becomes less distorted with increasing iron content in agreement with experimental observations. The equation of state is almost independent of the iron content and the arrangement of the iron atoms in the unit cell. The shear modulus on the other hand shows a more pronounced dependence on the iron content, it is reduced by 7.7% for 25 at% iron as compared to MgSiO_3 perovskite at 135 GPa, the pressure at the base of the earth's lower mantle. *This research was performed in collaboration with Renata Wentzcovitch.*

2:00 PM *D6.2

FIRST-PRINCIPLE SIMULATIONS OF THE STABILITY OF MgSiO_3 PEROVSKITE AT LOWER MANTLE CONDITIONS. S. Scandolo and R. Car, Princeton Materials Institute and Department of Chemistry, Princeton University, Princeton, NJ.

First-principles molecular dynamics simulations have been used to investigate the structural stability of MgSiO_3 perovskite, the major component of the Earth's lower mantle. Simulations were carried out at a constant pressure of 120 GPa, and at various temperatures up to 5000 K, i.e. well above the lower mantle geotherm. We find that MgSiO_3 persists in the low-temperature $Pbnm$ crystal structure up to the highest temperatures. Finite-temperature free-energy profiles for distortions away from the $Pbnm$ structure show that temperature-induced displacive transitions are unlikely at any temperature below melting. Other candidate phases for MgSiO_3 at high temperature are found to convert spontaneously to the $Pbnm$ structure during the simulation. In conclusion, first-principles simulations robustly indicate that MgSiO_3 retains the low-temperature / high-pressure $Pbnm$ crystal structure at the temperatures of relevance for the deep mantle.

2:30 PM *D6.3

FIRST PRINCIPLES THERMOELASTICITY OF MgSiO_3 PEROVSKITE: CONSEQUENCES FOR THE INFERRED PROPERTIES OF THE LOWER MANTLE. Stefano de Gironcoli, Scuola Internazionale Superiore di Studi Avanzati (SISSA), Trieste, ITALY.

Some key thermoelastic properties of MgSiO_3 -perovskite (**pv**) have been determined at lower mantle (LM) pressures and temperatures using the quasi-harmonic approximation in conjunction with first principles phonon dispersions. The adiabatic bulk moduli (K_S) of **pv** and of an assemblage of 80 vol% **pv** and 20 vol% MgO were obtained along the thermodynamically inferred adiabat and compared with the seismic counterpart given by the preliminary reference Earth model (K_{PREM}). The discrepancy between calculated K_S 's and K_{PREM} in the deep LM suggests a super-adiabatic gradient, or subtle changes of composition, or phase, or all beginning at about 1200 km. The Anderson Grüneisen parameter, $\delta_S = (\partial \ln K_S / \partial \ln \rho)_P$, was predicted to decrease rapidly with depth (from 2.7 to 1.2 across the LM) supporting the thermal origin for the lateral heterogeneities throughout most of the LM. Research performed in collaboration with B.B. Karki, R.M. Wentzcovitch, and S. Baroni.

3:15 PM D6.4

ELASTIC CONSTANTS OF MgSiO_3 PEROVSKITE AT LOWER MANTLE PRESSURE AND TEMPERATURE CONDITIONS. M. Cococcioni^a, R.M. Wentzcovitch^{a,b}, S. de Gironcoli^a, B.B. Karki^b, and S. Baroni^a; ^aSISSA, Trieste, ITALY; ^bDept of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN.

Phonon dispersions of MgSiO_3 perovskite obtained using density functional perturbation theory are used to determine the thermal contribution to the Helmholtz free energy within the quasi-harmonic approximation, as a function of hydrostatic pressure and for a number of independent strained configurations. Energy-strain relations are then used to extract the individual elastic coefficients of MgSiO_3 perovskite throughout Earth's lower mantle (LM) pressure-temperature regime.

3:30 PM D6.5

QUASIHARMONIC FREE ENERGIES WITH SOFT MODES. Graeme Ackland and Neil Drummond, Dept. of Physics and Astronomy, University of Edinburgh, Edinburgh, SCOTLAND.

Equations of state for materials well below their melting point can be efficiently calculated using the quasiharmonic approach, in which phonon frequencies are calculated at a range of volumes and the

modes populated according to Bose-Einstein statistics. By contrast to molecular dynamics and Monte Carlo approaches, the quasiharmonic method allows a properly quantum mechanical treatment of the phonon spectrum. Its analytic form enables the link between interatomic forces and structural properties to be elucidated, such that the changes in the former (material composition) required to produce specific changes in the latter (macroscopic properties) are laid bare. In perovskite materials, the quasiharmonic approach fails spectacularly: unstable phonons with imaginary frequencies lead to divergent free energies. Here, we present a method for addressing this, retaining the concept of well defined normal modes, but allowing the unstable-mode branch to be described by a quantised double well, whose parameters are immediately recovered by a static relaxation of the soft mode phonons. Within this model, an analytic expression for the free energy in terms of properties of the static lattice is retained. Phase transformations temperatures can be predicted, and the strength of the first-order nature of the transition arises naturally from the coupling of the phonons to the symmetry-breaking strain, which is present in the low symmetry phase and absent in the high symmetry case. The model is applied to perovskite, using both simple interatomic potential models and data from pseudopotential data and phonon frequencies calculated from lattice dynamics, using force constants from finite displacements.

3:45 PM D6.6

THE ORTHORHOMBIC PHASE OF CaSiO_3 PEROVSKITE.

Blanka Magyar-Köpe, Göran Grimvall, Theory of Materials, Department of Physics, Royal Institute of Technology, SCFAB, Stockholm, SWEDEN; Levante Vitos, Börje Johansson, Applied Materials Physics, Department of Materials Science and Engineering, Royal Institute of Technology, Stockholm, SWEDEN; János Kollár, Research Institute for Solid State Physics and Optics, Budapest, HUNGARY.

Ab initio total energy calculations combined with a global parametrization method for perovskites are used to investigate the instability of cubic CaSiO_3 perovskite against octahedral distortions. We propose a theoretical equilibrium crystal structure of orthorhombic $Pbnm$ symmetry with 7° average tilting of the SiO_6 octahedra relative to the cubic axis. The orthorhombic structure is lower in energy than the cubic phase with a barrier of 63 meV per formula unit. Albeit it is gradually reduced with hydrostatic pressure, the predicted octahedral distortion persists up to 150GPa. The possibility of stabilization through the vibrational entropy of the cubic structure is considered.

4:00 PM D6.7

COMPUTER MODELLING OF MgSiO_3 PEROVSKITE INTERFACES. L.M. Alfredsson, S.C. Parker, Department of Chemistry, University of Bath, Bath, UNITED KINGDOM; C.R.A. Catlow, The Royal Institution, London, UNITED KINGDOM.

Computer simulation techniques represent a powerful complementary tool for studying mineral interfaces. The aim of this presentation is to describe the recent progress in modelling the structure of magnesium silicate perovskite surfaces and grain boundaries at the atomic level. One consequence of the very high pressures and temperatures found in the earth's mantle is that the interface properties of minerals found under these extreme conditions are poorly understood, and yet the interfaces will control the microstructure and can potentially be an important location for impurities. The basis of these techniques is to use a combination of electronic structure and atomistic methods. The latter using Born Model of Solids where simple parameterised analytical equations are employed to describe the interactions between atoms. We will show that by comparing electronic structure and atomistic simulation methods, the atomistic simulation techniques need to include a representation of the electronic polarisability. In addition, the results to date, show that the most stable low index interfaces are those where the outermost atomic layer is magnesium rich. Finally, we will show how such complex interfaces can be generated and the solubility of impurities at these interfaces.

4:15 PM D6.8

SEMI-EMPIRICAL DENSITY FUNCTIONAL MODELS OF SILICATE PEROVSKITES. Sofia Akber-Knutson, Mark Bukowinski, University of California at Berkeley, Dept of Earth and Planetary Sciences, Berkeley, CA.

We explore the mechanism of impurity solubility in silicate perovskite and its pressure dependence. Our model extends the density-functional-based Variationally Induced Breathing (VIB) model, shown to be accurate when applied to highly ionic materials. Its efficiency allows practical simulations of crystals containing hundreds of structural degrees of freedom, making it ideal for application to materials containing small concentrations of impurities. However, VIB overestimates the compressibility of silicates because it overestimates the Si-O repulsive interaction. To correct for this, we include in the

Si-O interaction a semi-empirical covalent correction, which allows the equalization of electronegativities by optimizing the charge transfer between ions. We choose covalent parameters such that the calculated equation of state of stishovite agrees with those derived from recent experiments. We find these parameters also yield excellent results for the model Earth's lower mantle silicate perovskites: MgSiO_3 ($T = 300\text{K}$, $V_o = 162.63 \pm 0.03 \text{ \AA}^3$, $K_o = 257.0 \pm 1.1 \text{ GPa}$, $K' = 4.05 \pm 0.01$, $Z = 4$) and CaSiO_3 ($T = 300\text{K}$, $V_o = 45.90 \pm 0.02 \text{ \AA}^3$, $K_o = 227.5 \pm 2.0 \text{ GPa}$, $K' = 4.28 \pm 0.01$, $Z = 1$). In the Earth, these perovskites also contain some Al and Fe, believed to significantly affect the properties of these minerals. We report progress on simulations designed to examine the effects of aluminum concentration on the structure, density, and compressibility of MgSiO_3 perovskite. We also compare the energetics of various substitution mechanisms of aluminum into the Mg and Si sites in the lattice, including those which introduce oxygen vacancies. Preliminary calculations for an Al substitution of both Mg and Si at an Al concentration of 12.5% ($\text{Mg}_{7/8}\text{Al}_{1/4}\text{Si}_{7/8}\text{O}_{24}$) suggest that the replacement of Mg by the smaller and more highly charged Al changes the sense of tilt of the neighboring SiO_6 octahedra, from $+- -$ to $++ -$, in the notation of Glazer (1972). The calculated volume and compressibility of this perovskite nearly match those of the pure magnesian end-member. However, calculations including large concentrations of oxygen vacancies indicate significant increases in the volume and compressibility.

SESSION D7: POSTER SESSION SYNTHESIS AND GROWTH AND MAGNETORESISTIVE PEROVSKITES

Chair: Chris Leighton

Wednesday Evening, April 3, 2002

8:00 PM

Salon 1-7 (Marriott)

D7.1

EFFECTS OF STRONTIUM MODIFICATION ON DIELECTRIC PROPERTIES PZT THIN FILMS WITH DIFFERENT Zr/Ti RATIOS. Dong Heon Kang, Sang Hyun Shin, Young Ho Kim, Sang Keun Gil, Ki Woon Park and Bong Hee Cho, TICEM and Dept of Electronic Materials Engineering, The University of Suwon, Suwon, KOREA.

$(\text{Pb}_{1-x}\text{Sr}_x)(\text{Zr}_{0.8}\text{Ti}_{0.2})\text{O}_3$ (PSZT80) and $(\text{Pb}_{1-x}\text{Sr}_x)(\text{Zr}_{0.6}\text{Ti}_{0.4})\text{O}_3$ (PSZT60) thin films were fabricated via the metallorganic solution deposition technique on Pt/Ti/SiO₂/Si(100) substrates. Their crystal structure, microstructure and dielectric properties were investigated as a function of strontium (x) content. All films, regardless x content and Zr/Ti ratio, possessed a polycrystalline and dense microstructure with no evidence of secondary phase formation by annealing at 700°C. With increasing x, the lattice constant tended to be decreased and grain size became slightly larger for both PSZT compositions, while the effect of strontium on dielectric properties was found to be different with Zr/Ti ratio. For the PZT(60/40), dielectric constant and remanent polarization showed the decreasing tendency with increasing x. While for the PSZT80 films, the dielectric constant and remanent polarization improved from 530 and 20 $\mu\text{C}/\text{cm}^2$ to 1020 and 23 $\mu\text{C}/\text{cm}^2$, respectively with adding x up to 0.1 and then decreased with further addition. The stable dielectric loss, below 0.02 was observed for all compositions. Especially the apparent improvement in fatigue behaviors was observed for the PSZT80 film by adding strontium. These results were explained in terms of polarization characteristics occurring in the mixed ferroelectric and antiferroelectric electric phases.

D7.2

EPITAXIAL PEROVSKITE LaVO_3 /BST/PLZT/LSCO HETERO-STRUCTURES FOR FERROELECTRIC FIELD EFFECT MEMORY DEVICES. Woong Choi and Tim Sands, University of California, Dept of Materials Science & Engineering, Berkeley, CA.

The ferroelectric field effect transistor (FET) configuration permits a nonvolatile memory element with nondestructive readout. However, the reliable performance of ferroelectric field effect transistors based on silicon has yet to be demonstrated, mainly because of the screening of the field effect by the interface states between the ferroelectric thin film and the silicon. The use of epitaxial oxide heterostructures has been suggested as a way of circumventing this problem. Epitaxial thin films of several semiconducting oxides such as $(\text{La,Sr})_2\text{CuO}_4$ and $(\text{La,Ca})\text{MnO}_3$ have been used by previous researchers to build epitaxial heterostructures in a ferroelectric FET configuration. In contrast to these heavily doped or degenerate semiconducting oxides, LaVO_3 can be synthesized with a relatively low ionized hole concentration ($\sim 10^{18} / \text{cm}^3$) that could make the ferroelectric field effect more pronounced. Earlier work showed the optimal ferroelectric properties of epitaxial $\text{LaVO}_3/(\text{Ba,Sr})\text{TiO}_3$ (BST)/(Pb,Lu) Zr_2TiO_7

(PLZT)/(La,Sr)CoO₃ (LSCO) heterostructures on a perovskite substrate along with the modulation of the depletion layer in LaVO₃ layer. In this continuing study, the channel resistance through the LaVO₃ layer is measured as a function of the poling voltage to indicate ferroelectric switching. The thickness of the LaVO₃ layer is optimized to achieve and enhance memory effect.

D7.3

INFLUENCE OF VANADIUM DOPING ON STRUCTURAL AND FERROELECTRIC PROPERTIES OF LASER ABLATED SrBi₂Ta₂O₉ THIN FILMS. Rasmi R. Das, P. Bhattacharya, W. Pérez and Ram S. Katiyar, Physics Department, University of Puerto Rico, San Juan, PR.

Bismuth layered ferroelectric SrBi₂Ta₂O₉ (SBT) is a prime candidate for non-volatile memory applications due to its fatigue free nature for up to 10¹² switching cycles. In this report, we have doped certain concentration (0, 5, 10, 15, 20%) of vanadium at Ta-site of SBT thin films and study their influence on the structural and electrical characteristics. Individual compositions of vanadium doped targets with 5% excess bismuth were synthesized by a conventional solid state route. Thin films were grown on platinumized silicon substrates using an excimer laser (KrF, 248 nm) with an energy density of ~2.5 J/cm². During deposition the substrate temperature was maintained at 500°C with an oxygen pressure of 200 mTorr. As-grown films were annealed at temperatures ranging from 650 to 800°C. X-ray diffraction and micro-Raman spectroscopy was used to study the structural changes in SBT films with vanadium concentration. The increase of orthorhombic lattice parameters of SBT films confirms the vanadium substitution at Ta-site. The ferroelectric properties of SBT films were enhanced with the doping concentration. SBT films show dielectric constant of about ~300 with tangential loss of 0.02 at a frequency of 100 kHz. Dielectric constant increases with increase in V-concentration. The leakage current density of the films was of the order of ~10⁻⁸ A/cm². Detailed results of structural and electrical properties will be presented in close correlation with the inherent characteristics of doped V⁵⁺ ion.

D7.4

EPITAXIAL GROWTH AND PROPERTIES OF (Ba,Sr)TiO₃ THIN FILM ON SAPPHIRE FOR HIGH FREQUENCY CAPACITOR APPLICATIONS BY COMBUSTION CHEMICAL VAPOR DEPOSITION (CCVD) TECHNOLOGY. Todd A. Polley, Yong Dong Jiang, Erika Moore, Andrew T. Hunt, MicroCoating Technologies, Atlanta, GA.

Perovskite, ferroelectric thin films have excellent dielectric properties that make them ideally suited for a wide range of capacitor applications. One of the most important applications recently recognized is for advanced electronic packaging, such as high frequency signal de-coupling capacitors. Also, due to the dielectric constants dependence on applied voltage, perovskite materials offer an enticing prospect for incorporation into frequency-agile microwave electronic components, such as phase shifters and tunable filters. For these applications, (Ba,Sr)TiO₃ (BST) is attracting more and more attention because of its high permittivity, low loss, low leakage current and high tunability. BST thin films have already been deposited on a variety of substrates by vacuum-based deposition techniques. In this study, a novel, low-cost, open-air deposition technology, Combustion Chemical Vapor Deposition (CCVD), was employed to deposit BST thin films and (La,Sr)CoO₃ (LSC) bottom electrodes on sapphire substrates, which is an intrinsic low loss substrate for high frequency applications. X-ray diffraction 2θ scan and pole figure analysis were utilized to determine the phases and crystal orientations present in the deposited films. It was found that both the LSC and BST thin films were epitaxial with (111) plane parallel to the substrate surface. Scanning Electron Microscopy (SEM) showed that the deposited films were smooth and dense. Also, in this study, composition was determined by XPS and EDX, and surface roughness was measured using optical profilometry. Electrical properties will be also presented in this paper.

D7.5

PROPERTIES OF Ba-Sr-Ti-O THICK FILMS. Peter Kr. Petrov, Kumaravinathan Sarma, and Neil McN. Alford, Physical Electronics and Materials Centre, EEIE, South Bank University, London, UNITED KINGDOM.

Ferroelectric thick films of SrTiO₃ (STO) and BaTiO₃ (BTO) and their solid solution Ba_xSr_{1-x}TiO₃ (BSTO) are the subject of considerable research and show some promise in tuneable microwave devices. The sintered, non-epitaxial BSTO films made by ceramics technology, despite the comparatively inferior electrical properties (high loss level, low tuning ratio), are still attractive for many applications because of their low fabrication cost and good reproducibility. There are two main methods for sintering of BSTO films: Method 1 is a mixture (with the appropriate Ba/Sr ratio) of

BaCO₃, SrCO₃ and TiO₂ source powders, and method 2 is a mixture of BaTiO₃ and SrTiO₃ powders. This paper presents the results of a comparative study of structural and electrical properties of BSTO films made by the both methods. The films were sintered at temperatures between 900°C and 1350°C. Their structural properties were investigated using X-ray diffraction and SEM. The microwave and RF electrical properties were examined in temperature range between 250K and 350K. Our preliminary results shown that method 1 is preferable for low temperature sintering. The BSTO films sintered at 900°C with powder-mixture 1 have one well-presented BSTO phase and almost no secondary phases. The BSTO phase is absent in all samples made by method 2 while the peaks from STO and BTO phases are clearly evident on the XRD patterns. Also, when compared, samples made by method 1 exhibited better electrical performance. For sintering at high temperatures, there was almost no difference in structural perfection of BSTO films made by both methods. The measurements of electrical properties of these samples are in progress.

D7.6

Abstract Withdrawn.

D7.7

STUDY OF FIELD EMISSION CHARACTERISTICS OF SILICON FIELD EMITTER ARRAYS COATED WITH FERROELECTRIC MATERIAL. M. Hajra, N.N. Chubun, C.E. Hunt, A.G. Chakhovskoi, Electrical and Computer Engineering Dept., University of California, Davis, CA; R.G. Polcawich, US Army Research Laboratory, Adelphi, MD.

Silicon has been a promising cathode material for field emission arrays (FEAs) because of its compatibility with the integrated circuit technology. However, the noise and instability characteristics of bare silicon emitters suggest that surface modification or coating could improve emission. Various materials have been employed for Si tip coating to enhance the emission properties. Ferroelectric materials are among the candidates of interest as a coating material for silicon emitters. They exhibit properties such as low electron affinity, moderate band gap and an induced internal polarization electric field. We investigate here ferroelectric material on Si field emission cathodes using Lead Zirconate Titanate (PZT) ferroelectric thin film coating. The silicon array is coated with sol-gel PZT solution using standard spinning techniques. The thickness of a single layer of PZT was measured to be 50nm. The electrical characteristics of the uncoated and coated silicon emitter arrays are compared and evaluated using I-V measurements in the diode configuration.

D7.8

INTEGRATION OF SINGLE CRYSTAL EPITAXIAL NdNiO₃ WITH Si(100). Ashutosh Tiwari, C. Jin, J. Narayan, Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC.

We have succeeded in growing epitaxial NdNiO₃ film on Si(100) substrate under ambient oxygen pressure using a pulsed laser deposition method. The integration of NdNiO₃ with Si(100) was accomplished by lattice matching epitaxy of MgO and SrTiO₃ and domain matching epitaxy of TiN on Si(100). During domain matching epitaxy, four lattice constants of TiN match with three of silicon across the TiN/Si(100) interface. High quality epitaxial NdNiO₃ film on SrTiO₃/MgO/TiN/Si(100) showed a very sharp metal-insulator (M-I) phase transition at 200 K. Observed M-I transition in epitaxial NdNiO₃ is much sharper than that usually observed in bulk and polycrystalline films with more than four orders of magnitude change in resistivity. This Metal-insulator transition is understood to arise because of the opening of charge transfer gap between Ni³⁺ (3d) and O²⁻ (2p) band. Fabrication of thin NdNiO₃ film on silicon is likely to open numerous opportunities for perovskite based microelectronics.

