# SYMPOSIUM U

## Multiferroic Materials

November 27 - 30, 2005

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# TUTORIAL

**FTT/U/W: Smart Materials – Fundamentals and Applications**
**Sunday, November 27, 2005**
**9:00 AM - 12:30 PM**
**Room 200 (Hynes)**

This tutorial will focus on the broad range of inorganic and organic functional materials that are being studied for applications as “Smart Materials,” including piezoelectrics, multiferroics, and electroactive polymeric materials. The tutorial aims to give the attendee a broad perspective of the various materials and their fundamental science, and then finish up with a summary discussion of their applications. Each segment will include background information, a description of the method, the current state of the art, new trends, and unique advantages and limitations (e.g., for fabrication of particular materials or devices, scalability, unusual geometries, and integration in multistep hybrid device fabrication schemes). The intention of the tutorial is to give the attendees a fundamental background on each method, the strengths of each technique, the ease/difficulty/cost of setting up, and future directions.

*Fundamentals of Piezoelectric Materials* – Trolier-McKinstry
*Multiferroics* – Viehland
*Electroactive Polymers* – Cheng
*Applications and Examples* – Madden

**Instructors:**
**Z. Y. Cheng**
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**John Madden**
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**Susan Trolier-McKinstry**
The Pennsylvania State University

**Dwight Viehland**
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SESSION U1: Ferromagnetic Shape Memory Theory
Chair: Eckhard Quandt
Monday Morning, November 28, 2005
Republic A (Sheraton)

**8:00 AM** ***U1.1**
**Martensitic Transformations and Magnetocaloric Effects in Ni-Mn Based Heusler Alloys.** Eberhard F. Wassermann, Thorsten Krenke and Mehmet Acet; Physics, Universitaet Duisburg-Essen, Duisburg, Germany.

Although Ni-Mn based Heusler alloys have been extensively studied over nearly 80 years in relation to their ferromagnetic properties, it was not until recent that interesting magnetoelastic and thermal properties giving rise to giant magnetic shape memory behavior and magnetocaloric effect have been discovered. We will briefly review the basic magnetic shape memory properties in the archetype Ni-Mn-Ga Heusler alloys, and then show how as a function of the electron concentration one can achieve a systematic knowledge about the structure and magnetism in the existing Heusler systems. On this basis, we have started a search for new potential Heusler alloys with adequate magnetic shape memory properties, i.e., Curie temperatures above martensitic transformation temperatures. Two systems have been found, Ni-Mn-In and Ni-Mn-Sn, which have shown magnetoelastic properties that are favorable in fulfilling the requirements stated above. We report on structural and magnetic transformations on these systems by x-ray diffraction, optical microscopy, differential scanning calorimetry, magnetization, and magnetostriction studies. Further neutron diffraction experiments in magnetic fields have been carried out to investigate the microscopic properties of the field induced strains. The austenite state in Ni-Mn-Sn and Ni-Mn-In has the L21 structure, while the martensite has a 10M, 14M, or L10 structure depending to the Sn or In compositions. The structural and magnetic phase diagrams of these systems have been constructed and fit into the existing electronic concentration scheme mentioned above. Other than magnetic field induced strains, large inverse magnetocaloric effects have been observed in both systems in the vicinity of room temperature, making these material attractive for high temperature magnetic cooling [1]. The large inverse magnetocaloric effect has its origin in a martensitic phase transformation that modifies the magnetic exchange interactions through the change in the magnitude of the lattice parameter. [1] Inverse magnetocaloric effect in Ni-Mn-Sn alloys, Th. Krenke et al., Nature Mat. (2005).

**8:30 AM** ***U1.2**
**Mesoscopic Modeling of Multiferroic Materials.**
Avadh B. Saxena, Los Alamos National Lab, Los Alamos, NM, New Mexico.