D7.9

EPITAXIAL INTEGRATION OF PEROVSKITES VIA A CONDUCTING SrRuO₃ BOTTOM ELECTRODE WITH Si USING MBE. J.H. Haeni, J. Lettieri, D.G. Schlom, Dept of Materials Science and Engineering, Penn State University, University Park, PA; W. Tian, X.Q. Pan, Dept of Materials Science and Engineering, University of Michigan, Ann Arbor, MI; B.T. Liu, V. Nagarajan, K. Maki, R. Shreshtha, and R. Ramesh, Dept of Materials Science and Engineering, University of Maryland, College Park, MD.

With the goal of integrating the active properties of perovskites (e.g., ferroelectricity, pyroelectricity, and piezoelectricity) with silicon integrated circuit technology, several methods have been used to deposit perovskites on silicon. Key among these methods are epitaxial approaches in which the directionality of the active properties of perovskites can be exploited to the greatest extent. Although fully-epitaxial routes utilizing thin transition layers have been developed to integrate perovskites with silicon, those developed to date use insulating layers or layers that do not survive the oxidizing

conditions required for the deposition of epitaxial perovskite oxides. An important enabler for a broader range of perovskite-based devices or devices with improved integration density and performance is the ability to have a conducting epitaxial contact to the underlying silicon. We have achieved such a conductive contact by using epitaxial SrRuO₃ layers grown on Si (100) using molecular beam epitaxy. Vertical transport measurements show that the SrRuO₃ forms an ohmic contact with the silicon substrate, although cross section TEM indicates there is a thin, amorphous interfacial Sr-Si-O layer at the substrate / film interface. This metallic perovskite SrRuO₃ buffer layer serves as a template for the subsequent growth of an epitaxial La_{1-x}Sr_xCoO₃ / Pb_{1-x}Zr_xTiO₃ / La_{1-x}Sr_xCoO₃ stack. This ferroelectric stack exhibits increased values of d₃₃ compared to a polycrystalline counterpart grown on a Pt electrode, as well as excellent fatigue-free ferroelectric properties up to 10¹⁰ cycles. The growth conditions, as well as structural and electronic characterization of these structures by RHEED, four-circle x-ray diffraction, high-resolution TEM, and ferroelectric and vertical transport measurements of these films will be presented.

D7.10

LAYER-BY-LAYER EPITAXY OF Nb-DOPED STO STUDIED BY AN OBLIQUE-INCIDENCE OPTICAL REFLECTIVITY DIFFERENCE TECHNIQUE. X.D. Zhu, Univ. of California, Dept. of Physics, Davis, CA; Yiyang Fei, Huibin Lu, Guozhen Yang, Zhenghao Chen, Institute of Physics, Laboratory of Optical Physics, Chinese Academy of Science, Beijing, CHINA.

We studied the kinetics of epitaxy of 10% Nb-doped strontium titanate (STO) on a (001) face of strontium titanate substrate. The epitaxy was performed under pulsed laser deposition condition. By monitoring in-situ the optical reflectivity difference signal from the growth surface in oblique-incidence geometry, we were able to find the growth condition that supports a nearly perfect layer-by-layer epitaxy of Nb-doped STO. At the substrate temperature of 655 degrees Celsius and in a molecular oxygen ambient of 0.000043 Pa and 0.00025 Pa, we observed oscillatory responses in the optical reflectivity difference signal as a function of averaged thickness of the deposits, indicative of a layer-by-layer growth. The layerwise growth sustained for hundreds of molecular monolayers. Compared to a simultaneously monitored RHEED intensity, we found that the condition for a sustained oscillatory response in the optical reflectivity difference signal is more stringent than for RHEED, presumably due to the fact that the optical signal is more prone to the accumulation of defects and to the state of oxidation of the unit cell as the film thickness increases. This means that the optical technique can be used as a better in-situ gauge for the quality of the epitaxy of perovskite oxides or other multi-component materials. From the optical reflectivity difference signal versus the deposit thickness over 1000 Å, we were able to extract the real and imaginary parts of the optical dielectric constant of the epitaxially grown Nb:STO film. We found that the optical dielectric constant for a film grown under oxygen deficient condition (0.000043 Pa) is different from that for a film grown under oxygen sufficient condition (0.00025 Pa) by roughly 20%. From the evolution of the optical signal after the deposition of one monomolecular layer, we were able to determine the complex oxidation kinetics that involve both adsorption of ambient oxygen on the growth surface and the diffusion of bulk oxygen to the growth surface.

D7.11

STABILITY AND REDUCTION BEHAVIOR OF NICKEL-BASED PEROVSKITES AS EPITAXIAL FILMS AND MULTILAYERED STRUCTURES. Lane Martin, Trong-Duc Doan, Balasubramanian Kavaipatti, Andrew Francis, Paul A. Salvador, Carnegie Mellon University, Department of Materials Science and Engineering, Pittsburgh, PA.

Residual strains that exist in epitaxial films can be exploited to control their *ex-situ* topotactic reduction pathways, leading to highly metastable compounds. In this research, a modified two-step synthesis route is developed in an effort to stabilize rare-earth nickel oxides RENiO₂, which are isostructural and isoelectronic with high temperature superconducting layered copper oxides. Nearly all compositions in the RENiO_{3-x} family but LaNiO₃ are metastable and difficult to synthesize, particularly RENiO₂. In the first step, thin films of both stable LaNiO₃ and metastable NdNiO₃ were grown on various single crystal perovskite substrates using pulsed laser deposition, and some were capped with SrTiO₃ or YMnO₃ as protective layers. In a second step, the films were subjected to both *in-situ* and *ex-situ* reducing treatments. The films are compared in terms of their stability both in the as-grown state and after reduction under different temperatures and atmospheres. A marked increase in the stability of the capped thin films against structural decomposition is observed. Topotactic reduction pathways are discussed with respect to epitaxial (structural) relationships between oxygen sub-stoichiometric films and the under- and over-layer materials, as well as the reductive conditions employed. Emphasis is placed on

understanding and achieving the complete topotactic reduction of RENiO₃ thin films to RENiO₂.

D7.12

MECHANISMS OF HETERO-EPITAXIAL NUCLEATION OF YBa₂Cu₃O_x AT THE BURIED PRECURSOR/SrTiO₃ INTERFACE IN THE POST-DEPOSITION REACTION PROCESS. L. Wu, V.F. Solovoyov, H.J. Wiesmann, Y. Zhu, M. Suenaga, Brookhaven Nat'l Lab. Mater. Sci. Dept., Upton, NY.

The BaF₂ process is an *ex situ* process for the synthesis of YBa₂Cu₃O₇ (YBCO) films. In this process a precursor film, which is a stoichiometric mixture of Y, Cu, and BaF₂, is deposited on a substrate by electron-beam evaporation and then heated to form YBCO in a flowing inert-gas atmosphere containing O₂ and H₂O. It is easy to grow thin epitaxial YBCO films with the *c*-axis orientation which is required for their high critical current densities. However, the growth of the *c*-axis oriented films becomes very difficult when the films exceed ~2 micrometers in thickness. (The required thickness is ~ >5 micrometers.) This is one of the main concerns for this processing method becoming a commercially viable fabrication process for technological YBCO conductors. To understand this problem, we investigated the hetero-epitaxial nucleation of YBCO in the quenched specimens with various precursor thickness utilizing TEM and XRD techniques. Through this study, we have identified the nucleation mechanisms of YBCO at the buried interface between a precursor film and SrTiO₃, the substrate. It is shown that the preferential nucleation of YBCO at the interface is due to (1) the strong chemical affinity of the (Y,Ba)-oxy-fluoride, an intermediate phase, to SrTiO₃ and (2) the epitaxial alignment of its (111) planes with SrTiO₃'s (001) surface which reduces the activation barrier for the formation of YBCO. In thin films (<2 micrometers) the YBCO nuclei, whose *c*-axes are perpendicular to the SrTiO₃ surface, form directly from this aligned oxy-fluoride. In thick films (5 micrometer), however, this oxy-fluoride decomposes into a disordered transitory cubic phase which then orders to form tetragonal YBCO nuclei with three orientational variants, one with its *c*-axis perpendicular and two with their *c*-axes parallel to the (001) plane of SrTiO₃.

D7.13

EPITAXIAL GROWTH OF YBa₂Cu₃O_{7-x} FILMS WITH LIQUID FLUXED STRUCTURE BY IN-SITU E-BEAM DEPOSITION. Jeong-uk Huh^{a,b}, Tsuyoshi Ohnishi^a, William Jo^a, Robert Sinclair^b, Robert H. Hammond^a, Malcolm R. Beasley^a, ^aGeballe Laboratory for Advanced Materials, Stanford University, Stanford, CA; ^bDepartment of Materials Science and Engineering, Stanford University, Stanford, CA.

High temperature superconductor YBa₂Cu₃O_{7-x} is deposited using in-situ electron beam evaporation over a wide range of rates (1-20 nm/sec). Although deposited under oxygen pressure of 5 × 10⁻⁵ Torr, YBa₂Cu₃O_{7-x} is stable owing to the higher activity of atomic oxygen and has critical current density greater than 1 MA/cm². TEM analysis shows different microstructures of the YBa₂Cu₃O_{7-x} depending on the growth temperature and deposition rate. It is found that the defect free microstructure is caused by layer-by-layer growth and the defected region is grown when island growth mechanism is dominant. The microstructure of the film indicates that YBa₂Cu₃O_{7-x} was grown in Ba-Cu-O liquid flux layer. It is found that critical currents of the films show a strong dependence on microstructure. Secondary phases such as CuO and Y₂O₃ are found in the interface or the surface and in the matrix of the film, respectively. It is interesting to observe that (103) orientation of YBa₂Cu₃O_{7-x} and formation of other phases increase when the oxygen activity is large or the deposition rate is high.

D7.14

ULTRAVIOLET-ASSISTED PULSED LASER DEPOSITION OF BARIUM STRONTIUM TITANATE ON Si: CHARACTERIZATION OF THE INTERFACIAL LAYER. Valentin Craciun, Joshua M. Howard, Nabil D. Bassim, Chad Essary, Rajiv K. Singh, Materials Science and Engineering, University of Florida, Gainesville, FL.

Barium strontium titanate (BST) is one of the most studied materials for capacitors due to its very high bulk dielectric constant. However, thin BST films always exhibit much lower dielectric constant values than those measured for the bulk because of the presence of fine grain, mechanical stresses, formation of interfacial layers, or rough interfaces. The formation of the interfacial layer is of particular concern for the growth of BST films directly on Si substrates because of the high temperatures and oxygen pressures required during deposition. An ultraviolet-assisted pulsed laser deposition (UVPLD) technique has been developed which allows the growth of high quality-high dielectric constant films on Si at much lower temperatures than those usually employed. To account for the observed improvement in electrical, structural and optical properties, a detailed investigation of the grown BST films and of the interfacial

layer were performed and the results are presented here. According to our investigations the oxygen trapped inside the film is the main source for the formation during growth and any further annealing treatments of the interfacial layer. We have investigated using x-ray photoelectron spectroscopy, x-ray diffraction and reflectometry, high-resolution transmission electron microscopy and Rutherford backscattering spectrometry techniques the quantity of oxygen trapped inside BST films grown by the UVPLD technique and the thickness and characteristics of the interfacial layer. Our results show that some of the formed SiO_x is being homogeneously mixed with the first monolayers of the growing BST films.

D7.15

PULSED LASER DEPOSITION OF $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 THIN FILMS AND HETEROSTRUCTURES. Guy Garry, Albert Lordereau, Ceramics & Packaging Dept, Thales Research & Technology, Orsay, FRANCE.

$\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 (PMN-PT) thin films have been deposited on MgO (001) and Al_2O_3 (00.1) substrates by Pulsed Laser Deposition. Oxygen pressure and substrate temperature were found to be the most sensitive parameters for controlling composition of the film. X-ray characterizations were carried out on thin films deposited at three different pressures and for temperatures between 400°C to 650°C. For all oxygen pressures investigated, X-ray diffraction measurements showed that the films crystallize into a polycrystalline pyrochlore phase for the lowest temperatures moving into a textured perovskite phase for the highest temperatures. In the latter case, the films were found to be (100) and (111) oriented respectively on MgO (001) and Al_2O_3 (00.1). Dielectric and ferroelectric characterizations of these layers require electrodes on both sides of the films. We carried out epitaxial growth of PMN-PT / RuO_2 bilayers on Al_2O_3 (00.1) substrates. Both layers exhibit a (111) orientation with good crystalline quality. Preliminary results of dielectric and ferroelectric measurements of these bilayers will be given.

D7.16

CRYSTAL GROWTH OF QUATERNARY RUTHENIUM AND OSMIUM CONTAINING PEROVSKITES FROM REACTIVE HYDROXIDE FLUXES. Hans-Conrad zur Loye, Katharine E. Stitzer, Mark D. Smith, University of South Carolina, Department of Chemistry and Biochemistry, Columbia, SC.

The utilization of high temperature solutions has been very effective for the growth of oxide single crystals containing virtually all elements in the periodic table with a wide range of oxidation states. Oxide crystals have been grown from many different high temperature solutions, including alkali and alkaline earth carbonates, halides, peroxides, super oxides, and hydroxides. Of these diverse solvent systems, the hydroxide melts have proven to be the most advantageous for obtaining crystals containing elements in unusually high oxidation states. Our group has been concentrating on the use of such melts to incorporate members of the platinum group metals into oxide structures. To that end, we have synthesized new quaternary osmium and ruthenium containing perovskite oxides from reactive hydroxide fluxes. Specifically, the crystal growth, structural characterization, and magnetic properties of Ba_2MO_6 ($\text{M} = \text{Li}, \text{Na}$) and $\text{Ba}_3\text{MRu}_2\text{O}_9$ ($\text{M} = \text{Li}, \text{Na}$) will be discussed. Of particular interest is the coupled structural and magnetic transition that $\text{Ba}_3\text{NaRu}_2\text{O}_9$ undergoes at low temperatures.

D7.17

FORMATION ENTHALPIES OF TETRAVALENT LANTHANIDE PEROVSKITES BY HIGH TEMPERATURE OXIDE MELT SOLUTION CALORIMETRY. S.V. Ushakov, J. Cheng, A. Navrotsky, Thermochemistry Facility, Department of Chemical Engineering and Materials Science, University of California at Davis, Davis, CA; J. Wu, S.M. Haile, Materials Science Department, California Institute of Technology, Pasadena, CA.

Tetravalent lanthanide perovskites, MLnO_3 , where $\text{M} = \text{Ba}, \text{Sr}$ and $\text{La} = \text{Ce}, \text{Pr}, \text{Tb}$ represent an unusual case of lanthanide stabilization in octahedral coordination of interest due to their ionic and proton conducting properties. While enthalpies of MLnO_3 formation from oxides follow the usual trend for perovskites namely decreasing stability with increasing structural distortion, BaPrO_3 was reported to be anomalously stable. The formation enthalpies of BaCeO_3 are of dispute in the literature. We used high-temperature oxide melt solution calorimetry to determine formation enthalpies for several MLnO_3 compounds. BaPrO_3 and BaCeO_3 perovskites were synthesized from chemical solution methods followed by calcination at 1100-1300°C. PrO_2 was synthesized by oxidation of Pr_6O_{11} in an oxygen flow at 280°C. The samples were characterized by X-ray diffraction, thermogravimetric and differential thermal analyses. Drop solution enthalpies were measured in a Calvet type twin microcalorimeter, using $3\text{Na}_2\text{O} \cdot 4\text{MoO}_3$ solvent at 702°C. The obtained value for molar formation enthalpy of BaPrO_3 from oxides is

about -67 ± 4 kJ at room temperature. This value falls on the normal trend of energetics versus tolerance factor and does not show any special stabilization of BaPrO_3 relative to other MLnO_3 perovskites. Ongoing experiments to quantify the effects of deviation in stoichiometry of BaCeO_3 on thermodynamic stability will be discussed.

D7.18

THE SYNTHESIS OF LAYERED PEROVSKITES AND PEROVSKITE-RELATED MATERIALS IN MOLTEN SALT FLUXES. Margret J. Geselbracht, Jeanette M. Blaine, Dept of Chemistry, Reed College, Portland, OR; E. Sarah Cowell, Dermot O'Hare, Inorganic Chemistry Laboratory, Oxford, UNITED KINGDOM.

Layered perovskites and perovskite-related materials are typically prepared by high temperature solid state synthesis methods. In some cases, for example the Ruddlesden-Popper type layered perovskites Sr_2TiO_4 and $\text{Sr}_3\text{Ti}_2\text{O}_7$, the reaction temperatures are as high as 1400-1500°C. Lower temperatures would be advantageous for many reasons. We have explored one approach to lowering the reaction temperature, the use of molten salt fluxes to enhance the reactivity of starting materials. We will describe an overview of our results so far on the use of molten salt fluxes to synthesize titanate and niobate-based layered perovskites and perovskite-related materials. Specific examples will include the synthesis of $\text{RbCa}_2\text{Nb}_3\text{O}_{10}$, Sr_2TiO_4 and $\text{Sr}_3\text{Ti}_2\text{O}_7$ from molten chloride fluxes and the synthesis of $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ from a low temperature precursor isolated from a molten hydroxide flux.

D7.19

HIGH-PRESSURE AND HIGH-TEMPERATURE SYNTHESIS OF A NOVEL PEROVSKITE COMPOUND: MAGNETIC AND ELECTRIC PROPERTIES OF THE RHODIUM OXIDE SrRhO_3 . K. Yamaura, E. Takayama-Muromachi, National Institute for Materials Science, Superconducting Materials Center, Tsukuba, JAPAN; D.P. Young, Dept of Physics and Astronomy, Louisiana State Univ, Baton Rouge, LA.

Polycrystalline rhodium(IV) oxide perovskite SrRhO_3 was synthesized by high-pressure technique at 6 GPa and 1500°C, followed by measurements of the magnetic susceptibility, electrical resistivity, thermopower, and specific heat. Rietveld study (x-ray) found a distorted perovskite structure, GdFeO_3 -type, was reasonable to SrRhO_3 ; space group was $Pnma$ and lattice parameters were $a = 5.5394(2)$ Å, $b = 7.8539(3)$ Å, and $c = 5.5666(2)$ Å. Oxygen vacancies in the perovskite were quantitatively investigated by thermogravimetric analysis and found to be insignificant. The title compound shows Fermi-liquid behavior in its electrical resistivity. The magnetic susceptibility is large [$\chi(300\text{K}) \sim 1.1 \times 10^{-3}$ emu/mol-Rh], and the character seems to be intermediate between enhanced Pauli- and CW-type paramagnetism.

D7.20

STRAIN EFFECTS IN EPITAXIALLY GROWN $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ THIN FILMS. A.Y. Ramos, H.C.N. Tolentino, LNLS, Campinas, BRAZIL; E. Favre-Nicolin, L. Ranno, Lab. Louis Neel, CNRS, Grenoble, FRANCE.

Sr-doped manganites, of composition close to $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO), are receiving a great deal of interest due to their potential use for a new generation of spin-based devices. It has been observed that the ferromagnetic coupling and mobility of the eg electron in manganese thin films differs from the values obtained on bulk specimens. The conduction bandwidth is directly connected to the geometry of the Mn-O-Mn bond so slight crystallographic distortions are expected to have drastic effects on magnetism and transport. LSMO films grown over a monocrystalline SrTiO_3 (STO) substrate have been studied by X Ray Diffraction (XRD) and EXAFS. The mismatch between the cell parameter of STO (cubic $a=0.3905$ nm) and LSMO (pseudocubic $a=0.387$ nm) is of about 1%. The XRD study has shown that for film thickness below 1000Å the epitaxial growth of LSMO over STO substrate results in an expansion of in-plane cell parameters and, correlatively, an out-of-plane compression. This anisotropy has been tentatively associated to anisotropy variations in the Mn-O-Mn angle, but without any experimental evidence at the local scale. In this study, we used Mn K-edge P-EXAFS, to get specific information on the in-plane and out-of-plane local structure around Mn atoms of a 600Å-thick LSMO/STO film. The results are compared to those obtained in the same geometrical conditions in a reference film of LSMO of the same thickness grown over a MgO (MO) substrate, out of the conditions of epitaxy, where no strain effect has been observed by XRD. The Mn-O distance remains unchanged for both samples. The Mn-Mn bond length suffers an in plane elongation of about 3% in LSMO/STO (and consequently an increase of Mn-O-Mn angle). On the other hand, no out-of-plane MnMn bond length compression has been observed.

D7.21

THE CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF $\text{Ba}_4\text{Mn}_3\text{O}_{10}$. C.A. Moore and P.D. Battle, Inorganic Chemistry Laboratory, University of Oxford, Oxford, UNITED KINGDOM; V.G. Zubkov, A.P. Tyutyunnik, I.F. Berger, V.I. Voronin and G.V. Bazuev, Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences, Ekaterinburg, RUSSIA.

A structural and magnetic investigation has been conducted on a polycrystalline sample of nominal composition $\text{Ba}_4\text{Mn}_3\text{O}_{10}$. It has been shown that $\text{Ba}_4\text{Mn}_3\text{O}_{10}$ adopts the orthorhombic $\text{Ba}_4(\text{Ti}, \text{Pt})_3\text{O}_{10}$ structure rather than that of the $n=3$ Ruddlesden-Popper phase, $\text{Ca}_4\text{Ti}_3\text{O}_{10}$. The crystal structure represents one of a number in which neither corner nor face sharing of octahedra is dominant completely, but instead a mixture of hexagonal and cubic stacking exists. The essential features are zig-zag layers parallel to the xz plane, where the layers are composed of trimers of face sharing MnO_6 octahedra. Each $[\text{Mn}_3\text{O}_{12}]$ unit is connected to four others by sharing two of the three corners at each end of the trimer. Structurally, $\text{Ba}_4\text{Mn}_3\text{O}_{10}$ bears a close resemblance to the 9R-polytype of the hexagonal perovskite BaMnO_3 . Both materials contain trimeric $[\text{Mn}_3\text{O}_{12}]$ units, and in both cases these units share apices ($\text{Ba}_4\text{Mn}_3\text{O}_{10}$ in two directions, 9R BaMnO_3 in three). Whereas 9R BaMnO_3 is composed solely of close packed layers of $[\text{BaO}_3]$ stacked along c according to the sequence $(\text{hhc})_3$, in the case of $\text{Ba}_4\text{Mn}_3\text{O}_{10}$ the layers are anion-deficient $[\text{Ba}_4\text{O}_{10}]$ and are of two types: the perovskite-like hexagonal array mixed with the more rare orthorhombic packing for $[\text{AX}_3]$ composition. SQUID magnetometry studies reveal two features in the molar susceptibility *vs.* temperature trace of $\text{Ba}_4\text{Mn}_3\text{O}_{10}$; one a broad maximum in the high temperature region and the other a divergence of the zero-field cooled and field cooled susceptibilities at ~ 70 K. To investigate this further, a low-temperature neutron diffraction study was carried out which showed the presence of magnetic scattering. A model that correctly predicts the positions and intensities of the magnetic reflections is based on an antiferromagnetic coupling of the spins on the d Mn^{4+} cations within the layers.

D7.22

SPIN-GLASS BEHAVIOR AND MAGNETIC PHASE DIAGRAM IN A STRONGLY CORRELATED ELECTRON $\text{La}_{0.7}(\text{Ba}_{1-x}\text{Pb}_x)_{0.3}\text{MnO}_3$ SYSTEM. Yu-Sheng Wang, Shi-Zong Gong and Ming-Fong Tai, National Chung Cheng Univ., Dept. of Physics, Chia-yi, TAIWAN.

The crystallographic structure, magnetic order and the distorted perovskite $\text{La}_{0.7}(\text{Ba}_{1-x}\text{Pb}_x)_{0.3}\text{MnO}_3$ ($0.0 \leq x \leq 1.0$) system with a constant ratio of $\text{Mn}^{4+} / \text{Mn}^{3+} \sim 0.7$ are extensively studied by x-ray crystallographic analyses and dc magnetic measurements. The detailed crystallographic parameters of all the samples are obtained by the refinements of the powder x-ray diffraction data using a Rietveld program. All samples crystallize in the rhombohedral $\text{R}\bar{3}\text{C}$ structure with the lattice parameters of $a \sim 5.50 \text{ \AA}$ and $c \sim 13.38 \text{ \AA}$. The spin glass behavior was significantly observed in low magnetic fields in all our samples. The Pb^{2+} substitution on Ba^{2+} site does not significantly affect the ferromagnetic transition temperature T_C but strongly affect the spin glass transition temperature T_g due to the disorder distribution of Pb additions.

D7.23

COMPARISON OF STRUCTURAL AND MAGNETIC PROPERTIES BETWEEN $\text{La}_{1-x}\text{Pb}_x\text{MnO}_3$ and $\text{La}_{1-x}\text{Pb}_x\text{CoO}_3$ BOTH PEROVSKITE-LIKE SYSTEMS. Yi-Ling Hsieh, Ming-Fong Tai, National Chung Cheng Univ., Dept. of Physics, San-Hsing, Chia-Yi, TAIWAN.

Two Pb-doping transition-metal oxide systems, $\text{La}_{1-x}\text{Pb}_x\text{TO}_3$ ($T = \text{Mn, Co}$; $0.0 < x < 0.5$), were prepared by a conventional solid-state reaction method. The both systems exhibit the same Rhombohedral $\text{R}\bar{3}\text{C}$ crystal structure with similar lattice parameters of $a = b \sim 5.4 \text{ \AA}$ and $c \sim 13.1 \text{ \AA}$. The partial substitution of Pb^{2+} ion on La^{3+} ion induces a mixed-valence state of T^{3+} and T^{4+} . It also leads to the occurrence of the chemical and charge disorder in the (La, Pb) sites as well as 3d orbital disorder of $\text{T}^{3+/4+}$ ions. As a result, a rich variety of magnetic and transport properties are observed. The spin-glass behavior and the coexistence of ferromagnetic (FM) and antiferromagnetic (AFM) interactions are remarkably observed in the both systems. The results of magnetic experiments show that the stronger FM exhibits in the Mn-based system than in the Co-based one. Due to the large difference in strength of FM and AFM interactions among $\text{Mn}^{n+}\text{-O}^{2-}\text{-Mn}^{m+}$ bonds, the strong ferromagnetism and the higher T_C are observed in the Pb-doped manganese. However, the much weak ferromagnetism is observed in the coblates. It is attributed to the competition of FM and AFM interactions among the $\text{Co}^{n+}\text{-O}^{2-}\text{-Co}^{m+}$ ($n, m = 3, 4$) bonds. It also leads to the spin-glass behavior appears in an extensively wider range of temperature and magnetic field.

D7.24

$\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$: A BIRD'S-EYE VIEW OF STRUCTURAL, MAGNETIC, AND ELECTRONIC STATES. J.F. Mitchell, C.D. Ling, D.N. Argyriou, J.E. Millburn, Materials Science Division, Argonne National Laboratory, Argonne, IL; J. Linton, Advanced Photon Source, Argonne National Laboratory, Argonne, IL; H. Bordallo, Intense Pulsed Neutron Source, Argonne National Laboratory, Argonne, IL.

Study of the delicate balance among charge, lattice, and spin in layered perovskite colossal magnetoresistive (CMR) manganites requires a broad picture of the available structural and magnetic states. Using special synthetic techniques, we have succeeded in extending the available range of layered manganites beyond the known $0.3 \leq x \leq 0.5$ range in the $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ solid solution. Using the complementary strengths of x-rays and neutrons, we have used these novel materials to study the extended phase diagram. The result is a wide-angle view of the interplay among charge, structure and magnetism in this system. These diffraction studies reveal three areas of particular significance to manganite physics: (1) $x = 0.5-0.6$. In this region, ferromagnetically (FM) aligned layers of Mn ions alternate to give the so-called A-type antiferromagnetic (AFM) structure. In this regime, a conductive A-type structure competes with a "charge-ordered" checkerboard array of these mixed-valent ions. These materials are allowing us to explore metallicity in a layered perovskite antiferromagnet and the relative stability of localized and itinerant states. (2) $x=0.66-0.75$. No long-range order is observed at any temperature above 5 K in this unexpected region. It is possible that long-range order is replaced by either a mixture of short-range-ordered A-type and C-type regions or by a disordered "stacking-fault" array of either A or C-type. Neutron pair distribution function studies (S. Billinge, Mich. State Univ.) show an orthorhombic strain in this tetragonal structure, a necessary condition for the validity of these structural disorder models. (3) $x=0.75-0.9$. In this region a structural phase transition from tetragonal to orthorhombic signals an orbital ordering along the b-axis. Superexchange rules show that this orbital arrangement is ideally suited to host the observed C-type AFM structure.

D7.25

GRAIN SIZE DEPENDENT MAGNETORESISTANCE AND MAGNETOTHERMOELECTRIC POWER OF $\text{La}_{0.5}\text{Pb}_{0.5}\text{MnO}_3$ SHOWING METAL-INSULATOR TRANSITION. Aritra Banerjee, Sudipta Pal, and B.K. Chaudhuri, Department of Solid State Physics, Indian Association for the Cultivation of Science, Kolkata, INDIA.

Grain size dependent transport properties (resistivity and thermopower) of $\text{La}_{0.5}\text{Pb}_{0.5}\text{MnO}_3$ has been investigated both in presence and in absence of magnetic field $B=0.0-1.5\text{T}$ (maximum). All the samples show metal-insulator transition (MIT) with a peak at the MIT temperature (T_p). Magnetic field decreases the resistivity with an increase in the peak temperature T_p . Grain size, conductivity and T_p of the sample increase with increasing annealing time. Resistivity decreases whereas, DC magnetic susceptibility increases with increasing grain size. Grain size also influences the magnetoresistance. High temperature semiconducting (insulating) part of the resistivity curve is divided into two distinct regimes. Resistivity data for $T > \theta_D/2$ (θ_D is Debye temperature), can be well fitted with the nearest neighbor small polaron hopping (SPH) model. Polaron hopping energy (W_H) decreases but polaron radius (r_p) increases with increase of grain size. The lower temperature part ($T_p > T > \theta_D/2$) of the semiconducting (insulating) regime is found to follow variable range hopping (VRH) model. With the increase of grain size, the temperature range of validity of the VRH conduction mechanism decreases. The low temperature metallic regime (for $T < T_p$) of the resistivity (both in absence and in presence of field) data fit well with $\rho = \rho_0 + \rho_{2.5}T^{2.5}$ and transport mechanism in this region is mainly dominated by magnon-carrier scattering ($\sim T^{2.5}$). Grain size has, however, comparatively little effect on Seebeck coefficient (S). In all the samples with different grain sizes, S changes sign below T_p . In contrast to magnetoresistance, application of magnetic field increases S at low temperature ($T < T_p$) for these samples. Similar to the resistivity results, thermopower data in the metallic phase (both for $B=0.0$ and 1.5T) can also be analyzed by considering magnon-scattering term along with an additional spin-wave fluctuation term ($\sim T^4$). Though variable range hopping (VRH) mechanism is supported from the resistivity data (for $T_p > T > \theta_D/2$), no signature of the validity of the VRH mechanism is obtained from the thermoelectric power data in this temperature range.

D7.26

FERROMAGNETIC ORDERING IN RUDDLESDEN-POPPER MANGANATES. Daniel Gallon, Peter Battle, Andrew Fergus, Inorganic Chemistry Laboratory, University of Oxford, Oxford, UNITED KINGDOM; Matthew Rosseinsky, Department of Chemistry, Liverpool University, Liverpool, UNITED KINGDOM.

There has been considerable recent research into manganate perovskites, in the search for compounds displaying colossal magnetoresistance. This has often been associated with the onset of ferromagnetism. Most studies have focussed on members of the $n = \infty$ (perovskite) and the $n = 2$ Ruddlesden-Popper (RP) series. However the members of the series with $n = 1$ have been largely ignored. Recently we have demonstrated that ferromagnetism can be induced in a rhodium doped $n = 1$ RP manganate upon application of a magnetic field, with associated subtle changes in the crystal structure. Here we describe the synthesis and structure of a new $n = 1$ RP manganate series which shows remarkably similar properties. Squid magnetometry shows that some members of the iridium doped Sr/La/Mn/O system display a sharp increase in magnetisation at low temperatures in fields as low as 100 Oe. However neutron diffraction experiments conducted in zero field display no evidence of this ordering. Neutron diffraction experiments in a cryomagnet have shown there to be additional contributions to the intensity of Bragg peaks as a result of ferromagnetic ordering in an applied magnetic field. We present the results of our analyses of the crystal structure under various conditions, and we discuss the effect of the applied field on the magnetic properties.

D7.27

JAHN-TELLER COUPLING IN THE PEROVSKITE MANGANITES. S. Satpathy, Dept of Physics, University of Missouri, Columbia, MO.

The Jahn-Teller effects in the manganites is studied from density-functional and model calculations. The static JT coupling is shown to produce the observed orbital ordering in $LaMnO_3$, with the band structure effects taken into account, while the dynamical JT coupling involving the quantum-mechanical motion of the oxygen octahedra leads to the experimentally observed isotope shift of the T_C .

D7.28

ORDER OF MAGNETIC TRANSITION IN $La_{2/3}A_{1/3}MnO_3$ (A = Ca, Sr and Ba) OXIDES. Yuebin Zhang, Sean Li, Nanyang Technological Univ, School of Materials Engineering, SINGAPORE; Shixue Dou, Univ of Wollongong, Institute for Superconducting and Electronic Materials, AUSTRALIA.

The magnetic phase transition behaviors of colossal magnetoresistance $La_{2/3}A_{1/3}MnO_3$ (A = Ca, Sr and Ba) perovskite oxides at Curie temperature (T_C) are explored through a systematic study of thermal, magnetic, and electronic properties. It is found that the ferromagnetic-paramagnetic transition changes from first order to second order as the ionic radius of doped alkaline earth elements, such as Ca, Sr and Ba, increases. Likewise, an orthorhombic (Pbnm) lattice structure existing in $La_{2/3}Ca_{1/3}MnO_3$ oxide changes to a rhombohedral ($R\bar{3}c$) structure in both $La_{2/3}Sr_{1/3}MnO_3$ and $La_{2/3}Ba_{1/3}MnO_3$ oxide. Lattice structure, not an electronic-polaronic conduction transition occurring in three oxides, may play an important role in the order of magnetic transition.

D7.29

STUDY OF CORRELATED IONIC MOTIONS AND DISORDER IN CRYOLITE RELATED SYSTEMS USING SOLID STATE NMR AND MOLECULAR DYNAMICS SIMULATION TECHNIQUES. Santanu Chaudhuri, Lin-Shu Du, Clare P. Grey, State University of New York, Department of Chemistry, Stony Brook, NY; Michael Castiglione, Mark Wilson, Paul Madden, University of Oxford, Physical and Theoretical Chemistry Laboratory, Oxford, UNITED KINGDOM.

Cryolite, Na_3AlF_6 , is an industrially important mineral used in aluminum extraction as a molten electrolyte. Cryolite has a double perovskite structure (ABO_3) with Na in both octahedral and distorted cubic sites. Cryolite and related isostructural oxyfluorides show interesting properties including motion of Na ions and perovskite tilting of AlF_6^{3-} octahedra. Our and previous [1] ^{19}F MAS NMR results show that there is no long range motion of fluoride ions; the high mobility of fluoride ions can be explained by the rocking and rotation of AlF_6^{3-} octahedra as a whole without breaking the Al-F linkages. The variable temperature ^{23}Na multiple quantum MAS (MQMAS) NMR results show that the exchange between octahedral and cubic sodium ions starts around 175°C. Molecular dynamics (MD) simulation with the Polarizable Ion Model can be used to simulate motions of AlF_6^{3-} octahedra. In order to simulate cryolite, we have looked into AlF_3 systems for developing a standard Al-F potential. The α - AlF_3 MD simulation results show a phase transition from a room temperature rhombohedral form to cubic AlF_3 due to the rocking motion of AlF_6^{3-} octahedra similarly found in cryolite. The structure factors and different vibrational modes in the AlF_6^{3-} were calculated as a function of simulation temperature starting with a rhombohedral simulation cell consisting of 1200 atoms. A similar potential has been used to simulate cryolite and shows rotation and

rocking of AlF_6^{3-} octahedra and the motion of the sodium ions on the simulation timescale. We are currently exploring the possibility of calculating quadrupolar coupling constant and orientation of Electric Field Gradients to compare them with experimental values measured by NMR. [1] V. Lacassagne, C. Bessada, D. Massiot, P. Florian, J. P. Coutures, J. Chim. Phys., 95, 322, 1998.

D7.30

EPITAXIAL THIN FILM OF HIGH-DIELECTRIC-CONSTANT MATERIAL $CaCu_3Ti_4O_{12}$ BY PULSED-LASER DEPOSITION. Weidong Si, Evelyn M. Cruz, C.C. Homes, Peter D. Johnson, Dept. Phys., Brookhaven National Lab, Upton, NY; Art P. Ramirez, Los Alamos National Lab, Los Alamos, NM.

Epitaxy thin films of newly-found high-dielectric-constant material $CaCu_3Ti_4O_{12}$ have been grown successfully on various substrates and conducting buffer layers, like $LaAlO_3$, YBCO and $La_{2-x}Sr_xCuO_{4+\delta}$, by pulsed-laser deposition. Thin film has a similar property as compared to single crystal, although the dielectric constant is much lower. However, it is higher than that of thin films of most other materials at room temperature. This means it is still a very promising material for various applications.

D7.31

ENHANCED STABILITY OF CHARGE AND ORBITAL ORDER IN $La_{0.8}Sr_{0.2}Mn_2O_7$. B.J. Campbell, D.N. Argyriou, J.F. Mitchell, R. Osborn, Materials Science Div., Argonne National Laboratory, Argonne, IL.

Due to its lower dimensionality, the bilayered perovskite manganite system $La_{2-2x}Sr_{12x}Mn_2O_7$ exhibits unusual ordering phenomena that are not observed in the corresponding three-dimensional perovskite systems. $LaSr_2Mn_2O_7$ ($x = 0.5$), for example, exhibits a long-range ordering of the e_g electrons into a zig-zag orbital configuration at 210 K, which then makes a reentrant disappearance at 100 K in the face of competing antiferromagnetic order. No long-range magnetic or charge/orbital (C/O) order is observed in this system in the range $0.66 < x < 0.75$, but nonstoichiometric doping levels just above 0.5 are relatively unexplored. Here, we map out the competing C/O and magnetic orderings of $La_{0.8}Sr_{0.2}Mn_2O_7$ ($x = 0.6$) and describe their evolution vs. temperature. We find that the stability of the C/O order is significantly enhanced, rather than degraded, relative to $x = 0.5$. This work was supported by the U.S. DOE Office of Science contract No. W-31-109-ENG-38.

D7.32

HALL EFFECT AND NOVEL MAGNETORESISTANCE IN $Nd_{1-x}Sr_xMnO_3$ CRYSTALS. H. Kuwahara^{a,b}, R. Kawasaki^a, K. Noda^a, Y. Ashikawa^a and Y. Hirobe^a, ^aSophia University, Dept. of Physics, Tokyo, JAPAN; ^bPRESTO, Japan Science and Technology Corporation (JST), Tokyo, JAPAN.

We have investigated Hall effect and magnetotransport properties of Nd-based manganite crystals with controlled band filling ($0.30 \leq x \leq 0.80$) grown by the FZ method. We have determined normal (R_H) and anomalous Hall (R_S) coefficients from the Hall resistivity ρ_{xy} as a function of temperature in a ferromagnetic metallic state of the samples with $0.40 \leq x \leq 0.48$. The obtained effective carrier number ($1/eR_H$) is about 1.0 hole/Mn site, which does not depend on the nominal hole concentration x . R_S is found to be proportional to ρ_{xx}^α ($1.4 \leq \alpha \leq 1.9$) and to $(M_S - M)^\gamma$ ($1.7 \leq \gamma \leq 2.2$), where M_S is the saturated magnetization. In addition, we have measured magnetoresistance (MR) in the overdoped samples ($0.50 \leq x$) showing various magnetic structures. We have found a large positive MR just below T_N in the A-type-antiferromagnetic (AF) sample ($x=0.60$), which is not the conventional negative CMR near T_C in manganites. The observed positive MR arises from magnetic-field-induced suppression of AF interaction, i.e., transition temperature (T_N) from paramagnetic high-resistive state to AF low-resistive one decreases with magnetic field intensities. In C-type-AF insulating states ($0.63 \leq x$), the $\rho - T$ curve below 40K is well explained by the variable-range hopping (VRH) mechanism. A large negative MR, which is increased with decreasing temperature, was observed in VRH region. The localization length from the characteristic temperature of VRH increases with magnetic field, which indicates that application of magnetic field induces a reduction of energy gap from E_F to the mobility edge by the Zeeman shift. The phase separation near the phase boundary ($x=0.62$) between the above mentioned two phases, the A-type-AF metal with monoclinic symmetry and the C-type-AF insulator with tetragonal one, will also be discussed.

D7.33

NEW LAYERED MANGANESE OXYCHLORIDES. Christopher S. Knee and Mark T. Weller, Department of Chemistry, University of Southampton, UNITED KINGDOM.