Using the Ginzburg-Landau level mesoscopic modeling with multiple coupled order parameters (e.g. strain, magnetization, polarization, shuffle modes) we investigate the inhomogeneous microstructure in shape memory alloys, ferroelectrics, magnetoelastics, functional perovskites including the multiferroics with direct coupling of polarization and magnetization. The role of long-range, anisotropic forces such as those arising from either the elastic compatibility constraints or the (polar and magnetic) dipolar interactions in determining the microstructure as well as physical properties is discussed. We also model their thermodynamic response and compare with experimental observations. In collaboration with: T. Lookman, S.R. Shenoy, A.R. Bishop, R.C. Albers, R. Ahluwalia, W. Cao, T. Castan, and A. Planes.

**9:00 AM** **U1.3**
**The Impact of Twin Boundary and Domain Wall Mobility on the Macroscopic Response of Ferromagnetic Shape Memory Alloys.** Antonio DeSimone, International School for Advanced Studies, SISSA, Trieste, Italy.

Ferromagnetic shape memory alloys (FSMAs) such as Ni2MnGa or Fe3Pd undergo a reversible first order martensitic phase transformation upon coooling, at temperatures below the Curie temperature. The crystallography of twinning implies that neighboring variants have nearly perpendicular easy axes. Therefore, a specimen can be biased towards one or another variant by applying a magnetic field. Because the transformation is first order, unlike in ordinary or giant magnetostrictive materials, very large strains can be produced by variant redistribution. Large and reversible field-induced strains are typically observed in materials with high magnetic anisotropy. This is because, in these circumstances, the magnetization stays parallel to the easy axes even as the magnetic field is increased, ensuring a significant driving force on twin boudaries. Although much is known about the energetics of these magnetoelastic domains, the understanding of how twin boundaries and domain walls move is much less satisfactory. In particular, the derivation of microstructurally based criteria to ensure highly mobile twin boundaries would be of great technological relevance. In this work, a model for the kinetics of magnetoelastic interfaces is presented and validated by comparison with the available experimental evidence on the macroscopic response of FSMAs. The basic framework of the model is the high anisotropy limit of micromagnetics proposed and discussed in [1] and [2]. The theory is extended to the analysis of the motion of magnetoelastic interfaces by the use of configurational forces and of microstructurally-based kinetic laws. The role of pinning heterogeneities and of ohmic losses in determining the observed macroscopic response of FSMAs is critically assessed. References: [1] A. DeSimone and R.D. James: A constrained theory of magnetoelasticity. Journal of the Mechanics and Physics of Solids, vol. 50 (2002), pp. 283-320. [2] A. DeSimone and R.D. James: Energetics of magnetoelastic domains in ferromagnetic shape memory alloys. Journal de Physique IV (France), vol. 112 (2003), pp. 969-972.

**9:15 AM** **U1.4**
**Multi-scale theoretical model for phase transformations in ferromagnetic shape memory alloys.** Vesselin Stoilov, Mechanical, Automotive and Materials Engineering, University of Windsor, Windsor, Ontario, Canada.

The large magnetic-field-induced strains observed in martensitic phases based on Ni2MnGa and in other ferromagnetic shape memory alloys are believed to arise from reorientation of the martensitic variants accompanied with the process of twin-boundary motion. The present work has been aimed at connecting atomistic level model to continuum theory of phase transformations in ferromagnetic shape memory alloys. A first principles theoretical model for the magnetization process and field-induced strain by twin boundary motion is proposed for strong, weak and intermediate anisotropy cases The author has developed a formulation of the Helmholtz free energy potential based on one dimensional atomic Ising model of the magnetic materials. The developed thermodynamic potential is used in the context of the sharp phase front-based continuum framework proposed by Stoilov et. el. Acta Mat. 2002 to study the micro-macro transition during the martensitic transformations in Ni2MnGa single crystals. The developed model has been successfully used to predict the response of 2D and 3D single crystal systems. Nucleation of domains and propagation of domain walls were investigated under combined magneto-mechanical loading and compared to recent experiments.

**9:30 AM U1.5**
**Anomalous Vibrational Effects in Magnetic Shape Memory Heusler Alloys.** Peter Entel[1], Alexey T. Zayak[2,1], Karin M. Rabe[2], Waheed A. Adeagbo[1] and Markus E. Gruner[1]; [1]Physics Department, University of Duisburg-Essen, Duisburg, Germany; [2]Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey.

First-principles calculations are used in order to investigate phonon anomalies in magnetic Ni- and Co-based Heusler alloys. Phonon dispersions for several systems in their cubic L21 structure were obtained along the [110] direction. We consider compounds which exhibit phonon instabilities and compare them with their stable counterparts. The analysis of the electronic structure allows us to identify the characteristic features leading to structural instabilities. The phonon dispersions of the unstable compounds show that, while the acoustic modes tend to soften, the optical modes disperse in a way which is significantly different from that of the stable structures. The optical modes that appear to disperse at anomalously low frequencies are Raman active, which is considered an indication of a stronger polarizability of the unstable systems. We show that phonon instability of the TA2 mode in Heusler alloys is driven by the strong interaction (repulsion) with the low energy optical vibrations. The optical modes show their unusual behaviour due to covalent interactions which are additional bonding features incommensurate with the dominating metallicity in Heusler compounds. As a consequence we observe that the optical vibrations show unusual inversion of their modes. Analysis of the force constants revealed that negative force constants are present in all unstable systems. We conclude that the inversion of optical modes appears to be the driving force for the acoustic anomaly and, hence, for the premartensitic effects and the martensitic transformation. Preliminary results have been published in [1-3]. [1] A. T. Zayak, P. Entel, J. Enkovvaara, A. Auela, and R. Nieminen, Phys. Rev. B 68 (2003) 132402 [2] J. Enkovaara, A. Ayuela, A. T. Zayak, P. Entel, L. Nordstrom, M. Dube, J. Jalkanen, J. Impola, and R. M. Nieminen, Mater. Sci. Eng. A 378 (2004) 52. [3] A. T. Zayak and P. Entel, J. Magn. Magm. Mater. 290-291 (2005) 874.

**9:45 AM U1.6**
**Comparative Study of Precursor Modulated Patterns in Magnetic and Structural Ferroic Materials.** Antoni Planes[1], Marcel Porta[1], Teresa Castan[1] and Avadh Saxena[2]; [1]Estructura i Constituents de la Materia, Universitat de Barcelona, Barcelona, Spain; [2]Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico.

Phase transitions in multiferroic materials are often preceded by nanoscale textures which occur through local symmetry breaking effects that mimic the symmetry of the incoming low-temperature phase. Typical examples are ferromagnetic Heusler shape-memory alloys where magnetic and structural modulated patterns have been observed above their martensitic (and in some cases magnetic) transitions. We discuss the basic ingredients required for these phenomena to occur and show that they are likely to be fulfilled for a large variety of ferroic materials regardless of the specific physical variables involved in their description. We propose Landau-type free energy models that incorporate these required ingredients for structural and magnetic systems. In particular, we show that symmetry characteristics of the precursor modulated patterns are determined by the nature of the long range interactions arising from compatibility constraints in the material. Finally, we compare representative numerical simulation results obtained for these two systems.

SESSION U2: Ferromagnetic Shape Memory Alloys I
Chair: Yasubumi Furuya
Monday Morning, November 28, 2005
Republic A (Sheraton)

**10:30 AM *U2.1**
**Lorentz Microscopy of Magnetic Domain Configurations in Multiferroic Materials.** Sai Prasanth Venkateswaran and Marc De Graef; Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania.