The synthesis, structure and preliminary magnetic characteristics of the new layered manganese oxide chlorides, $\text{Sr}_2\text{MnO}_3\text{Cl}$ and $\text{Sr}_4\text{Mn}_3\text{O}_{8-y}\text{Cl}_2$ are reported. $\text{Sr}_2\text{MnO}_3\text{Cl}$ adopts a K_2NiF_4 type structure with sheets of MnO_5 square based pyramids linked through oxygen and separated by SrCl layers; it is the end member of a new family of Ruddlesden-Popper type manganese oxide halides which includes the 3-layer member $\text{Sr}_4\text{Mn}_3\text{O}_{8-y}\text{Cl}_2$. These materials demonstrate the extension of mixed anion chemistry to manganese and will increase flexibility in designing and controlling oxidation states of new GMR materials. In $\text{Sr}_2\text{MnO}_3\text{Cl}$ the manganese is formally co-ordinated to oxygen in a square pyramidal arrangement with a much longer interaction to chloride while for $\text{Sr}_4\text{Mn}_3\text{O}_{8-y}\text{Cl}_2$ a central MnO_6 octahedron is bonded through its apices to two MnO_5Cl units similar to those present in $\text{Sr}_2\text{MnO}_3\text{Cl}$. The manganese environments, determined from Rietveld analysis of powder X-ray data, are in all cases distorted from a regular environment as might be expected for structures based on a Jahn-Teller ion such as Mn(III) . For example $4 \times 1.9452(8) \text{ \AA}$ Mn-O(1) basal bonds and apical interactions at $2.019(6) \text{ \AA}$ (Mn-O(2)) and $3.184(4) \text{ \AA}$ (Mn-Cl) for $\text{Sr}_2\text{MnO}_3\text{Cl}$. Bond valence analysis indicate that the 3 layer material $\text{Sr}_4\text{Mn}_3\text{O}_{8-y}\text{Cl}_2$ exhibits considerable potential as a new GMR material, with a level of Mn^{4+} localized on the central MnO_6 octahedron. The results of a powder neutron study of the materials aimed at accurately determining the oxygen content/distribution and hence manganese oxidation states within both materials will also be presented.

SESSION D8: FERROELECTRIC, PIEZOELECTRIC,
AND FERROELASTIC PROPERTIES I

Chair: Andrew M. Rappe
Thursday Morning, April 4, 2002
Golden Gate A2 (Marriott)

8:00 AM *D8.1

FIRST-PRINCIPLES CALCULATIONS OF PIEZOELECTRICITY AND POLARIZATION ROTATION IN PZT. Henry Krakauer and Michael Wu, College of William and Mary, Dept. of Physics, Williamsburg, VA.

Technologically important solid solution perovskite piezoelectrics such as PZT are found to have optimal electromechanical properties at compositions near the morphotropic phase boundary (MPB) separating rhombohedral and tetragonal symmetry. Recently, Noheda *et al.* [1] have discovered a new monoclinic phase within a narrow compositional range at the MPB that acts as a bridge between the rhombohedral and tetragonal phases. This discovery suggests that polarization rotation [2] may be responsible for the large piezoelectric constants found in PZT. We have used first-principles methods to investigate this. Bulk spontaneous polarization and piezoelectric stress tensor elements of $\text{PbZr}_{1/2}\text{Ti}_{1/2}\text{O}_3$ (PZT 50/50) were determined from ground-state Berry's phase calculations as a function of ϵ_3 strain, while constraining the symmetry to monoclinic Cm. Extremely large piezoelectric response is found as the polarization rotates within the mirror plane away from tetragonal symmetry. These piezoelectric constants are more than an order of magnitude larger than previously calculated first-principles co-linear piezoelectric constants. Polarization rotation is thus shown to be a key feature of the large electromechanical response of PZT.

[†] Supported by the Office of Naval Research.

[1] B. Noheda, D.E. Cox, G. Shirane, S-E. Park, L.E. Cross and Z. Zhong Phys. Rev. Lett. **86**, 3891 (2001).

[2] H. Fu and Cohen, Nature **403**, 281 (2000).

8:30 AM D8.2

SUPPRESSION OF THE PHASE TRANSITION IN Ca-DOPED SrTiO_3 WITH MODEST PRESSURE. E.L. Venturini and G.A. Samara, Sandia National Laboratories, Albuquerque, NM; W. Kleemann, Applied Physics, Univ. of Duisburg, Duisburg, GERMANY.

We report dramatic changes under modest hydrostatic pressure in the nature of the phase transition for a single crystal of SrTiO_3 doped with 0.7 mol % CaTiO_3 . The Ca cation dopants generate polar clusters within the soft, readily polarized host crystal. At ambient pressure the cluster size increases with decreasing temperature, leading to a dispersive (relaxor) ferroelectric transition at 18 K. However, the application of modest pressure stiffens the host lattice, limits cluster growth and, thus, suppresses the relaxor transition. AC dielectric constant and loss data were employed to monitor the low temperature behavior of these polar domains as a function of pressure and static electric field. The transition temperature is lowered by 20% under 0.1 kbar He pressure but retains relaxor character. However, under 0.5 kbar or greater pressure the relaxor transition is not observed. Rather, a temperature- and frequency-independent dielectric response reflects quantum paraelectric behavior. Application

of a static electric field increases the transition temperature and substantially decreases the dielectric constant in the relaxor regime but has little effect on the quantum paraelectric response. These data demonstrate the extreme sensitivity to pressure and static field of relaxors with low transition temperatures and provide additional insight into polar cluster dynamics. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Department of Energy under Contract No. DE-AC04-94AL85000.

8:45 AM *D8.3

PEROVSKITE ULTRATHIN FILMS AND SUPERLATTICES FROM FIRST PRINCIPLES. Karin M. Rabe, Rutgers Univ, Dept of Physics and Astronomy, Piscataway, NJ.

With continuing advances in algorithms and computer capabilities, first-principles density-functional calculations of structure, polarization, phonon dispersion, dielectric and piezoelectric response can now be carried out not just for bulk oxides, but for ultrathin films and simple superlattices. The effects observed can be partially interpreted in terms of the properties of component materials under appropriate mechanical and electrical boundary conditions. However, surface and interface layers, which make up a significant volume fraction of these systems, can exhibit novel behavior that might dramatically modify the properties of interest. Some recent calculations for BaTiO_3 - SrTiO_3 and PbZrO_3 - PbTiO_3 superlattices and Sr-Ti-O Ruddlesden-Popper phases will be presented. Extensions to more complex superlattices and finite temperatures through first-principles modeling will be discussed.

9:15 AM D8.4

PHASE TRANSITIONS OF SELF-POLARIZED PZT THIN FILMS. Gunnar Suchanek, Gerald Gerlach, Dresden Univ of Technology, Institute for Solid State Electronics, Dresden, GERMANY; Alexandre Deineka, Lubomir Jastrabik, Institute of Physics, Academy of Sciences of the Czech Republic, Prague, CZECH REPUBLIC; Sul Khan, T. Davitadze, Boris A. Strukov, Moscow State Univ, Moscow, RUSSIA.

Ferroelectric films prepared by various techniques exhibit a self-polarization. This self-polarization occurs due to the presence of an internal electric field, which is at least as large as the coercive field at the Curie temperature. As a consequence the film is poled whenever it is cooled down below the paraelectric-ferroelectric transition temperature. Little is known about the properties of self-polarized PZT thin films. To examine phase transitions in self-polarized PZT thin films deposited by sputtering on platinized silicon wafers the temperature dependence of refractive (n) and absorption (k) indexes were measured at various wavelengths in whole visible range at elevated temperatures up to 500°C. Optical measurements were performed with the J.A. Woollam spectral ellipsometer working on rotating analyzer mode. The optical gap E_{03} was obtained from isoabsorption curves at $\alpha=1000 \text{ cm}^{-1}$. The temperature dependence of the optical gap dE_{03}/dT was described by the electron-phonon interaction and the thermal lattice expansion. Three important temperature points of dE_{03}/dT were obtained in the range from room temperature (RT) to 500°C. A second order (order-disorder) phase transition obtained at 200°C could be caused by the appearance of mobile charged lattice defects in the film, probably oxygen vacancies. At 290°C phase changes of excess lead oxides were observed. The first order phase transition at 400°C was attributed to the ferroelectric/paraelectric phase transition. A suitable method to study thermal properties of thin film deposited onto massive substrates is the ac heater strip method which is also called 3ω method. The temperature dependence of heat capacity determined by this method showed peculiarities at 195°C, 285°C and a first order phase transition at 390°C.

9:30 AM D8.5

PIEZOELECTRIC LEAD ZIRCONATE TITANATE (PZT) THICK FILMS FOR MICROACTUATORS AND MICROSENSORS. Qing-Ming Wang, Dept of Mechanical Engineering, University of Pittsburgh, Pittsburgh, PA.

As a direct electromechanical transduction material with high electromechanical coupling effect, piezoelectric lead zirconate titanate (PZT) material in the form of thick film (thickness $>1\mu\text{m}$) has drawn much attention for a variety of microactuator and microsensor applications. In this paper, PZT thick film deposition methods including multiple layer sol-gel spin-on coating, RF magnetron sputtering, and hydrothermal processing will be discussed. It will be demonstrated that the electromechanical properties of PZT films can be tailored by crystal orientation control during the film deposition processing to better fit the need for the fabrication of micro-devices. The effect of electrode, deposition conditions and seed layer on the PZT film orientation and properties will be discussed. This paper will present a few PZT thick film microactuator and microsensor devices, which are currently pursued in our Laboratory.

10:15 AM *D8.6

THEORY OF FERROELECTRIC PHASE TRANSITIONS IN PURE AND MIXED PEROVSKITES. Yizhak Yacoby and Yakov Girschberg, Racah Institute of Physics, Hebrew University of Jerusalem, Jerusalem, ISRAEL.

We present a microscopic theory of ferroelectric phase transitions and spontaneous off-center displacements in the paraelectric phase in perovskites. We show, that the inclusion of strong intraband electron-phonon interaction (i.e. the existence of small polarons) into the framework of the interband theory of displacive like ferroelectrics, leads to local spin like structural distortions in the paraelectric phase. Their interaction with the soft mode induces spin-spin coupling through the soft phonon leading to a spin ordering phase transition. The resulting theory is shown to quantitatively explain both displacive like and order-disorder like features in two representative perovskites: KNbO_3 and PbTiO_3 . We have further extended this theory to explain the properties of mixed incipient ferroelectrics with small concentrations of ferroelectricity inducing ions such as $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$. We show that the non-uniform strong intraband electron-phonon interaction leads to the localization of virtual conduction band electrons around the Nb ions and to the off-center displacements of these ions. We consider the off-center displacements as pseudo-spins and show that their interaction with the soft phonon mode of the host lattice (KTaO_3) plays a fundamental role in the phase transition dynamics. The model quantitatively reproduces the basic experimental data in the quantum regime: the temperature dependence of the inverse dielectric function, the impurity and temperature dependence of the renormalized soft mode vibrational frequency and the impurity concentration dependence of the transition temperature T_c . In particular we show that, the critical concentration for $T_c=0$ is determined by the ion tunneling frequency, the bare soft mode parameters and the pseudospin-phonon coupling constant.

10:45 AM *D8.7

FROM FERROELECTRIC TO QUANTUM PARAELECTRIC: $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ (KTN), A MODEL PEROVSKITE SYSTEM. G.A. Samara, Sandia National Laboratory, Albuquerque, NM.

The ABO_3 perovskite oxides constitute an important family of technologically important ferroelectrics whose relatively simple chemical and crystallographic structures have contributed significantly to our understanding of ferroelectricity. They readily undergo structural phase transitions involving both polar and non-polar distortions from the ideal cubic lattice. This presentation will focus on the mixed perovskite system $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$, or KTN, which has turned out to be a model system. While the end members KTaO_3 and KNbO_3 might be expected to be similar, in reality they exhibit very different properties. Their mixed crystals, which can be grown over the whole composition range, exhibit a rich set of phenomena whose study has added greatly to our current understanding of the phase transitions and dielectric properties of these materials. Included among these phenomena are soft mode response, ferroelectric (FE)-to-relaxor (R) crossover, quantum mechanical suppression of the transition and the appearance of a quantum paraelectric state. Each of the phenomena will be discussed and illustrated. Some emphasis will be on the unique role of pressure in elucidating the physics involved. *Supported jointly by the Division of Materials Sciences and Engineering, Office of Science, U.S. Department of Energy (DOE) and by Research Foundations, Sandia National Laboratories. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the DOE under Contract DE-AC04-94AL85000.

11:15 AM D8.8

CROSSOVER BETWEEN FERROELECTRIC AND QUANTUM PARAELECTRIC IN SrTiO_3 BOTH BY ISOTOPIC SUBSTITUTION AND HYDROSTATIC PRESSURE. Ruiping Wang, Smart Str Res Center, AIST, Ibaraki, JAPAN; Mitsuru Itoh, Mat Str Lab, Tokyo Inst Tech, Yokohama, JAPAN.

Oxygen isotope substitution and application of hydrostatic pressure on quantum paraelectric SrTiO_3 could reversibly control the two states between ferroelectric and quantum paraelectric. Oxygen isotope substitution has evolved a ferroelectricity in SrTiO_3 , which involves no macroscopic structural change and no observable heat anomaly at T_c . The isotopically induced ferroelectricity in SrTiO_3 could be well correlated to the suppression of the quantum fluctuation. On the contrary, no change in the ferroelectric interaction was observed. The depression and vanishing of T_c above $P_c=0.75$ kbar could be explained by the increase in the quantum fluctuation keeping the dipole interaction a constant. These results are discussed compared with the doped ferroelectric SrTiO_3 , in which strong local dipole is incorporated in the lattice. Finally, possible mechanism for isotopically induced ferroelectric transition is discussed.

11:30 AM D8.9

MASSIVE ELECTROSTRICTION IN BARIUM AND LEAD

TITANATE SINGLE CRYSTALS. Rongjing Zhang, Guruswaminaidu Ravichandran and Kaushik Bhattacharya, Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA.

This paper reports on an approach to attain massive electrostriction in single crystals of Barium Titanate and Lead Titanate single crystals through controlled domain wall motion. Using a novel experimental setup, which applies constant compressive stress and cyclic electric field to suitably oriented single crystals, Burcu, Ravichandran and Bhattacharya recently demonstrated strains as large as 1% in Barium Titanate. We demonstrate even larger strains in Lead Titanate using the same experimental setup. We demonstrate through in-situ polarized microscopy that these large strains are attained through controlled domain wall motion. We study the effect of changing frequency and compressive stress on the electrostriction, the hysteresis and domain wall motion. We explore the interior of the hysteresis loops. This paper also reports on a series of experiments which studies piezoelectricity by applying cyclic electric field in addition to a constant mean applied stress and electric field. The implications of these results for the design of novel microactuators are discussed.

11:45 AM D8.10

NIOBIUM POLARIZATION IN RELAXOR FERROELECTRIC PEROVSKITES PZN-PT AND PMN. Eugene Mamontov, Wojtek Dmowski, Takeishi Egami, Univ of Pennsylvania, Dept of Materials Science and Engineering, Philadelphia, PA; Thomas Gog, Chitra Venkataraman, CMC-CAT, Advanced Photon Source, Argonne National Laboratory, Argonne, IL; Paul William Rehrig, Leslie Eric Cross, Materials Research Laboratory, Pennsylvania State Univ, University Park, PA.

The atomic-level mechanism of the relaxor ferroelectricity in materials with perovskite structure is discussed. Using XANES measurements performed on the poled single crystals we demonstrate that Nb polarization in relaxor ferroelectric perovskite $(\text{Pb}(\text{Zr}_{1/3}\text{Nb}_{2/3})\text{O}_3)_{0.85}(\text{PbTiO}_3)_{0.15}$ (PZN-PT) is small compared to that in conventional ferroelectric perovskite KNbO_3 . Additionally, the neutron pair-distribution function data show that Nb polarization in relaxor ferroelectric perovskite $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) is much smaller than in KNbO_3 , and ferroelectric polarization is dominated by Pb. These findings do not support conventional view of ferrorelaxor behavior in perovskites as a result of disruption of the connectivity of polarizable ions by their non-polarizable counterparts. Instead, they speak in favor of theory in which ferrorelaxor behavior is caused by randomness of the local direction of Pb polarization due to chemical disorder on the B-sites of the perovskite structure.

SESSION D9: MAGNETORESISTIVE PEROVSKITES II

Chair: Nicola A. Hill

Thursday Afternoon, April 4, 2002
Golden Gate A2 (Marriott)

1:30 PM *D9.1

ATOMIC SCALE ENGINEERING OF MAGNETIC AND SUPERCONDUCTING PEROVSKITE HETEROSTRUCTURES. A.M. Goldman, University of Minnesota, Minneapolis, MN.

It has been possible to adapt molecular beam epitaxy techniques used to grow semiconductors such as GaAs to the growth of complex oxides such as high temperature superconductors, insulating and conducting oxides, and perovskite manganites that exhibit the phenomenon of colossal magnetoresistance. The approach is called ozone-assisted molecular beam epitaxy. A wide variety of materials have been found to be epitaxially compatible. As a consequence it has been possible to carry out atomic scale engineering of tunneling junctions and bilayer and multilayer heterostructures involving various combinations of these materials. This MBE approach to the fabrication of heterostructures appears to have some advantages over more common methods of growing films such as pulsed laser deposition and sputtering. Several examples of these engineered structures will be discussed, including combinations of superconductors and perovskite manganites, which have permitted the study of spin injection in superconductors, and combinations of perovskite manganites and metallic oxides, which have permitted investigation of exchange coupling in these complex materials. For the latter work both multilayer heterostructures and spin valve configurations were produced. Physical results from the study of these structures will be presented.

Work performed in collaboration with P.A. Kraus, A. Bhattacharya, K.R. Nikolaev, I.N. Krivorotov, A.Yu. Dobin, E.D. Dahlberg, and R.M. Wentzcovitch.

Supported in part by supported by the National Science Foundation Materials Research Science and Engineering Centers Program under

grant no. NSF/DMR-9876816 and by Office of Naval Research under grant no. N/N00014-98-1-0098.

2:00 PM **D9.2**

HIGH PRESSURE PULSED LASER DEPOSITION OF OXIDE THIN FILMS. Gertjan Koster, Theodore H. Geballe, Stanford Univ, Stanford, CA; and Ivan Bozovic, Oxxel GMBH, Technologiepark Universitaet, Bremen, GERMANY.

There have been a number of phases which have been synthesized at high pressures (~ 10 GPa) which it would be nice to have available as well ordered and aligned thin films. For example, it is of interest to compare the dependence of critical current of stoichiometric $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ upon grain boundary angle with that $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, which exists with a large range of oxygen stoichiometry. Other phases of interest include $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_x$ ($\text{Cu}1234$, $T_c \sim 120\text{K}$), which to date has only been synthesized in bulk form at high pressure. We developed a system where a thin layer of the constituent cations are pulsed laser deposited at low temperature and standard pressure (typically at 400°C and $200\text{-}300\text{ Torr}$), which is periodically annealed by moving a high pressure cell onto the film. This cell allows in situ annealing up to 700°C and a maximum pressure of about 100 Torr (O_2 , O_3 , Hg , Tl or Mg). The deposition of material is synchronized with the annealing cycles, which duration can be varied. The amount of material deposited at low temperatures in each cycle can be varied from sub-monolayer to greater than 5 layers. Thus we will be able to study both surface and bulk diffusion and ordering. We also expect to see effects on the growth behavior of diffusion and ordering in the regime in between bulk diffusion and surface diffusion. This can be studied as a function of temperature, pressure and layer thickness (i.e., deposited each cycle). In this paper we will report on the synthesis of the high pressure phases mentioned above and perhaps phases such as the Hg-cuprates, MgB_2 and others as a function of temperature, pressure, layer thickness, dwell time and ambient atmosphere.

2:15 PM **D9.3**

EPITAXIAL GROWTH OF $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ THIN FILM ON BUFFERED $\text{Si}(100)$ SUBSTRATE. Ashutosh Tiwari, Amit Chug, C. Jin, D. Kumar, A. Kvit and J. Narayan, Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC.

We have successfully deposited an epitaxial layer of $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ on Si by using a multilayered thin film buffer medium. Buffer medium consists of TiN, MgO and SrTiO_3 . This combination of layers was motivated by the fact that TiN grows epitaxially on Si substrates by domain matching epitaxy; four lattice constants of TiN match well with three of Si. TiN has good lattice matching with MgO, which in turn has good lattice matching with SrTiO_3 and $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$. Thin film deposition was performed in a multitarget pulsed laser deposition system where TiN, MgO, SrTiO_3 and $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ were ablated one after the other using a KrF excimer laser. The deposition of TiN was performed in vacuum (2×10^{-7} Torr) and the substrate temperature was 580°C . MgO was deposited at 0.05 mTorr oxygen pressure at 600°C . For SrTiO_3 deposition, substrate temperature was 750°C and oxygen pressure was 1 mTorr . $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ was deposited at 720°C with oxygen pressure of 250 mTorr . The films were characterized using x-ray diffraction, transmission electron microscopy and electrical resistivity measurements. We found that the properties of these $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ films are comparable to the properties of $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ films grown on conventional oxide substrates.

2:30 PM **D9.4**

SYNTHESIS, STRUCTURES, AND PHYSICAL PROPERTIES OF YTTRIUM-DOPED STRONTIUM MANGANESE OXIDE FILMS. Andrew J. Francis, Balasubramanian Kavaipatti, Paul A. Salvador, Carnegie Mellon University, Department of Materials Science and Engineering, Pittsburgh, PA.