Characterization of the magnetic microstructure of magnetic multiferroic materials by means of electron optical methods is not an easy task. Lorentz transmission electron microscopy (LTEM) and electron holography (EH) are among the more commonly used observational techniques. In this talk, we will first introduce the theoretical foundation of the imaging process in the electron microscope. The basic quantity underlying all magnetic observations in the TEM is the phase of the electron wave, which contains information about the electromagnetic fields inside and surrounding the thin foil. Reconstruction of this phase from measured intensities is a significant component of quantitative work in this field, and we will highlight a recently developed phase reconstruction method, the so-called Transport-of-Intensity Equation. From the phase, we can obtain quantitative magnetic microstructure information at the nanometer length scale. We will discuss examples of phase reconstructed LTEM images, as well as the limitations of the technique. The second half of this talk will focus on the application of these techniques, in particular phase reconstructed LTEM, on ferromagnetic shape memory alloys in both the Ni-Mn-Ga and Co-Ni-Ga systems. We will present LTEM observations on both the martensitic and austenitic states of both alloy systems. In particular, we will present evidence for the presence of magnetoelastic tweed contrast. This contrast, which is only visible in the Lorentz imaging mode, is due to the presence of modulations in the local magnetization. We will conclude the talk with a review of image simulation methods for Lorentz TEM.

**11:00 AM U2.2**
**Electron Diffraction and HREM Imaging of the Martensitic Phase in $Ni_2MnGa$.** Debashis Mukherji[1], Myriam Aguirre[1], Peter Mullner[2] and Gernot Kostorz[1]; [1]Angewandte Physik, ETH Zurich, Zurich, Switzerland; [2]Materials Science and Engineering, Boise State University, Boise, Idaho.

In the near-stoichiometric $Ni_2MnGa$ alloys, the parent $\beta$ phase ($L2_1$ structure) transforms to a long-periodic martensite. The close-packed basal planes of the martensite which originate from the {110}-type planes of the parent cubic phase are stacked along the c axis of the martensite unit cell. In both magnetic-field- and stress-induced martensitic structures, a superstructure with long periodicity is revealed by superlattice reflections in X-ray, neutron and electron diffraction. Periodic displacements of the basal planes and various modulations of the periodic structure, e.g. 5 fold (10M) and 7 fold (14M) have also been observed in $Ni_2MnGa$ alloys. However, details of these periodic displacements, e.g. whether they are a result of a periodic shuffling or a periodic shear of the planes, remain controversial. Results of high-resolution electron microscopy (HREM) and electron diffraction on different non-stoichiometric compositions of the $Ni_2MnGa$ phase will be presented. Models of (*i*) a sinusoidal shuffling and (*ii*) a discrete periodic shift of the basal planes in the modulated long-periodic structures will be considered. The experimental results will be compared with computer simulations of different 10M and 14M martensitic structure models. The periodic shuffling and the periodic shear models which give different atomic positions (and therefore different structure factors) in the martensite unit cell have been tested by a quantitative matching of intensities in experimental and simulated diffraction patterns. For a quantitative comparison, diffraction patterns were recorded on imaging plates, with the advantage of recording the intensity variation linearly over a large dynamical range. Thereby, very weak superlattice reflections are resolved in the presence of strong reflections. Diffraction analysis results have been complemented by lattice-resolved HREM images of [010]-oriented $Ni_2MnGa$ martensite to directly reveal the structural modulations. The present work favours the periodic-shift model.

**11:15 AM *U2.3**
**Ni-Mn Based Ferromagnetic Shape Memory Alloys.** Ryosuke Kainuma[1], Yuji Sutou[2], Katsunari Oikawa[1] and Kiyohito Ishida[1]; [1]Department of Materials Science, Tohoku University, Sendai, Miyagi, Japan; [2]Biomedical Engineering Reasearch Organization, Tohoku University, Sendai, Miyagi, Japan.

Ferromagnetic shape memory alloys (FSMAs) have attracted considerable attention as a new type of magnetic actuator materials. Among the various FSMAs, the NiMnGa alloy system, which shows a large magnetic field-induced strain over 6%, has been extensively studied. Until now, some Ni-Mn based FSMAs besides the NiMnGa have been reported in NiMnX (X: Al, In, Sn and Sb) systems. In the present paper, characteristic features on the martensitic and magnetic transformations of these Ga-free NiMn-based FSMAs will be reviewed in contrast with those of the NiMnGa alloy.

**11:45 AM U2.4**
**Martensitic Transformation Characteristics of CoNiGa Ribbon and Bulk Alloys.** Yoichi Kishi[1], Zenjiro Yajima[1], Ken-ichi Shimizu[1], Teiko Okazaki[2], Yasubumi Furuya[2] and Manfred Wuttig[3]; [1]AMS R&D Center, Kanazawa Institute of Technology, Hakusan, Ishikawa, Japan; [2]Faculty of Science and Technology, Hirosaki University, Hirosaki, Aomori, Japan; [3]Department of Materials Science and Engineering, University of Maryland, College Park, Maryland.

Microstructures, phase transformation behavior and magnetic properties of CoNiGa ribbons prepared by melt-spinning are investigated and contrasted with those of CoNiGa bulk alloys. Rapidly solidified 40 $\mu$m-thin ribbons of the alloys were prepared by electro-magnetically controlled single-rolled melt-spinning. Transformation characteristics of the ribbons resemble those of the bulk alloys. Coercive force of the ribbons strongly depends on the direction of the applied magnetic field. Maximum coercive force is obtained at $\theta = 70°$ ($\theta$ is the angle between the magnetic field and the ribbon plane). Bird-view and cross sectional SEM observations show that martensite variants tend to be formed at high angles. This anisotropy of the magnetic properties appears to be related to the formation angles of martensite variants.

SESSION U3: Ferromagnetic Shape Memory Actuators
Chair: Emmanouel Pagounis
Monday Afternoon, November 28, 2005
Republic A (Sheraton)

**1:30 PM** *U3.1
**Influence of Temperature on Ni-Mn-Ga Magnetic Shape Memory Alloys.** Herbert Schmidt[1], Manuel Koehl[1,2] and Joerg Ihringer[2]; [1]Corporate Sector Research and Advance Engineering, Robert Bosch GmbH, Gerlingen-Schillerhoehe, Germany; [2]Inst. for Geosciences, Eberhard-Karls-University, Tuebingen, Germany.

Magnetic shape memory alloys present a comparatively new class of active materials with qualitatively new properties. In order to identify promising applications, it is fundamentally important to develop an understanding of the temperature variations of key materials properties. These include passive properties (e.g. thermal expansion) and active properties (e.g. maximum Field-Induced Strain (FIS), twinning stress, switching field, and hysteresis). In this study, thermal expansion was determined using differential dilatometry on a- and c-axis oriented single crystals, finding macroscopic shape change in agreement with scattering data on the temperature evolution of the unit cell. Temperature evolution of the tetragonal distortion is derived from the aforementioned data over a wide range of temperatures (approx. −150...+200°C), and is found to closely correspond to the maximum FIS over the studied temperature range (approx. −20...+50°C). From quasistatic strain-stress experiments in an external transverse field under controlled-temperature conditions it is found that with increasing temperature (within the latter temperature range) all of the following properties decrease: maximum FIS, twinning stress, switching field, and hysteresis. At low temperature (the actual value strongly depends on the twinning stress of a given sample) the material becomes magnetomechanically inactive. In samples displaying comparatively large twinning stress (about 1 MPa at room temperature) the disappearance of the magnetic shape memory effect is directly observed experimentally.

**2:00 PM** *U3.2
**Development Multi-ferroic Actuator/Sensor Material and Device for Intellligent/Smart Technology.** Yasubumi Furuya and Teiko Okazaki; Department of Intelligent Machines and System Engineering, Hirosaki University, Hirosaki, Japan.