Cubic strontium manganese oxide is an end-member of the colossal magnetoresistive (CMR) family of manganese-based perovskites, $\text{RE}_{1-x}\text{Ae}_x\text{MnO}_3$. Because normal synthesis conditions lead to the 4H hexagonal perovskite polymorph, high-pressure conditions are typically used to obtain the cubic perovskite polymorph. In this work, we describe the synthesis and structural/physical characterization of the cubic perovskite form of the high-alkaline-earth containing phases of $\text{Y}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x \geq 0.7$) as epitaxial thin films. Thin films of various stoichiometries were grown on single-crystal perovskite substrates of SrTiO_3 , NdGaO_3 , and LaAlO_3 , using pulsed laser deposition. After optimizing deposition conditions, the perovskite polymorph is obtained for all compositions, as demonstrated by x-ray and electron diffraction. Epitaxial relationships and film quality will be discussed. The physical properties of these n-type doped manganese oxides are discussed in relation to the known behavior of bulk perovskites, particularly the $\text{RE}_{1-x}\text{Ca}_x\text{MnO}_3$ compounds,

which are well known and well characterized. The films display insulator-like electrical properties with little to no magnetoresistive behavior. The results are discussed in terms of the use of such layers as sub-units in artificial superlattices and multilayer device structures requiring lattice-matched insulators.

3:15 PM **D9.5**

UNDERSTANDING THE BIAS DEPENDENCE OF MAGNETORESISTANCE IN THE MAGNETIC TUNNEL JUNCTION $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{SrTiO}_3/\text{Co}$. M. Bowen, A. Barthelemy, J.P. Contour, A. Fert, F. Petroff, E. Jacquet, J. Humbert, A. Vaures, UMP CNRS-Thales, Orsay, FRANCE; R. Bertacco, M. Portalupi, M. Marcon, L. Duo, F. Cicacci, INFN-Dipartimento di Fisica, Politecnico de Milano, Milan, ITALY.

In the six years of renewed activity, the field of magnetic tunnel junctions has matured slowly, fueled by junctions integrating an amorphous barrier of Al_2O_3 [1] yet hindered by the experimental difficulty of producing epitaxial junctions [1] which are accessible in a theoretical approach. The nearly ideal system, comprised of a half-metallic manganite electrode of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3(001)$ with only a d (band crossing the Fermi level, grown in an epitaxial bilayer with an insulating barrier of $\text{SrTiO}_3(001)$ which allows efficient transmission of d electronic states, and capped with a counterelectrode such as (111)-textured Co, has already proven itself of interest for fundamental tunneling studies [2]. To explain the unique features in the bias dependence of the magnetoresistance for such a system, we have first performed inverse photoemission experiments to determine the influence of the spin-polarized unoccupied density of states of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3(001)$. Then, with an aim to investigate the influence of the Co density of states, we will present a set of comparative tunneling experiments on junctions with a counterelectrode of CoCr - Cr impurities introduce virtual bound states in the Co matrix density of states, and thus affect in a controlled manner the resulting bias dependence of the magnetoresistance. The role of the crystallinity of the SrTiO_3 barrier will also be discussed using $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ -based junctions with amorphous SrTiO_3 . [1] M. Bowen, V. Cros, F. Petroff, A. Fert, C. Martínez Boubeta, J.L. Costa-Krämer, J.V. Anguita, A. Cebollada, F. Briones, J.M. de Teresa, L. Morellón, M.R. Ibarra, F. Güell, F. Peiró, A. Cornet., App. Phys. Lett. 79, 11 p. 1655 (2001). [2] J.M. De Teresa, A. Barthelemy, A. Fert, J.P. Contour, R. Lyonnnet, F. Montaigne, P. Seneor, and A. Vaurès, Phys. Rev. Lett. 82 4288 (1999), Science 286 (1999).

3:30 PM ***D9.6**

ELECTRONIC MANIFESTATIONS OF MULTIPHASE COEXISTENCE IN MIXED-VALENT MANGANITE THIN FILMS. Satish Ogale^a, University of Maryland, Center for Superconductivity Research, Department of Physics, College Park, MD. ^a Also at Department of Materials Science.

New insights are gained into the behavior of mixed-valent manganite thin films via use of direct electrical probes. An electric field effect study on different manganite channels reveals a significant composition sensitivity of the electroresistance (with a maximum effect of about 76% at 4×10^5 V/cm in the $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ channel), and a complementarity of the electric and magnetic field effects¹. These observations suggest a strong role of electronic phase separation. Frequency dependent dielectric measurements on $\text{Pr}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ show strong response features at all the key ordering transitions in the system², emphasizing multiphase nature of the phase transformations in this system. Similar studies on $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and $\text{La}_{1-x}\text{Pr}_x\text{Ca}_{0.3}\text{MnO}_3$ films offer further support to this physical picture. Direct imaging of undoped and Pr doped $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ films via magnetic and electric force microscopies (MFM/EFM)³ reveals the coexistence of (ferromagnetic) metallic and insulating (possibly charge ordered) domains in these films, and their evolution as a function of temperature. 1. T. Wu, S.B. Ogale, J.E. Garrison, B. Nagaraj, Amlan Biswas, Z. Chen, R.L. Greene, R. Ramesh, T. Venkatesan, A.J. Millis, Phys. Rev. Lett. 86, 5998 (2001). 2. L.V. Saraf, S.B. Ogale, Z. Chen, R.P. Godfrey, T. Venkatesan and R. Ramesh, Phys. Rev. B. (Rapid Commun) 62, R 11 961 (2000). 3. S.H. Chung, S.R. Shinde, S.B. Ogale, T. Venkatesan, R.L. Greene, M. Dreyer and R.D. Gomez, J. Appl. Phys. 89, 6784 (2001). Work supported by MRSEC grant #DMR-00-80008.

4:00 PM **D9.7**

ADJUSTABLE MAGNETORESISTANCE WORKING RANGE IN $\text{La}_{2/3}\text{Ca}_{1/3-x}\text{Sr}_x\text{MnO}_3$ PEROVSKITE. Anders Reves Dinesen and Soren Linderth, Materials Research Department, Risoe National Laboratory, Roskilde, DENMARK.

The perovskite manganites $\text{La}_{2/3}\text{A}_{1/3}\text{MnO}_3$ ($\text{A} = \text{Ca}$ or Sr) are known to exhibit a large negative magnetoresistance (MR) in an interval around the their Curie temperature ($T_C \simeq 270$ and 350 K , respectively). For both substances, this temperature working range constitute a rather narrow interval around T_C . For some practical

purposes it may be of importance to try to extend the working range, e.g. by using mixtures of materials with different T_C and overlapping MR peaks. We have studied the magnetoresistance and other properties of polycrystalline $\text{La}_{2/3}\text{Ca}_{1/3-x}\text{Sr}_x\text{MnO}_3$ powders prepared by a glycine-nitrite combustion method. The gradual substitution of Ca with Sr leads to structural changes and a variation of the Curie temperature in the temperature interval of 270-350 K. The samples have a large negative magnetoresistance (10-20%) in a temperature interval of about 20 K around the Curie point. The MR peaks overlap and a combination of these materials would provide a working range of about 100 K around room temperature with a considerable magnetoresistance.

SESSION D10: POSTER SESSION
FERROELECTRIC, PIEZOELECTRIC, AND
FERROELASTIC PROPERTIES II
Chair: Kenneth R. Poeppelmeier
Thursday Evening, April 4, 2002
8:00 PM
Salon 1-7 (Marriott)

D10.1

AB INITIO STUDIES ON PHASE BEHAVIOR OF BARIUM-TITANATE. Mustafa Uludoğan, Physics Department, METU, Ankara, TURKEY; Tahir Çağın, William A. Goddard, III, Materials and Process Simulation Center, Caltech, Pasadena, CA.

Using DFT methods we have studied the structure, equation of state, and phase behavior of BaTiO_3 . We have identified the pressure induced phase transitions from rhombohedral to orthorhombic at ca. 5 GPa, from orthorhombic to tetragonal at ca. 6 GPa and from tetragonal phase to cubic phase at ca. 7.5 GPa.

D10.2

WAFER BONDING AND LAYER TRANSFER FOR THIN FILM FERROELECTRICS. Cecily A. Ryan, Harry A. Atwater, California Institute of Technology, Thomas J. Watson Laboratories of Applied Physics, Pasadena, CA.

The transfer of thin films of LiNbO_3 and BaTiO_3 via wafer bonding and layer transfer is being investigated as a means of obtaining high quality ferroelectric thin films on Si substrates. High quality ferroelectric thin films have applications as modulator and actuator devices. The layer transfer technique allows for the study of the ferroelectric domain structure and optical properties of high quality single crystal LiNbO_3 and BaTiO_3 thin films manufactured with bulk crystal quality. Epitaxial film growth of ferroelectrics on Si(001) is challenging due to the lattice mismatch. In this study z-cut LiNbO_3 and (001) BaTiO_3 are used. We have successfully demonstrated hydrophilic wafer bonding between bulk z-cut LiNbO_3 and $\text{SiO}_2/\text{Si}(001)$. LiNbO_3 and BaTiO_3 crystals were implanted with H^+ at 80 keV to doses of $1 \times 10^{17} \text{cm}^{-2}$, $8.4 \times 10^{16} \text{cm}^{-2}$, $6.7 \times 10^{16} \text{cm}^{-2}$ and $5 \times 10^{16} \text{cm}^{-2}$ to create a H-rich damage layer at 450-550nm. Blistering studies were performed to characterize H_2 bubble formation for the various doses. Thermal cycling to 450°C at atmospheric pressure to induce layer splitting at the damaged layer will be reported [1] as well as AFM and optical microscopy used to image domains in the bulk crystals and resulting thin films. Bonding on different substrates such as borosilicate glass and metallic strain-relaxation layers will be investigated to minimize thermomechanical stress due to mismatch in the coefficient of thermal expansion of the ferroelectrics and the Si substrate. This will add versatility in processing for actuator and modulator applications by allowing a larger range of thermal variation during fabrication.

1. Aspar, B., *et al.*, The Generic Nature of the Smart-Cut Process for Thin Film Transfer. *Journal of Electronic Materials* **30**(7), 834-840(2001).

D10.3

FABRICATION AND PROPERTIES OF INTEGRATED METAL/FERROELECTRICS/METAL CAPACITORS FOR FeRAM APPLICATIONS BY COMBUSTION CHEMICAL VAPOR DEPOSITION (CCVD). Yong Dong Jiang, Tim Metzger, Xiao Xu, Todd A. Polley, Andrew T. Hunt, MicroCoating Technologies, Atlanta, GA.

Ferroelectric random access memories (FeRAMs) are new types of memories especially suited for mobile applications due to their unique properties, such as non-volatility, small cell size, fast read/write, low voltage and low power consumption. Perovskite ferroelectric materials, such as $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) and La-doped PZT (PLZT), are well suited for FeRAM applications because of their high switchable charge, control of crystallographic texture, low temperature processing. This paper will present the properties of the

deposited Pt, $(\text{La,Sr})\text{CoO}_3$ (LSC) and PZT thin films on Si as well as a detailed description of the low-cost, open-atmosphere CCVD technique used to deposit them. Stoichiometric compositions of PZT and LSC were achieved in this study. The ferroelectric capacitor structure investigated was composed of LSCO/Pt bottom electrodes, PZT ferroelectric thin films and Ag or Al top electrodes. While the bottom LSC layer serves as part of bottom electrode, it can also promote the preferred growth of PZT thin film and prevent migration and deterioration of the Pt thin film during the PZT deposition. X-ray diffraction 2θ scans and pole figure analysis were utilized to determine the identities and crystal orientation of the phases present in the deposited films. Preferred (111) textured structures were obtained for the Pt, LSC and PZT films. Film surface morphology and thickness were examined using SEM. Surface roughnesses were measured using optical profilometry. Preliminary ferroelectric measurements showed a saturation polarization of $12.4 \mu\text{C}/\text{cm}^2$, a remnant polarization of $8.0 \mu\text{C}/\text{cm}^2$, and a coercive voltage of 1.6 V.

D10.4

FORMATION OF PAIRED-PLATE PRECIPITATE STRUCTURES IN $\text{Pb}_{0.91}\text{La}_{0.09}\text{Zr}_{0.65}\text{Ti}_{0.35}\text{O}_3$ FILMS GROWN ON SAPPHIRE SUBSTRATES. Cengiz S. Ozkan, University of California at Riverside, CA; Bahadır Tunaboylu, Ken Ring, Sadik Esener, University of California at San Diego, CA; Ali Ata, Gebze Institute of Technology, Kocaeli, TURKEY.

PLZT films are of great interest for applications in pyroelectric, memory and electro-optic devices and the microstructure of the film directly influences the device properties and their performance. In this paper, we report on the phase transformation behavior of $\text{Pb}_{0.91}\text{La}_{0.09}\text{Zr}_{0.65}\text{Ti}_{0.35}\text{O}_3$ PLZT films grown on r-sapphire substrates using transmission electron microscopy (TEM). A complex microstructure results in these PLZT thin films depending on deposition and annealing conditions. A random equiaxed polycrystalline grain morphology ($\sim 600\text{nm}$) were observed after rapid thermal annealing (RTA) or furnace annealing when the as-deposited (rf-magnetron sputtering) films were predominantly pyrochlore. Precipitate splitting (or pair-plate formation) was observed after furnace annealing in PLZT films that were deposited at high temperatures ($>490^\circ\text{C}$). The average size of such a split precipitate was 35 nm in width and 150 nm in length. We believe that this is related to the internal stress in the films due to both the lattice mismatch and the thermal expansion mismatch between the film and the sapphire substrate.

D10.5

OPTICAL AND ELECTRICAL PROPERTIES OF SOL-GEL PROCESSED Gd DOPED FERROELECTRIC PLZT THIN FILMS. Reji Thomas, Shoichi Mochizuki, Toshiyuki Mihara and Tadashi Ishida, AIST Kansai, National Institute of Advanced Industrial Science and Technology, Osaka, JAPAN.

Gadolinium (Gd) doped ferroelectric lead lanthanum zirconate titanate (PLZT 8/65/35) thin films were prepared by sol-gel spin coating technique. Fused silica and platinumized silicon were used as substrates. Pyrolysis and annealing temperature were optimized through the x-ray diffraction studies to prepare films in single perovskite phase. Effect of excess Pb on the crystallization and microstructure were studied. Crystallinity of the pyrolyzed films increased with annealing temperature and its orientation strongly depends on the pyrolyzing temperature, rather than annealing temperature. Infrared and X-ray diffraction data for films heat treated above 650°C showed that the material is free from carbonates and crystalline. Compositional analysis was done with AES and the depth profile showed uniform elemental distribution along the thickness except the surface region. Optical transmission spectra were recorded and from this, refractive index, extinction coefficient and thickness were calculated for films on fused silica annealed at different temperatures. In addition, the resultant films showed more than 60% transmission in the visible region. The electrical measurements were conducted on metal-ferroelectric-metal (MFM) capacitors. Ferroelectric properties were studied by plotting the P-E hysteresis loop and the effects of Gd content on the dielectric and ferroelectric behavior also will be discussed.

D10.6

HYDROTHERMAL SYNTHESIS OF BISMUTH TITANATE POWDERS. Huiwen Xu, Elliott Slamovich, Keith Bowman, Purdue Univ, School of Materials Engineering, West Lafayette, IN.

Bismuth titanate powders were synthesized by reacting nanocrystalline TiO_2 in alkaline aqueous solutions of bismuth nitrate at temperatures ranging from 200-240°C. The influence of Bi/Ti molar ratio, pH, and mineralizing agent (e.g., KOH, NaOH, $(\text{CH}_3)_4\text{NOH}$) on the powder composition and morphology was examined. Energy dispersive spectroscopy and X-ray diffraction were used to examine the phase composition and crystal structure of each

powder. Using KOH to control pH resulted in a mixture of Bi₄Ti₃O₁₂ and Bi₅Ti₄O₁₅ phases, with the relative amount of Bi₅Ti₄O₁₅ increasing with increasing KOH concentration. The particle morphology was investigated by light scattering, BET, SEM and TEM. Typical powders have an average size of approximately 0.6-0.7 μm , with a distribution ranging from 0.04-2 μm . SEM and TEM studies showed that the particles exhibit elongated platelet morphology, and electron diffraction was used to characterize the phase distribution of Bi₄Ti₃O₁₂ and Bi₅Ti₄O₁₅ within the powders.

D10.7

POSSIBLE QUANTUM BEHAVIORS IN NANOCRYSTALLINE BaTiO₃. J. Yu, X.J. Meng, J.L. Sun, C.P. Jiang, S.L. Guo, and J.H. Chu, National Laboratory for Infrared Physics, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, Shanghai, CHINA.

Nanostructured materials are striking ones' attentions, not only because they advance devices toward miniaturization, but also their performances may be controlled by quantum mechanism. In a crystal, if at least one of its dimensions is smaller than the length scale of some properties, the properties is confined and becomes dependent on the size and shape of what is now called a "quantum crystal". In semiconductor nanocrystals and low-dimensional electron gas system, quantum size confinement are most often referred to discuss the observed distinctive physical properties. On the other hand, quantum effects such as zero-point fluctuation on the displacive-type phase transformation are investigated and assigned in ferroelectrics at low temperature and under pressures, in which "quantum paraelectricity" and "quantum ferroelectricity" are named. Now, when the crystallite size reduces to the same order of or less than the correlation length of the long-range interaction in ferroelectrics, what would happen is an interesting problem. In this report, possible quantum behaviours in nanocrystalline BaTiO₃ (nc-BaTiO₃) are discussed. BaTiO₃ ultrafine powders are prepared using low-temperature/ambient-pressure hydrothermal process below 100°C. The phase structural changes and lattice dynamics are characterized with heat treatment at various temperature. In Raman scattering experiments, some low temperature lattice vibrational modes are recorded in nc-BaTiO₃, their changes with annealing temperature and the relaxation of Raman selection rules are discussed with the structural changes in nanocrystals. Using the terms of the long-range interaction altered by particle size in covalent ionic nanocrystals, the phase transition, the lattice expansion and the bonding character change in nc-BaTiO₃ with decreasing particle size can be predicted, which are consistent with the present experimental results. Analogizing with the structural change and lattice vibrational properties in BaTiO₃ induced by pressure and size effects, some quantum behaviors such as on the nature of phase transition and the temperature dependence of dielectric constant are proposed in nc-BaTiO₃. And the temperature dependent dielectric properties in those nanocrystalline system are also preliminarily measured.

D10.8

SOFT PHONON DYNAMICS IN THE ISOTOPICALLY INDUCED FERROELECTRIC PHASE TRANSITION OF STRONTIUM TITANATE. Toshiro Yagi, Masaru Kasahara, Yuhji Tsujimi, Hiroki Hasebe, Research Institute for Electronic Science, Hokkaido University, Sapporo, JAPAN; Masashi Yamaguchi, UCLA Riverside, Riverside, CA; Ruiping Wang, Smart Structure Center, National Institute for Advanced Industrial Science and Technology, Tsukuba, JAPAN; Mitsuru Itoh, Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, JAPAN.

The quantum paraelectricity of SrTiO₃ (STO) has attracted a lot of interest of many researchers since the quantum-mechanical stabilization of the paraelectric phase below 4K was pointed out as a macroscopic quantum effect on the suppression of the phase transition.¹⁾ Recently a ferroelectric phase transition has been reported in the isotopically exchanged STO (STO18) where the natural oxygen ¹⁶O has been exchanged for its isotope ¹⁸O.²⁾ The difference of mass between ¹⁶O and ¹⁸O seems to suppress the quantum fluctuations and to bring a divergent peak of the dielectric constant at a temperature T_m . The value of T_m depends strongly on the isotope concentration. In the present study, the soft-phonon dynamics of 87% exchanged STO18 has been studied by both Raman and Brillouin scattering.³⁻⁵⁾ The Brillouin scattering study found anomalous temperature dependence of the acoustic mode near T_m ; On cooling run, at several degrees above T_m the spectrum of the c_{44} mode in the paraelectric-tetragonal phase begins to split into two components. One of them shows a drastic softening with a dip on the spectrum characteristic for coupling with a central peak component, though the other is independent of temperature. Though the soft A_{2u} mode is Raman inactive in the paraelectric phase, the Raman scattering observed the A_{2u} mode spectra in the $x(yz)$ -x geometry. This indicates a local symmetry breaking near T_m . Below T_m , a hardening behavior of the soft mode was observed. The ferroelectric phase transition of STO18 is primarily caused by the soft mode dynamics and secondarily by some inhomogeneous factors in the

crystal. 1) K.A. Muller and H. Burkard: Phys. Rev. B19 (1979) 3593. 2) M. Itoh, R. Wang, Y. Inaguma, T. Yamaguchi, Y.-J. Shan and T. Nakamura; Phys. Rev. Lett. 82 (1999) 3540. 3) M. Yamaguchi, T. Yagi, R. Wang and M. Itoh: Phys. Rev. B63 (2001) 2102. 4) Y. Tsujimi, H. Hasebe, R. Wang, M. Itoh and T. Yagi: Ferroelectrics (2001) in print. 5) M. Kasahara, R. Wang, M. Itoh and T. Yagi: J. Phys. Soc. Jpn. 70 (2001) 648.

D10.9

ELECTROMECHANICAL PROPERTIES OF BARIUM-MODIFIED STRONTIUM CALCIUM SODIUM NIOBATES WITH TUNGSTEN BRONZE STRUCTURE. Rong-Jun Xie, Yoshio Akimune, Kazuo Matsuo, Tastuo Sugiyama, Smart Structure Research Center, National Institute of Advanced Industrial Science and Technology, Tsukuba, JAPAN; Naoto Hirotsaki, Advanced Materials Lab., National Institute for Materials Science, Tsukuba, JAPAN.

Many tungsten bronze compounds have been reported to be ferroelectrics and find applications in electro-optic, photorefractive, pyroelectric and piezoelectric devices. Among these compounds, calcium-modified strontium sodium niobates (SCNN) possess relatively higher piezoelectric properties, enabling them to find applications in sensors and actuators. Meanwhile, these materials contain no lead and thus environmental friendly, being promising candidates to replace the widely used lead-based perovskite materials. However, it is difficult to prepare highly dense ceramics by the normal sintering techniques. In this work, a novel sintering technique, spark plasma sintering, was attempted to densify barium-modified SCNN $(1-x)SCNN-xBNN$ ceramics, and their electromechanical properties were evaluated. Sintering was carried out at 1200°C for 5 min under 35 MPa in vacuum, followed by annealing at 1000°C for 10h in air. The Curie point increased but the dielectric constant and ferroelectric properties decreased as the calcium concentration increased. Both the Curie point and the peak dielectric constant decreased with increasing barium content until $x = 0.5$ was reached. Ferroelectricity was clearly observed in all barium-modified samples, with the remanent polarization being about 3.0 $\mu\text{C}/\text{cm}^2$. The maximum piezoelectric properties were found at $x = 0.4$, with the electromechanical coupling coefficients k_t and k_p and the piezoelectric constant d_{33} being 50%, 9.0% and 110 pC/N, respectively.

D10.10

CRYSTALLINE PROPERTIES OF FERROELECTRIC-RELAXOR PZN-PT THIN FILMS BY PULSED LASER DEPOSITION. Sushil Kumar Singh, Pam A. Thomas, Stuart B. Palmer, Dept of Physics, University of Warwick, Coventry, UNITED KINGDOM.

Relaxors are a special class of perovskite ferroelectrics and exhibit a broad, large dielectric constant and high electromechanical coupling constant. The piezoelectric properties of the $\text{Pb}(\text{Zn}_{0.33}\text{Nb}_{0.66})\text{O}_3$ (PZN) be enhanced by the addition of PbTiO_3 (PT). The PZN-PT thin films were deposited on Pt/Ti/SiO₂/Si substrates at a temperature 700°C - 800°C and oxygen pressure of 50-100 m torr by pulsed laser ablation method. The XeCl excimer laser (308 nm wave-length, 30 ns pulse width) was operated at a repetition rate of 10 Hz. In this study, the orientation of PZN-PT thin films was controlled by laser parameters and the effect of the orientation on the piezoelectric and dielectric properties was investigated. X-ray diffraction patterns of the films shows the pyrochlore phases are depends upon the substrate temperature and it can reduce after annealing films at 800°C for 15 min. The growth of tetragonal phase in the rhombohedral phase were observed and at the phase transition the (002) peak jumps from near the expected rhombohedral position to near the expected tetragonal peak position. The change of the relative permittivity as a function of temperature at different frequencies for PZN-PT films have study. Relaxor behaviour, clearly evident, including a broad maximum and frequency dispersion below temperature of the dielectric peak. The permittivity of the PZN-PT films are depends upon the % of PT present in the films. The more investigation are in progress and results will be present during conference.

D10.11

EFFECTS OF SEED LAYERS ON FERROELECTRIC PROPERTIES OF SOL-GEL DERIVED SBT THIN FILMS. Ching-Chieh Leu, Chao-Hsin Chien, Tiao-Yuan Huang, National Nano Device Laboratories, Hsinchu, TAIWAN; Hung-Tao Lin, Chen-Ti Hu, National Tsing-Hua University, Dept of MS&E, Hsinchu, TAIWAN.

The effects of a seed layer on the crystallization of strontium-bismuth-tantalite (SBT) thin films prepared by sol-gel deposition technique were investigated. Seed layers of various thicknesses were deposited on top of Pt/TiO₂/SiO₂/Si substrates using magnetron sputtering. The seed layer served to provide nucleation site for the growth of ferroelectric films. Homogeneous crystalline SBT films of perovskite structure with fine grains were successfully obtained by 750°C rapid thermal annealing in O₂ ambient. The ferroelectric

properties of SBT films with seed layer were improved significantly in comparison with those without the seed layer. The remnant polarization ($2P_r$) and coercive field ($2E_c$) of SBT films without and with the seed layer annealed at 750°C were 15.56 and 24.92 mC/cm², 159 and 160 kV/cm at an applied voltage of 5 V, respectively. In addition, the seed layer also results in lower nucleation temperature. SBT films with seed layers exhibited good ferroelectric properties even after 700°C annealing. Finally, crystalline orientations and microstructures of SBT films were strongly dependent on the thickness of the seed layer. With an optimized seed layer thickness, SBT film showed (220)-preferred orientation and a homogeneous film structure with fine grains on the (111)-oriented Pt/TiO₂/SiO₂/Si substrates.

D10.12

LOW TEMPERATURE SINTERING OF PEROVSKITE PZT THICK FILMS DERIVED FROM A NOVEL SOL-GEL ROUTE. W. Zhu, Z.H. Wang, C.L. Zhao, and O.K. Tan, Microelectronics Center, School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore, R. OF SINGAPORE.

Low sintering temperature is always the trend in commercial production of electronic ceramic, especially for multilayer device. Developing a new process to fabricate crack-free perovskite PZT thick films on silicon substrates at a low process temperature is also critical for potential applications in microelectromechanical systems (MEMS). Dispersing very fine particles into a sol-gel matrix to get a thick 0-3 composite coating layer is a promising process among all attempts. In this paper, we have further improved this modified sol-gel process by nanocrystalline composite technique. Dense perovskite Pb(Zr, Ti)O₃ thick films of 10 to 50 nm in thickness have been obtained on the platinum-coated silicon substrates by spin-coating at sintering temperature of 600-700°C and fully developed submicron-sized grains have been demonstrated in screen-printing piezoelectric film on alumina substrates at sintering temperature of 700-800°C. The dependence of various properties such as microstructure, crystallinity, ferroelectric and piezoelectric properties of such made thick films on the processing parameters have been investigated. To a 10 nm-thick film spin-coated on silicon wafer, the dielectric loss and relative permittivity are 0.010 and 1024, respectively, at 1 kHz. The remnant polarization (Pr) and the coercive field (Ec) are 13.6 mC/cm² and 34.5 kV/cm, respectively. Obviously, such made perovskite piezoelectric thick film has comparable properties with bulk PZT ceramic. This novel technique can be extensively used in sol-gel, screen-printing, tape-casting, even in traditional ceramic process to reduce the process temperature.

D10.13

HYDROTHERMAL SYNTHESIS OF I:V PEROVSKITE THIN FILMS. Gregory K.L. Goh, Institute of Materials Research and Engineering, Opto- and Electronic Systems Cluster, SINGAPORE.

Although epitaxial II:IV perovskite films like BaTiO₃ and PZT have been grown by the hydrothermal method, there are no reports on the growth of I:V perovskite systems by this low temperature technique. In this study, thin films of KNbO₃, NaNbO₃ and KTaO₃ were grown on (100) oriented single crystal SrTiO₃ substrates by the hydrothermal method at 200°C and below. X-ray diffraction (XRD) revealed that the as-synthesized films were of an epitaxial nature with a (100)_{pc} out of plane orientation. Scanning electron microscopy (SEM) showed that the films formed by an island growth mechanism. KTaO₃ was also used as a buffer layer in the growth of KNbO₃ films in order to investigate the effect of lattice parameter on surface morphology and epitaxial quality, as determined by SEM and XRD rocking curve measurements, respectively.

D10.14

CHEMICAL SOLUTION DEPOSITION OF EPITAXIAL SrTiO₃-BASED THIN FILMS ON BIAXIALLY TEXTURED Ni (200) SUBSTRATES. Ryan J. Ong, University of Illinois at Urbana-Champaign, Dept. of Materials Science and Engineering, Urbana, IL; Jeffrey T. Dawley, Paul G. Clem, Michael P. Siegal, Donald L. Overmyer, Sandia National Laboratories, Albuquerque, NM.

A novel chemical solution deposition (CSD) approach was utilized to fabricate highly (200)-oriented SrTiO₃ (STO) and (Ba,Sr)TiO₃ (BST) thin films on biaxially textured Ni (200) tapes. Dense, smooth films with a high-degree of biaxial texture were fabricated at moderate temperatures in a highly reducing atmosphere. The chemical evolution, oriented growth, and film microstructure were controlled through chelating agents, doping, fluorination, and esterification. Emphasis was placed on maximizing oriented perovskite cube-on-cube growth on the (200) Ni substrate through exploration of the BaTiO₃-SrTiO₃ pseudo-binary system. Potential applications for highly (200)-oriented STO films are as buffer layers in HTSC coated conductor tapes and as dielectric layers in base metal electrode capacitors. Sandia is a multiprogram laboratory operated by Sandia

Corp., a Lockheed Martin Company, for the US Dept. of Energy under contract DE-AC04-94A185000.

D10.15

THE ROLE OF GRAIN BOUNDARY ON THE RESISTIVITY OF Pb(Fe_{1/2}Nb_{1/2})O₃ AT ROOM TEMPERATURE. Sang-Bop Lee, Kwang-Ho Lee, Hwan Kim, Seoul National Univ, School of Materials Science and Engineering, Seoul, KOREA.

Pb(Fe_{1/2}Nb_{1/2})O₃ has been regarded as an attractive candidate for multilayer capacitor material due to its large capacitance and low sintering temperature. However low resistivity, which results in high dielectric loss, prevents the practical usage of this system. The previous studies have reported that low resistivity is attributed to the hopping electron between Fe²⁺ and Fe³⁺ driven by the reduction of Pb(Fe_{1/2}Nb_{1/2})O₃. In this study, the previous theory was reconsidered, and the contribution of the grain boundary to the total resistivity of Pb(Fe_{1/2}Nb_{1/2})O₃ was investigated through the influence of sintering temperature on the electrical properties. At room temperature, the dc resistivity of 1150°C-sintered specimen was ~10⁷Ω-cm smaller than that of 1050°C-sintered specimen, but converged over 300°C, which couldn't be explained by the previous theory. Complex impedance spectroscopy revealed that there was no significant decrease of bulk resistivity from room temperature to 350°C. Furthermore, the resistivity of the specimen sintered at 1150°C showed similar behavior after it was annealed at 1050°C. It can be thought that this dramatic change of dc resistivity at room temperature is attributed to the change of composition at grain boundary due to the volatilization of Pb.

D10.16

CALCULATIONS OF ATOMIC AND ELECTRONIC STRUCTURE FOR (100) SURFACES OF SrTiO₃ PEROVSKITE. R.I. Eglitis, University of Osnabrueck, Dept. of Physics, Osnabrueck, GERMANY; E. Heifets, California Institute of Technology, Pasadena CA; E.A. Kotomin, Max Planck Institut fur Festkorperforschung, Stuttgart, GERMANY; G. Borstel, University of Osnabrueck, Dept. of Physics, Osnabrueck, GERMANY.

We present and discuss main results of the calculations for the surface relaxation and rumpling of SrTiO₃ surfaces with TiO₂ and SrO terminations using a wide variety of methods of modern computational physics and chemistry, including the shell model (SM) and *ab initio* methods based on Hartree-Fock (HF) and Density Functional Theory (DFT) [1,2]. The HF and DFT formalisms with different exchange-correlation functionals are implemented into Crystal-98 computer code using a Gaussian-type basis set. We demonstrate that a hybrid B3PW formalism gives the best results for the bulk SrTiO₃ properties. Results are compared with previous *ab initio* plane-wave LDA calculations, shell model calculations and LEED experiments. Our calculations demonstrate an increase of the covalency effects between Ti and O atoms near the surface [1].

References:

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2. E. Heifets, E.A. Kotomin, J. Maier, Surf. Sci. **462**, 19, 2000.

D10.17

THICKNESS AND DOPANT DEPENDENCE OF POLARIZATION PROFILES AND HYSTERESIS IN SEMICONDUCTING FERROELECTRIC THIN FILMS. V.B. Shenoy, Division of Engineering, Brown Univ, Providence, RI; K. Bhattacharya, Caltech, Pasadena, CA.

Ferroelectric thin films used in device and memory applications are modeled as wide band gap semiconductors. The electron affinities of these films are determined by the dopant concentration or density of crystalline defects such as oxygen vacancies. Using both analytical and finite-element methods, we determine the thickness dependence of polarization in thin ferroelectric capacitors by incorporating their semiconducting properties. In the case of a short circuited capacitor, depending on the doping level in the film and the type of metal used as the electrode of the capacitor, we find that the film can be either paraelectric, polarized ferroelectric or possess a novel head to tail domain structure. We also find that the switching properties/hysteresis loops depend strongly on the doping level and the thickness of the films. Our results provide a guide to tailoring the doping levels of the films to achieve optimum switching properties.

D10.18

A MESOSCOPIC ELECTROMECHANICAL THEORY OF FERROELECTRIC FILMS AND CERAMICS. Jiangyu Li, Dept. of Engineering Mechanics, University of Nebraska-Lincoln, Lincoln, NE; Kaushik Bhattacharya, Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA.

We present a multiscale modeling framework to predict the effective

electromechanical behavior of ferroelectric ceramics and thin films. This paper specifically focuses on the mesoscopic scale and models the effects of domains, domain switching and the intergranular constraints. Starting from the properties of the single crystal and the pre-poling granular texture, the theory predicts the domain patterns, the post-poling texture, the saturation polarization and strain as well as the electromechanical moduli. We demonstrate remarkable agreement with experimental data with no adjustable parameters. The theory also explains the superior electromechanical property of PZT at the morphotropic phase boundary. The paper concludes with the application of the theory to predict the optimal texture for enhanced dielectric and piezoelectric constants, coupling factors and high-strain actuation in selected materials.

D10.19

RAMAN STUDIES OF SrTiO₃ AND SrBi₂Ta₂O₉. Ran Liu, Motorola SPS, Advanced Process Development & External Research Laboratory, Mesa, AZ; Lyndee Hilt, Motorola Labs, Physical Sciences Research Laboratories, Tempe, AZ.

SrTiO₃ and SrBi₂Ta₂O₉ have attracted enormous interests in the semiconductor industry because of their great potentials in gate dielectric and memory applications. High-quality film growth on Si is necessary for successful integration of these materials with the mature Si technology. In this work, the crystal structure and phase transition of SrTiO₃ and SrBi₂Ta₂O₉ thin films on Si were studied and compared with single crystal bulk materials using Raman spectroscopy. UV-Raman spectra of high-quality MBE SrTiO₃ films mimic that of single crystal and are dominated by 2-phonon scattering, indicating excellent crystallinity of the films. The first order phonon modes are only weakly Raman-activated by threading dislocations. The polarized Raman spectra of SrBi₂Ta₂O₉ single crystals and spin-on thin films show most of the Raman phonon modes of the orthorhombic structure at room temperature. The orthorhombic to tetragonal phase transition is accompanied by the softening of an A₁ mode when samples heated up to the Curie temperature (~300°C).

D10.20

EFFECTIVE HAMILTONIAN STUDY OF PZT 95/5. K. Leung, Sandia National Laboratories, Albuquerque, NM; Eric Cockayne, Ceramics Division, National Institute of Standards and Technology, Gaithersburg, MD; A.F. Wright, Sandia National Laboratories, Albuquerque, NM.

An effective Hamiltonian H_{eff} is constructed for PbZr_{0.95}Ti_{0.05}O₃. It is parameterized using *ab initio* results computed in the virtual crystal approximation. The phase diagram depends sensitively on the energetic competition between the stable orthorhombic antiferroelectric (A_O) and the metastable "low temperature" rhombohedral ferroelectric (F_{R(LT)}) structures at zero Kelvin. By incorporating a temperature dependent lattice expansion term into H_{eff} and modifying H_{eff} to adjust the relative energies of the A_O and F_{R(LT)} phases, we obtain a ferroelectric phase intervening between the low temperature antiferroelectric ground state and the high temperature paraelectric phase, in qualitative agreement with experiments. We also discuss the temperature-dependent disordering of the oxygen octahedral tilts responsible for the experimentally observed space group of the ferroelectric phase.

D10.21

IN-SITU, REAL TIME STUDIES OF BST DEPOSITION ON MODIFIED Si SURFACES TO REDUCE INTERFACE LAYER FORMATION. A.H. Mueller, N.A. Suvorova, E.A. Irene, University of North Carolina at Chapel Hill, Department of Chemistry, Chapel Hill, NC; O. Auciello, Argonne National Laboratory, Material Science and Chemistry Division, Argonne, IL; J.A. Schultz, Ionwerks, Houston, TX.

The incessant push towards smaller and faster devices has led the semiconductor industry to explore the physical limits of SiO₂ technologies. The dielectric constant (K) of SiO₂ demands film thickness' which yield large leakage currents. In order to overcome the thickness restrictions associated with SiO₂ many alternative high K dielectrics have been investigated. The high dielectric constant exhibited by Ba_{0.5}Sr_{0.5}TiO₃ (BST) has made it a perennial favorite in the search for a SiO₂ replacement, yet BST exhibits the usual problems common to most other high K candidates. The most important problem is that the chemical reactivity of the Si substrate leads to reaction and interface formation during the deposition and subsequent processing of these films. This interface layer exhibits detrimental effects on the overall films' electrical properties, inhibiting the full exploration of the benefits of these high K materials. Pre-treatment of the Si surface has been shown to affect the formation of this interface. Restricting the Si surface's chemical reactivity by oxidation has been shown to slow the intermixing of the Si substrate with the deposited material. Real time, in-situ studies using spectroscopic ellipsometry and mass spectrometry of recoiled ions will

be presented for depositions on Si surfaces treated with the aim of reducing the reactivity of the substrate and thus restricting the formation of the aforementioned interface layer.

D10.22

STRUCTURAL CHARACTERISTICS AND DIELECTRIC PROPERTIES OF Ba(Zn_{1/3}Nb_{2/3})O₃-Ba(Zn_{1/2}W_{1/2})O₃ PEROVSKITE CERAMICS. Bostjan Jancar, "Jozef Stefan" Institute, Ljubljana, SLOVENIJA; P.K. Davies, University of Pennsylvania, Philadelphia, PA.

The commercially driven search for the replacement of high Q tantalate-based perovskite ceramics has resulted in the extensive research of other complex perovskites. With this in mind we have examined the structural and dielectric characteristics of the Ba(Zn_{1/3}Nb_{2/3})O₃-Ba(Zn_{1/2}W_{1/2})O₃ system. Very small additions of Ba(Zn_{1/2}W_{1/2})O₃ (<0.5 mole %) destabilize the 1:2 B-site cation order of Ba(Zn_{1/3}Nb_{2/3})O₃ and strongly stabilize 1:1 order. The τ_f and ϵ_r decrease with increasing concentration of tungsten. The increase in tungsten content also tends to destabilize the solid solution which results in the formation of secondary phases and defects inside the perovskite matrix. The nature of these secondary phases and the structure of the defects will be discussed in terms of their influence on microstructural development and dielectric properties.

D10.23

ORIENTATION DEPENDENCES AND E-FIELD EFFECT IN PHASE TRANSITIONS OF RELAXOR-BASED FERROELECTRIC CRYSTALS (PbMg_{1/3}Nb_{2/3}O₃)_{1-x}(PbTiO₃)_x (PMN-x%PT). Chi-Shun Tu, Fu Jen Univ, Dept. of Physics, Taipei, TAIWAN; V. Hugo Schmidt, Montana State Univ, Dept. of Physics, Bozeman, MT.

Dielectric permittivities, polarization-electric-field hysteresis loops and domain structures have been measured as a function of temperature in relaxor-based ferroelectric single crystals (PbMg_{1/3}Nb_{2/3}O₃)_{1-x}(PbTiO₃)_x (x=0.32) for <110> and <211> orientations. Contrary to the pure PbMg_{1/3}Nb_{2/3}O₃ (PMN), PMN-32%PT exhibits apparent crystallographic orientation dependences of dielectric permittivities, polarizations, domain structures and phase transitions. With a prior field-cooled treatment, a field-induced state, perhaps of orthorhombic symmetry, is evidenced and coexists with the rhombohedral symmetry in the low-temperature region. This field-induced phase is manifested by an extra dielectric peak. A relaxation mechanism which is responsible for the so-called diffuse phase transition, crosses a wide temperature region and results from fluctuations between rhombohedral and tetragonal states. In order of increasing temperature (without a prior field-cooled treatment), PMN-32%PT undergoes successive phase transformations: rhombohedral phase, coexistence of rhombohedral and tetragonal phases, tetragonal phase, coexistence of tetragonal and cubic phases, cubic phase.

D10.24

MICROSTRUCTURAL CHARACTERIZATION OF SINTERED Ba(Mg_{1/3}Ta_{2/3})O₃ MATERIALS BY TRANSMISSION ELECTRON MICROSCOPY AND CONVERGENT BEAM ELECTRON DIFFRACTION. J.W. Steeds, Department of Physics, University of Bristol, UNITED KINGDOM; and I-Nan Lin, Materials Science Center, National Tsing-Hua University, Taiwan, R.O.C.

Development of high performance dielectric materials is required to facilitate the trend towards miniaturization of microwave communications circuits. A novel two-step sintering process has been found that enhances the value of frequency Q-factor product. Detailed examination of samples densified in this way gives not only details of the grain size, defect content and state of order of the ordered perovskite grains but also reveals the presence of a number of previously unreported phases. These new phases have been examined by energy dispersive X-ray analysis to give them approximate chemical composition and by convergent beam electron diffraction to determine their crystallography. Large unit cells are found which are evidently related to compounds studied previously in the BaMaO_{3-x} system. The results will be discussed in relation to the enhanced performance of the materials that have been studied.

D10.25

OPTIMIZATION OF THERMAL PROCESSING AND CHEMISTRY IN THE FABRICATION OF A PZT BASED MEMS POWER GENERATOR. B.W. Olson, J.L. Skinner, C.D. Richards, R.F. Richards, and D.F. Bahr, Mechanical and Materials Engineering, Washington State University, Pullman, WA.

Thin films of lead zirconate titanate (PZT) are currently being used in a novel MEMS device to generate power. A piezoelectric stack consisting of platinum/PZT/gold is deposited by sputtering, spin coating, and subsequent heat treatments onto a thin silicon membrane, which is cyclically polarized by a flexing motion. The

membrane must withstand strains between 0.1% and 0.5% for several billion cycles, so we are interested in improving both mechanical and piezoelectric properties. This study has examined the processing-structure-property relationships in developing the PZT film for use in this device. In the sol-gel deposition of PZT, pyrolysis and crystallization temperatures have been shown to alter both microstructure and properties of the piezoelectric film. Optimization of these parameters has greatly improved mechanical reliability due to a reduction in flaws, as well as reducing the residual stresses in the membrane. The chemistry of the PZT film itself has been tailored to provide the highest possible piezoelectric output for this device, and a correlation is made to the ferroelectric properties measured for PZT film on bulk silicon, membranes, and freestanding structures.

D10.26

STRUCTURE AND POLARIZATION IN BaTiO₃/SrTiO₃ SUPERLATTICES FROM FIRST PRINCIPLES. J.B. Neaton, K.M. Rabe, Department of Physics and Astronomy, Rutgers University, Piscataway, NJ.

Structural and electronic properties of periodic, ultrathin [001]-oriented BaTiO₃/SrTiO₃ superlattices are calculated using density functional theory within the local density approximation. Spontaneous polarizations are evaluated using the Berry-phase theory of polarization. Motivated by recent experiments, we first report results for polarizations constrained to be parallel to the [001] stacking direction; the possibility of an additional perpendicular component is then also examined. The structure and polarization computed in BaTiO₃ layers exceeding three unit cells can be well described by strained bulk BaTiO₃. Important differences between SrTiO₃ layers and their bulk counterparts, however, are predicted to emerge with increasing BaTiO₃-layer thickness. In particular, the SrTiO₃ layers are found to develop a spontaneous polarization parallel to [001] having nearly the same magnitude as that in the BaTiO₃ layers, resulting in nearly constant polarizations throughout the superlattices. The modulation length and stacking periodicity are found to have a significant effect on the superlattice polarization. Finally, the implications for realizing a superlattice having a polarization larger than that observed in bulk BaTiO₃ are discussed in the context of recent experiments.

D10.27

NANOSCALE INVESTIGATION OF PHOTOINDUCED EFFECTS IN FERROELECTRIC THIN FILMS BY SCANNING FORCE MICROSCOPY. B.J. Rodriguez, A. Gruverman, A.I. Kingon, R.J. Nemanich, North Carolina State University, Depts. of Physics and Materials Science and Engineering, Raleigh, NC.

In this paper, piezoresponse force microscopy (PFM) is used to perform nanoscale studies of the photoinduced changes in ferroelectric and piezoelectric properties of lead titanate thin films. Both vertical and lateral PFM modes have been utilized to deduce the 3D orientation of polarization vectors in individual grains on a sub-micron scale. Local piezoelectric hysteresis loops of individual grains with out-of-plane polarization have been measured by superimposing the low-frequency switching voltage on the high-frequency imaging voltage. The hysteresis loops of negatively polarized grains are found to be symmetric while the hysteresis loops obtained from the positive grains are negatively biased. It has been found that illumination of the film with band-gap light leads to significant changes in the voltage shift of hysteresis loops with the sign of the shift determined by polarization of the grain. The relaxation behavior of UV-induced voltage shifts is qualitatively different in grains with opposite polarization. Domain pinning in negatively polarized grains as a result of combined application of a low (below coercive voltage) bias and UV illumination is observed. Results of this study are explained by the different screening conditions of positive and negative ends of the polarization vector by the photoinduced carriers and by the presence of the built-in bias at the bottom interface.

D10.28

MISFIT STRAIN DRIVEN PHASE TRANSFORMATIONS IN EPITAXIAL BARIUM STRONTIUM TITANATE FILMS. Z.G. Ban and S.P. Alpay, Department of Metallurgy and Materials Engineering and Institute of Materials Science, University of Connecticut, Storrs, CT.

We develop phase diagrams for single domain epitaxial barium strontium titanate films on cubic substrates as a function of the misfit strain based on a Landau-Devonshire phenomenological model similar to the one developed by Pertsev et. al [Phys. Rev. Lett. 80, 1988 (1998)]. With increasing misfit strain, a rotation of the polarization vector from the [001] direction of the film is expected. At critical misfit strains, phase transformations to unusual phases that are not possible in single crystals and bulk ceramics are predicted. The dielectric response of the films is calculated as a function of the misfit strain by taking into account misfit dislocation formation as to relieve

epitaxial stresses during deposition. Theoretical estimation of the dielectric constant of epitaxial Ba_{0.7}Sr_{0.3}TiO₃ (BST 70/30) films on Si, MgO, LaAlO₃, and SrTiO₃ substrates as a function of temperature and film thickness is provided. It is shown that by adjusting the misfit strain via substrate selection and film thickness, a high dielectric response can be obtained, especially in the vicinity of structural instabilities.

D10.29

DOPING AND SEEDING EFFECTS ON THE PROPERTIES OF (100) SrTiO₃ THIN FILMS FABRICATED BY CHEMICAL SOLUTION DEPOSITION. Jeffrey T. Dawley, Paul G. Clem, Ryan J. Ong, Michael P. Siegal, and Donald L. Overmyer, Sandia National Laboratories, Albuquerque, NM.

SrTiO₃ (STO) and STO-based thin films have been studied for a wide variety of applications, including dynamic random access memories (DRAM), tunable dielectrics, and as a buffer layer for superconducting tapes. For each of these applications the quality and specific crystallographic orientation of the STO is crucial for achieving desired properties. In this work, seeded nucleation and defect chemistry methods were applied to fabricate epitaxial (100)-oriented STO thin films on LaAlO₃(100) single crystal substrates and biaxially textured Ni(100) tapes using chemical solution deposition, to develop a buffer layer system compatible with YBa₂Cu₃O_{7-d} (YBCO). For this purpose, the STO films need to possess a high degree of (100) orientation, have low oxygen diffusivity, and prevent Ni poisoning of the YBCO. It was found that a solid-phase nucleation seeding process enhanced the epitaxial growth of (100)-oriented STO on Ni(100), which has a significant lattice mismatch of 11%. A dramatic enhancement in (100) orientation was observed in STO films grown using a novel liquid-phase seeding process. The effects of altering the crystal chemistry by adding acceptor and donor dopants, and the formation of a SrTiO₃-CaTiO₃ solid-solution on the oxygen diffusivity of the STO films was investigated using 18O in-diffusion. Sandia is a multiprogram laboratory operated by Sandia Corp., a Lockheed Martin Company, for the US Dept. of Energy under contract DE-AC04-94A185000.

D10.30

ELECTRIC FIELD-INDUCED DIELECTRIC SOFTENING AND STRUCTURAL STABILITY DURING FE(RH)/FE(RL) PHASE TRANSFORMATION. Pin Yang, Roger Moore, George Burns, Sandia National Laboratories, Albuquerque, NM.

An unusual field-induced dielectric softening near the FE(RH)/FE(RL) structural phase transformation was observed in a tin modified lead zirconate titanate solid solution (PSZT). Results show that the application of an external electric field stabilizes the low temperature rhombohedral phase to higher temperatures and changes the dielectric constant and loss tangent behavior near the structural phase transformation. Experimental observations on the field-induced dielectric softening and shifting transformation temperature under an external electric field will be reported. Structurally, the transformation from a high-temperature to a low-temperature rhombohedral phase is accomplished by oxygen octahedra tilting along the < 111 > direction. The additional (Zr,Ti)O₆ tilting in the adjacent cells permits the dipoles in the crystalline structure to be continuously developed in the low temperature rhombohedral structure as temperature decreases. It is believed that an increase in the dielectric dipole moment due to a field-enhanced piezoelectric effect near the structural phase transformation creates a structural instability, resulting in a dielectric softening and an increased coherent of the < 111 > oxygen octahedra rotations. Fundamental issues underlying the observed unusual behavior are discussed from the perspective of lattice dynamic theory. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

D10.31

LATTICE DYNAMICS STUDIES IN FERROELECTRIC THIN FILMS. X.X. Xi, D.A. Tenne, A. James, A. Sukiasyan, Department of Physics, The Pennsylvania State University, University Park, PA.

Lattice dynamics is of central importance for the mechanism of ferroelectricity. In particular, the soft mode behavior are directly related to many of their ferroelectric and dielectric properties. We report the experimental studies of the vibrational spectra of SrTiO₃ films grown by pulsed laser deposition. Raman scattering, with and without bias electric field, and Fourier-transform far-infrared ellipsometry were utilized. These results are compared with the low-frequency dielectric properties. We found that in the films the soft mode is harder compared to that in bulk crystals, in agreement with the Lyddane-Sachs-Teller formalism. The existence of local polar regions is proposed as an important factor determining the dielectric properties of ferroelectric thin films. The study was extended to

Ba_xSr_{1-x}TiO₃ films with Ba contents $x = 0.05, 0.1, 0.2$ and 0.5 . The temperature dependence of the soft mode frequency shows evidence of the ferroelectric phase transition in the films. Relative Raman intensity of hard phonon modes shows the ferroelectric phase transition occurs over a broad range of temperatures in thin films, which is different from bulk behavior. Comparison of temperature evolution of Raman spectra for films grown on SrTiO₃ and LaAlO₃ substrates shows the influence of strain on the temperature of ferroelectric phase transition.

D10.32

THEORETICAL PREDICTION AND EXPERIMENTAL CONFIRMATION OF CHARGE TRANSFER VIBRONIC EXCITONS AND THEIR PHASE IN ABO₃ PEROVSKITE CRYSTALS. R.I. Eglitis, Dept. of Physics, University of Osnabrueck, Osnabrueck, GERMANY; V.S. Vikhnin, A.F. Ioffe Physico Technical Institute, St. Petersburg, RUSSIA; E.A. Kotomin, Max Planck Institut für Festkörperforschung, Stuttgart, GERMANY; S.E. Kapghan, G. Borstel, Dept. of Physics, University of Osnabrueck, Osnabrueck, GERMANY.

The current theoretical and experimental knowledge of new polaronic-type excitons in ferroelectric oxides - CTVE - is discussed. It is shown that quantum chemical Hartree-Fock-type calculations using a semiempirical Intermediate Neglect of Differential Overlap (INDO) method as well as photoluminescence studies in ABO₃ perovskites confirm the CTVE existence. Our INDO calculations for KTaO₃ and KNbO₃ have demonstrated that the triplet exciton is a triad center containing one active O atom (O1) and two Ta atoms located on the opposite sites from this O atom. The total energy of a system is lowered by the combination of Coulomb attraction between electron and hole and the vibronic effect in this CTVE. According to our calculations, the oxygen ion O1 in KTaO₃ is displaced by 5.2% of lattice constant towards the Ta1 ion which is active in the CTVE formation. Simultaneously, this Ta1 ion reveals a displacement of 3.1% towards the O1 ion, whereas another Ta2 ion on the other side from the oxygen ion O1 along the (100) axis has a repulsion from the oxygen O1 and is displaced outwards by 4.5%. It is shown by means of our INDO calculations that polaronic-type CTVE in ferroelectric oxides could lead to the formation of a new crystalline phase. The ground state energy of this phase consisting of strongly correlated CTVEs lies within an optical gap of a pure crystal, and is characterized by a strong tetragonal lattice distortion, as well as by the ferroelectric ordering. It is also shown that clusters of the CTVE phase being stabilised by oxygen vacancies could be responsible for unusually strong optical SHG signal in nominally pure incipient ferroelectrics. Another experimental manifestation of CTVE is related to a drastic red shift with temperature of the fundamental absorption edge in SBN and KTaO₃ perovskite crystals observed at high temperatures. This effect could be explained by a thermal population of a low-lying bottom part of an additional valence band induced by the CTVE phase.

D10.33

MICROSTRUCTURE AND ELECTRICAL PROPERTIES OF BaTiO₃. Dae-Chul Park, Isao Sakaguchi, Naoki Ohashi, Hajime Haneda, Advanced Materials Laboratory, National Institute for Materials Science, Tsukuba, Ibaraki, JAPAN; Jun-ich Itoh, Mitsui Mining & Smelting Co., Ltd., Ageo-shi, Saitama, JAPAN; Toyohiko Yano, Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, Meguro, Tokyo, JAPAN.

Electrical properties and microstructure were investigated in BaTiO₃ ceramics with various additives, Ho₂O₃, MgO, 2Ho₂O₃/MgO, and La₂O₃. The dielectric constants were increased up to ≈ 4000 and ≈ 3000 at 25°C in the 1 mol% Ho-doped and 0.5 mol% Mg-doped BaTiO₃ materials, respectively. The BaTiO₃ ceramic coadded with 3 mol% Ho + 1.5 mol% Mg led to increase dielectric constant up to ≈ 6000 at 25°C and the dielectric constant peak around Curie temperature was suppressed at temperature range of from 25°C to 125°C. The size of BaTiO₃ grains was depended by the content and kind of an additive. Core-shell structure and secondary phase were also depended with an additive. Core-shell structure was formed completely in Ho-doped BaTiO₃ except for 0.5 mol%, but the structure was little observed in Mg-doped BaTiO₃ ceramic. Coadded BaTiO₃ ceramics also formed the core-shell grains. Grain size, mechanism of core-shell grain and sintering mechanism will be discussed.

SESSION D11: THEORY, MODELING, AND DESIGN OF PEROVSKITES

Chair: Renata M. Wentzcovitch
Friday Morning, April 5, 2002
Golden Gate A2 (Marriott)

8:00 AM *D11.1

COMPUTATIONAL DESIGN OF NEW MULTIFERROIC

PEROVSKITES. Nicola A. Hill, Alessio Filippetti, Materials Department, University of California, Santa Barbara, CA.

Multiferroic magnetolectrics are materials that are both ferromagnetic and ferroelectric in the same phase. As a result they have a spontaneous magnetization which can be switched by an applied magnetic field, a spontaneous polarization which can be switched by an applied electric field, and often some coupling between the two. Of the few that exist in nature, or have been synthesized in the laboratory, most are perovskite structure oxides. In this talk we use the multiferroic perovskites as model systems to explore the fundamental physics behind the scarcity of ferromagnetic ferroelectric coexistence. We find that in general the transition metal d electrons, which are essential for magnetism, reduce the tendency for off-center ferroelectric distortion. Consequently, an additional electronic or structural driving force must be present for ferromagnetism and ferroelectricity to occur simultaneously. We identify the chemistry behind this additional driving force, and describe the successful prediction and subsequent synthesis of a new multiferroic perovskite.

8:30 AM *D11.2

MAGNETIC COUPLING AND COLLECTIVE BEHAVIOR IN QUADRUPLE PEROVSKITE COMPOUNDS. W.E. Pickett, M.D. Johannes, Dept. of Physics, UC Davis, Davis, CA; R. Weht, Dept. of Physics, CNEA, San Martín, ARGENTINA.

Numerous double perovskite materials (perovskite ABO₃ → AA'BB'O₆) are known, and the small subset containing magnetic ions tend to have very interesting properties, e.g. half metallic Sr₂FeMoO₆. There is also a small but growing class of *quadruple perovskites* in which a Cu²⁺ drives a strong structural distortion that also tends to enforce good ordering on the various sublattices. This talk will address two such compounds. CaCu₃Mn₄O₁₂, observed to display potentially important magnetoresistance below its ordering temperature $T_C = 355$ K, is calculated to have a spin-asymmetric gap at low temperature (valence band maximum and conduction band minimum have different spin directions), which helps to account for its magnetoresistance. CaCu₃Ti₄O₁₂ has attracted attention due to its extremely high ($\sim 10^4$), T-dependent, dielectric constant in the kHz region. Here we discuss the magnetic coupling leading to antiferromagnetic alignment of Cu spins at $T_N = 25$ K, when magnetic coupling of both first and second Cu neighbors is forbidden by the symmetry of the Cu $d_{x^2-y^2}$ magnetic orbital.

9:00 AM D11.3

SUPERCONDUCTIVITY NEAR FERROMAGNETISM IN MgCNi₃. H. Rosner^a, R. Weht^{b,c}, M.D. Johannes^a, W.E. Pickett^a and E. Tosatti^{c,d}, ^aDepartment of Physics, University of California, Davis CA; ^bDepartamento de Física, CNEA, San Martín, ARGENTINA; ^cICTP, Trieste, ITALY; ^dSISSA and INFN/SISSA, Trieste, ITALY.

The antiperovskite MgCNi₃ was shown only very recently to be superconducting by He *et al.* [Nature **411**, 54 (2001)] The discovery of superconductivity above 8 K in MgCNi₃, which is primarily the ferromagnetic element Ni and is strongly exchange-enhanced, provides a probable new example of a possible coexistence of superconductivity and ferromagnetism which have been believed incompatible until the past 2-3 years. We have carried out full potential, all-electron density functional based calculations to understand the character of the charge carriers. An unusual quasi-two-dimensional heavy band mass van Hove singularity - almost completely Ni derived - lies very near the Fermi energy. Using supercell calculations, virtual crystal approximation and Stoner theory, it is shown that this compound is itself an incipient ferromagnet, which should be driven to ferromagnetism by partial ($\approx 12\%$) replacement of Mg with a monovalent metal such as Li or Na. This proximity of superconductivity to magnetism strongly suggests unconventional pairing, and the cross-over region between these phases will provide a novel playground in which to observe the competition, and possibly the coexistence, of these two intrinsically quantum mechanical - and usually antagonistic - collective phases.

9:15 AM D11.4

ELECTRONIC STRUCTURE OF PEROVSKITES AND TRANSITION METAL OXIDES BY MANY-BODY WAVE FUNCTION APPROACHES. Lubos Mitás, Lucas Wagner, Dept of Physics, North Carolina State University, Raleigh, NC.

We carry out a study of electronic structure of paradigmatic strongly correlated systems such as TMO transition metal oxides and perovskites. In particular, we compare several types of methods for capturing subtle effects such as magnetic ordering and ferroelectric/piezoelectric properties. We employ two types of methods and compare them: density functional approaches and modern quantum Monte Carlo methods. The quantum Monte Carlo approaches are qualitatively different from traditional methods since they are based on explicitly correlated many-body wave functions and stochastic

techniques of solving the Schrodinger equation. We discuss the impact of explicit correlation on ground and excited states, on geometries and electronic gaps. We point out the key roles of exact exchange and high accuracy treatment of electron correlation on the properties of these systems.

9:30 AM **D11.5**

COMPATIBLE TREATMENT OF BERRY PHASE POLARIZATION AND ELECTRIC-FIELD LINEAR RESPONSE IN FERROELECTRICS. Na Sai, Karin M. Rabe, and David Vanderbilt, Rutgers University, Department of Physics and Astronomy, Piscataway, NJ.

We have implemented a new formalism for computing the response of a periodic insulating system to an applied homogeneous, static electric field \mathcal{E} within density-functional perturbation theory (DFPT). The computed response is consistent with the discretized form of the Berry-phase polarization expression (R.D. King-Smith and D. Vanderbilt, Phys. Rev. B **47**, 1651 (1993)). Our approach facilitates the efficient minimization of the zero-field internal energy $U^{(0)}(\mathbf{P})$ at fixed spontaneous polarization \mathbf{P} . It can thus also be used to compute the electric enthalpy expanded to first order in electric field by minimizing $U(\mathcal{E}) = U^{(0)}(\mathbf{P}) - \mathcal{E} \cdot \mathbf{P}$ with respect to \mathbf{P} . Combining the modified DFPT scheme with the *ab-initio* pseudopotential technique, we present several applications to illustrate a variety of calculations that can be carried out for dielectric and ferroelectric systems. They include calculating the response of the internal structure to large ferrodistorptive modes; modeling the potential energy surface in the presence of electric fields and studying field-induced structural phase transitions; and directly computing the lattice contributions to the linear and the non-linear dielectric constants. We present examples of these applications in the context of simple perovskite systems that include BaTiO₃ and PbTiO₃, as well as for novel ferroelectric materials with compositionally broken inversion symmetries.

10:15 AM ***D11.6**

THE LOCAL STRUCTURE OF COMPLEX OXIDES WITH QUENCHED DISORDER. Ilya Grinberg, Valentino Cooper, Nathan R. Martin, Andrew M. Rappe, University of Pennsylvania, Department of Chemistry, Philadelphia, PA.

We perform a theoretical study of the perovskite material PbZr_{0.5}Ti_{0.5}O₃ (PZT) in order to understand its complex local structure. The Zr and Ti atoms are similar enough chemically that cation ordering is not observed in PZT. Therefore, any structural analysis must incorporate and understand the effect of quenched cation disorder. We have combined first-principles density functional theory (DFT) studies and Monte Carlo (MC) fitting of experimental data in order to develop a comprehensive picture of the local atomic distortions. By studying large supercells with DFT, we ascertain local chemical rules governing distortion patterns. These chemical rules are then incorporated in the MC analysis of experiment. Structures proposed by the MC calculations are tested for validity with DFT, and the cycle is repeated. In this way, theoretical and experimental evidence yield a unified picture of the response of PZT to quenched disorder.

10:45 AM **D11.7**

FIRST PRINCIPLES CALCULATIONS OF TWIST BOUNDARIES IN SrTiO₃. Roope K. Astala, Paul D. Bristowe, Univ of Cambridge, Dept of Materials Science and Metallurgy, Cambridge, UNITED KINGDOM.

The $\Sigma = 5$ (001) twist boundary in SrTiO₃ is a recently experimentally observed interface which possesses rich structural complexity. We have studied this grain boundary by performing lattice static DFT plane wave pseudopotential and empirical calculations. Various models with different boundary terminations and in-plane displacements were examined to identify the lowest-energy atomic geometries. The grain boundary has undercoordinated atoms and an open core structure which would make diffusion along the interface and point defect segregation likely. Also the electron structure differs from the bulk and the electrical activity of the grain boundary is discussed.

11:00 AM **D11.8**

AN ATOMISTIC MODEL FOR FERROELECTRIC SOLUTIONS. Marcelo Sepiarsky, Carnegie Institution of Washington, DC - IFIR, Conicet-UNR, Rosario, ARGENTINA; Ronald E. Cohen, Carnegie Institution of Washington, DC.

Atomistic modeling has shown capability to describe ferroelectric properties in perovskites [see for example S. Tinte *et. al.*, J. Phys.: Condens. Matter **11**, 9679 (1999)]. The possibility of the transferability of the parameters from pure systems to mixed compounds makes this kind of modeling an interesting alternative approach for the study of complex solutions. In the present work we use an *ab-initio* based shell model to test such ability. We apply the

parameters obtained for single ABO₃ compounds with different A and/or B substitutions to analyze the behavior of alloys where lead atoms are present. We compare the structural behavior, atomic distortions and ferroelectric properties with results obtained by available first principles calculations.

11:15 AM **D11.9**

POLARIZABLE FORCE FIELDS FOR MOLECULAR SIMULATION OF FERROELECTRICS. Qingsong Zhang, Tahir Çağın, and William A. Goddard III, Materials and Process Simulation Center, Caltech, Pasadena, CA.

In order to properly study the ferroelectric materials through molecular dynamics methods, we have developed a novel polarizable force field based on first principle quantum mechanics (QM). It is imperative for a force field to describe ferroelectricity in addition to the structural, thermal and mechanical properties of ferroelectrics. This new force field is novel especially in treating the electrostatic interactions. For electrostatic interactions, each atom is treated as follows: a fixed core charge with a Gaussian distribution and a variable shell charge with another Gaussian distribution. All the cores and shells interact with each other through coulomb law. This enables the proper treatment of the electronic polarization at the atomic level. The shell charges can flow within the whole system and described via the Charge Equilibration method, (QEq) [Rappe and Goddard, J. Phys. Chem. **95**, 3358 (1991)]. Hence, that variation of ionic polarization as a function of change in atomic configuration can be described. In addition to electrostatic interactions, a Morse potential is used to take care of the attraction due to dispersion and the repulsion due to Pauli Exclusion. Based on this model, we have derived Force fields for component oxides of BiTiO₃, TiO₂ (using QM studies on 3 polymorphs) and BaO (using QM studies on 4 different phases). We applied these force fields to component oxides and BiTiO₃. Furthermore, we have developed an algorithm to evaluation of charges via extended QEq for systems with large number of atoms, which is necessary to study the domain walls and domain wall mobility in ferroelectrics. This method reduces the computational cost from order N^3 to order N .

11:30 AM **D11.10**

COMPUTER SIMULATION OF DOMAIN PATTERN FORMATION IN 3-D. R. Ahluwalia, T. Lookman, A. Saxena, Theoretical Division, Los Alamos National Lab, NM; W. Cao, Department of Mathematics and Materials Research Institute, Pennsylvania State University, University Park, PA.

We study domain pattern formation in 3-D that results from a cubic to tetragonal transition, based on a Ginzburg-Landau approach. The free energy is written in terms of the polarization order parameter with an electrostrictive coupling to the elastic strain. The dynamics of the polarization fields is studied by solving over damped time dependent Ginzburg-Landau equations and the dynamics of strain fields is described by second order differential equations in time for the displacement fields, derived from a lagrangian formalism that incorporates a dissipational functional. Using this model, we have obtained stable and metastable domain patterns in 3-D that are formed in a cubic to tetragonal ferroelectric phase transition. It is found that the domain patterns are strongly influenced by the electrical and mechanical boundary conditions. We also simulated the electric field induced polarization reversal using this model, which sheds some light on the physical origin of the "domain engineering" process, recently used in fabricating super piezoelectric PMN-PT and PMN-PT multi-domain single crystals.

11:45 AM **D11.11**

CALCULATIONS OF THE ELECTRONIC AND ATOMIC STRUCTURE AND DIFFUSION OF POINT DEFECTS IN KNbO₃ PEROVSKITE CRYSTALS AND RELEVANT KTN SOLID SOLUTIONS. R.I. Eglitis, University of Osnabrueck, Dept. of Physics, Osnabrueck, GERMANY; E.A. Kotomin, Max Planck Institut fur Festkorperforschung, Stuttgart, GERMANY and Institute of Solid State Physics, University of Latvia, Riga, LATVIA; N.E. Christensen, Institute of Physics and Astronomy, Aarhus University, Aarhus-C, DENMARK; G. Borstel, University of Osnabrueck, Dept. of Physics, Osnabrueck, GERMANY.

In this paper we review our recent achievements in large scale computer simulations of point defects in advanced perovskite crystals. The results of calculations for mixed perovskite KNb_xTa_{1-x}O₃ solid solutions are presented and discussed. Analysis of the optimized atomic and electronic structure has clearly demonstrated that several nearest Nb atoms substituting for Ta in KTaO₃ – unlike Ta impurities in KNbO₃ – reveal the self-ordering effect, which probably triggers the ferroelectricity observed in KTN. The semiempirical INDO method based on the Hartree-Fock formalism predicts magnitudes of the Nb off-center displacements which are in good agreement with EXAFS measurements. Results are compared with *ab initio*

FP-LMTO first-principles calculations. The LMTO formalism and the semiempirical INDO methods were also combined for the study of the hole polarons in a cubic phase of KNbO_3 perovskite crystals. We predict the existence of both one-site and two-site (molecular) polarons with close optical absorption energies. Quantum chemical INDO calculations confirm the existence of the self-trapped electrons in both KNbO_3 and KTaO_3 associated with the lattice relaxation energy of 0.21 eV and 0.27 eV and estimated optical absorption of 0.78 eV and 0.75 eV, respectively. Lastly, we have calculated the defect migration energies using INDO method and classical shell model (SM) for the KNbO_3 cubic phase. The migration energies for the O vacancy obtained by means of these two quite different methods are reasonably close (0.68 eV and 0.79 eV, respectively) and also agree with the only experimental estimate available (ca 1 eV).

SESSION D12: FERROELECTRIC,
PIEZOELECTRIC, AND FERROELASTIC
PROPERTIES III

Chair: Karin M. Rabe
Friday Afternoon, April 5, 2002
Golden Gate A2 (Marriott)

1:30 PM *D12.1

CATION ORDER IN PEROVSKITE DIELECTRIC OXIDES.
Peter K. Davies, Dept. Materials Science, University of Pennsylvania, Philadelphia, PA.

With their ability to sustain an outstanding dielectric response in the microwave region and accommodate extensive chemical substitution, oxide perovskites are the most widely studied and technologically important family of microwave dielectrics. In mixed-metal perovskites a correlation between a high quality factor (low dielectric loss) and improved cation order has been clearly established. The lowest losses are observed in the 1:2 B-site ordered forms of $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ and $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$. However, there are relatively few examples of perovskites with this type of order and even in those cases the order is destabilized or modified by low concentrations of chemical additives. This paper will focus on identifying the critical factors responsible for the stabilization of cation order in perovskites with 1:1, 1:2, and 1:3 B-site stoichiometries. Examples of completely new families of B-site ordered dielectrics, based on a fractional A-site valence, will also be presented.

2:00 PM D12.2

TOPOGRAPHICAL EVOLUTION OF PZT THIN FILMS
PATTERNED BY MICROMOLDING IN CAPILLARIES.
Christopher Martin and Ilhan Aksay, Princeton University, Dept of Chemical Engineering and Princeton Materials Institute, Princeton, NJ.

Prior research has focused on the development of thin film fabrication technologies for piezoelectric materials for applications such as nonvolatile memory, sensors, actuators, and micromotors. The traditional microfabrication techniques used in silicon-based architectures are often not compatible with these materials. This presentation will demonstrate the utilization of the soft lithography technique of micromolding in capillaries[1,2,3] to the patterning of lead zirconate titanate ($\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$, PZT) thin films on length scales as small as one micrometer.[4,5] A PZT sol-gel is prepared and is patterned on a (100) Si wafer. Upon heat treatment, non-uniform shrinkage across the film due to the volatilization of organic components results in "double-peaked" film topographies that deviate from the shape of the original mold. Controlling the topography of the film through the drying and heat treatment conditions is critical for obtaining useful films for potential applications. Using the same framework used to understand the imbibition and flow of the infiltrating sol-gel in the capillary channels,[2,6] a model to explain the formation of the double-peak profile during drying and sintering has been developed. Atomic Force Microscopy measurements were used to quantify how the rate of gelation affects the topography and peak formation of the patterned thin films. Finally, modifications to the channel mold design are demonstrated that eliminate the peak formation, producing more homogenous patterns that better replicate the features of the mold.

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2. Y. Xia, E. Kim, and G.M. Whitesides, *Nature* **376** 581 (1995).
3. E. Kim, Y. Xia, and G.M. Whitesides, *Chem.Mater.* **8** 1558 (1996).
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5. J.S. Vartuli, M. Ozenbas, C.-M. Chun, M. Trau, and I.A. Aksay, *J.Mater.Res.* in press
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2:15 PM D12.3

IONIC DEFECT REDISTRIBUTION AND THE COMBINED

EFFECTS OF IMPRINT AND FATIGUE IN PZT THIN FILMS.

Lawrence F. Schloss and Paul C. McIntyre, Stanford University, Department of Materials Science and Engineering, Stanford, CA; Steven R. Gilbert, Agilent Laboratories, Palo Alto, CA; Jeffrey R. Roeder, Steven M. Bilodeau, and Bryan Hendrix, ATMI, Danbury, CT.

Through use of the oxygen isotope, ^{18}O , we have observed the redistribution of an introduced oxygen tracer profile within MOCVD-grown lead zirconate titanate (PZT) thin films during bipolar electrical stressing, or fatigue, at room temperature. We incorporated the tracer into the film during an exchange anneal prior to the top electrode deposition, and measured the oxygen isotope concentrations with depth-resolved secondary ion mass spectroscopy (SIMS). The effects of high temperature annealing prior to tracer exchange, and post-exchange anneals prior to fatigue will also be presented. In addition, the effect of static imprint on the switchable polarization, as measured by electrical pulse (PUND) testing, in thin film PZT has been found to have a magnitude and direction dependent on the relative amount of fatigue present prior to imprint. However, the effect of static imprint on fatigue appears transient, and after 1-3 decades of bipolar cycling fatigue levels in imprinted and non-imprinted samples converge. Results will be analyzed in light of proposed models for the mechanism of ferroelectric fatigue.

2:30 PM D12.4

TEXTURE AND STRAIN ANALYSIS OF PZT BY IN SITU NEUTRON DIFFRACTION. Ersan Ustundag, Robert Rogan, Bjorn Clausen, California Inst. of Technology, Department of Engineering and Applied Science, Pasadena, CA; Mark Daymond, ISIS, Rutherford Appleton Laboratory, Chilton, UNITED KINGDOM; Robert McMeeking, Univ. of California Santa Barbara, Materials Science Department, Santa Barbara, CA.

In situ neutron diffraction studies were performed on poled, doped PZT samples under various uniaxial compressive stresses. Rietveld analysis of the diffraction patterns provided data of the onset and culmination of domain switching through modeling of the sample texture. Calculated lattice parameters indicate significant residual stresses due to locked in domains, and individual peak analysis provides strain information specific to families of lattice planes.

2:45 PM D12.5

ELASTIC DEFORMATIONS IN FREESTANDING BaTiO_3 FILMS.
Jaya P. Nair, Natali Stavitski, Ilya Zon and Igor Lubomirsky, Weizmann Inst of Science, Rehovot, ISRAEL.

Perovskite films of BaTiO_3 are important for a number of applications such as high charge density capacitors, ferroelectric memory, microwave and optoelectronic devices. The dielectric properties of a thin film, however, depend not only on the ferroelectric material itself, but also on the substrate material, film thickness and mechanical stress. The last one is one of the most influential factors and experimental data on the effect of mechanical stress on dielectric constant, Curie temperature and spontaneous polarization, are numerous. Most of the data on mechanical stress in thin BaTiO_3 films are based on measurements of the *substrate curvature with and without the film*. In contrast, we report on measurements of the *film with and without the substrate*, i.e., we investigate *freestanding films*. BaTiO_3 films were prepared on bare silicon and on silicon, covered by a 120 nm thick, randomly oriented Al_2O_3 buffer. Films prepared on bare silicon by RF reactive sputtering are essentially stress-free. However, they disintegrate after substrate removal. In contrast, the films prepared on the Al_2O_3 buffer have tensile stress of 100-170 MPa but retain their structural integrity after separation from the substrate. Substrate removal is accompanied by film corrugation, indicating $\approx 0.5\%$ linear expansion of the films. At the same time, the freestanding films resonate mechanically, indicating a tensile stress of 2.2 GPa. This seeming contradiction can be understood on the basis of a recently developed theory of 2D clamping in thin ferroelectric films [N.A. Pertsev, A.G. Zembilgotov, and A.K. Tagantsev, *Phys Rev Lett* **80**, 1988 (1998)].

3:30 PM D12.6

STRESS INDUCED PHASE TRANSFORMATIONS IN (001) MOCVD-GROWN PZT THIN FILMS. Maxim B. Kelman, Paul C. McIntyre, Stanford Univ, Dept of Materials Science & Engineering, Stanford, CA; Bryan C. Hendrix, Steven M. Bilodeau, Jeffrey F. Roeder, ATMI, Danbury, CT; Alexei Gruverman, Department of Materials Science & Engineering, North Carolina State Univ, Raleigh, NC.

Structural and electrical properties of MOCVD-grown $\text{Pb}(\text{Zr}_{0.35}\text{Ti}_{0.65})\text{O}_3$ thin films with thickness varying from 700Å to 4000Å were investigated. X-ray diffraction showed that the stable PZT phase is dependent upon the film thickness. Hysteresis loop measurements showed that all of the films were ferroelectric. However,

while the thickest PZT films are at least partially tetragonal, with a-type and c-type peaks present, films thinner than 1500Å have neither of those peaks. Reflections detected in the XRD scan for the thinnest film were consistent with the film being rhombohedral. The relative volume fraction of the rhombohedral phase in the films was determined by integrating the area under the XRD peaks. For as-deposited PZT films, it was determined that the coercive field scales with the volume fraction of the rhombohedral phase. Piezoresponse imaging showed that at least for the thinnest films, each grain is in the single-domain state. X-ray diffraction also showed that the volume fraction of the rhombohedral phase in the films is affected by the annealing treatment performed on these films. As the annealing temperature is increased, the volume fraction of the rhombohedral phase increases and then decreases. The observed phase transformations can be attributed to the stresses present in the film. As described by N.A. Pertsev et. al (PRL '98), sufficiently high tensile stress can transform a single domain tetragonal ferroelectric into a distorted rhombohedral phase. Intermediate temperature anneals densify the film, increasing the tensile stress on the film and the volume fraction of the rhombohedral phase. Higher temperature anneals relieve those stresses, reversing this trend. Stress evolution in the PZT films was confirmed using wafer curvature methods.

3:45 PM D12.7

LEAD STEREOCHEMISTRY IN INCOMMENSURATE FERROELECTRIC PEROVSKITES AND IN INCOMMENSURATE LEAD MONOXIDE. Gianguido Baldinozzi, Jean-Marc Raulot,

Structures, propriétés et modélisation des solides, CNRS-Ecole Centrale Paris, Châtenay-Malabry, FRANCE; Ram Seshadri, Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore, INDIA; Vaclav Petricek, Dept of Physics, Czech Academy of Sciences, Praha, CZECH REPUBLIC; Dominique Grebille, Crismat Lab, CNRS-ISMRA Caen, FRANCE; Jean-Michel Kiat, Gilbert Calvarin, Structures, propriétés et modélisation des solides, CNRS-Ecole Centrale Paris, Châtenay-Malabry, FRANCE.

Our aim is to discuss some peculiar features concerning lead stereochemistry in lead based ferroelectric perovskites. Among these compounds, some of them present relatively sharp ferroic phase transitions towards a commensurate or an incommensurate phase (e.g. Pb_2CoWO_6 and $\text{Pb}_2\text{MgTeO}_6$). The superspace group approach and the analysis of anharmonicity (Gram-Charlier expansion) are rather sophisticated way to analyse the behaviour of Pb-O bonding in different sections of the commensurate or incommensurate structures. The possible phase transition mechanisms are reviewed and the bondings are compared to those in the incommensurate structure of *alpha*-lead monoxide. This is also consistent with the idea that a large portion of the ferroelectric polarization is provided by Pb displacements (to accommodate the lone-pair electrons), and these displacements are closely coupled to the rotation of the octahedra. Complex perovskite electronic structures are not easily accessible from diffraction experiments because of the heavy atoms sitting on the A site of the structure. Self consistent calculations of the electronic structure, charge distribution and electron localisation function in lead complex perovskites (elpasolites) and in lead monoxide provide better understanding of the behaviour of Pb-O bonding in these compounds. In particular, the covalency character of the bondings has a considerable impact on the softening of the interactions between the different ions in the structure, leading to the eventual appearance of potential minima sitting off of the cubic sites. Depending on the existence or not of this local minima, the phase transition character can be mostly order-disorder or displacive. The analysis of these bondings in these compounds allows us to discuss the common features of lead stereochemistry. This picture provides a possible framework for understanding relaxor behavior at the atomic level illustrating the effects of the coupling of the Pb polarization to the environment and the ease of rotation of the octahedra.

4:00 PM D12.8

PHYSICAL AND ELECTROMECHANICAL PROPERTIES OF SOL-GEL SYNTHESIZED EPITAXIAL PZT FILMS ON STO/Si SUBSTRATES. A. Talin, S.M. Smith, S. Voight, J. Finder, K. Eisenbeiser, D. Penunuri, Z. Yu, P. Fejes, T. Eschrich, J. Curless, D. Convey, A. Hooper, Motorola Labs, Tempe, AZ.

In this paper we report on the deposition and characterization of single-crystalline films of $\text{PbZr}_{.52}\text{Ti}_{.48}\text{O}_3$ (PZT) on (001)Si substrates with a thin, epitaxial interlayer of SrTiO_3 (STO), and subsequent performance of these films in surface acoustic wave resonator (SAW) structures. We use sol-gel method to deposit the PZT films, which range in thickness from 400Å to 1µm, have a typical surface roughness of 5Å, and exhibit well defined reflective high energy electron diffraction patterns characteristic of smooth epitaxial films. Using high resolution transmission electron microscopy and double-crystal X-ray diffraction we find that the PZT films are oriented with the c-axis normal to the (001)Si plane and with the a-axis lying along $\langle 110 \rangle_{\text{Si}}$ direction. SAW resonators are fabricated on our films using

an evaporated Al interdigitated transducer pattern with an electrode pitch of 1.2µm. The measured electromechanical coupling coefficient and the SAW velocity depend on the PZT film thickness and range from 0.5%-3%, and 2500m/s-3500m/s, respectively, and resulting in a SAW resonant frequency range of 1-1.8GHz. The PZT/STO/Si SAW characteristics are compared to previously published theoretical calculations for this system.