Two types of multi-ferroic actuator/sensor devices i.e. (1) magnetically driven composite actuator and (2) multi-functional surface acoustic wave (SAW) sensor by MEMS are presented for intelligent/smart technologies. The large-scale robust composite actuator (1) was designed to combine the ferromagnetic property with superelasticity of shape memory alloy(SMA) because it can be driven with high speed as well as large strain by applying the wireless magnetic field. The composite was reinforced by the superelastic fiber or lamellar of shape memory alloys(TiNi,CuAlMn) in the ferromagnetic metal(Ni,Fe) matrix. The actuator characteristics were investigated for 1)difference of the material properties and actuator performance, 2)strength of the composite material when changing the volume fraction of each elemental and 3)response speed in the alternative magnetic field. As a result, the considerable improvements of actuator perfomance such as higher speed response than SMAs and larger strain than conventional magnetostrictive alloy were experimentally comfirmed, but its large hysteresis problem should be improved for engineering actuator applications. Secondarily, multi-functional designed, multi-ferroic sensor device of surface acoustic wave(SAW) will be introduced. Piezoelectric LiNbO3 base material was used. IDT was made by lithography. On the surface part between IDTs, environmentally acticve material films such as SMA,FSMA and magnetostrictive alloy etc. were formed by magnetron-sputtering. Various environmental sensing parameters i.e. temperature, magnetic field strength, stress,loadig hysteresis and internal damage etc. could be evaluated nondetructively from the signal analysis of the amplitude and phase change of SAW, which indicates the effectiveness of our proposed multi-functional SAW device sensor. Consequently, these results show the possibility of a new type of multi-functional actuator and sensor based on multi-ferroic effect.

SESSION U4: Martensitic Microstructures and Microactuators
Chair: Florin Zavaliche
Monday Afternoon, November 28, 2005
Republic A (Sheraton)

**3:30 PM** *U4.1
**Martensitic Transformation and Rearrangement of Varians in Some Ferromagnetic Shape Memory Alloys under Magnetic Field.** Tomoyuki Kakeshita and Takashi Fukuda; Department of Materials Science and Engineering, Graduate School of Engineering, Osaka University, Suita, Osaka, Japan.

Some ferromagnetic shape memory alloys exhibit interesting behavior by the application of magnetic field because of their large magnetocrystalline anisotropy. One of such behavior is rearrangement of martensite variants (twinning plane movement) driven by magnetic field. We evaluated magentocrystalline anisotropy constant and twinning stress in a wide temperature range for some ferromagnetic shape memory alloys (iron based alloys and Ni-Mn-Ga). As a result, we have confirmed that the magnetic anisotropy energy is larger than the energy required for the twinning plane movement when the rearrangement of variants is driven by magnetic field and vice verse regardless of temperature and field direction. Another interesting behavior is concerned with magnetic field dependence of transformation temperature. We measured martensitic transformation temperatures under various magnetic fields in some Ni-Mn-Ga alloys, and found that the 10M and 14M transformation temperatures decrease in a low field region and then increase in a higher field region. Such characteristic field dependence is explained by the difference in magnetization between the parent phase and the martensite. That is, in a low field region, the magnetization of the martensite is smaller than that of the parent phase because of a large magnetocrystalline anisotropy of the martensite, but in a high field region the magnetization of the martensite is larger than that of the parent phase because the spontaneous magnetization of the martensite is larger than that of the parent phase.

**4:00 PM** U4.2
**Premartensitic Transition in Ferromagnetic Shape Memory Alloys.** Liyang Dai[1], Sai Prasanth Venkateswaran[2], Peng Zhao[1], Marc J. DeGraef[2] and Manfred Wuttig[1]; [1]Department of Materials Science and Engineering, University of Maryland, College Park, College Park, Maryland; [2]Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania.

Ferromagnetic shape memory alloys are a new class of active materials, which are technologically interesting due to the possibility of inducing large shape changes with an external applied magnetic field. Recently, premartensitic transitions in FSMAs were observed in FSMA systems such as FePd, $Ni_2MnGa$ and $Ni_2FeGa$, for example. In this paper, we focus on the premartensitic and martensitic transition of off-stochiometric $Ni_2MnGa$ of composition $Ni_{0.49}Mn_{0.23}Ga_{0.28}$ with a martensitic transition around $0^o$ C. The temperature dependence of the elastic constants was studied in the temperature range $140^o$ C>T>RT. Anomalous behavior in the austenite/s elastic constants and damping was observed indicating a premartensitic transition around $60^o$ C. XRD, neutron scattering and TEM studies revealed a structural condensation at this temperature. The neutron diffraction spectra, extended into the martensitic phase indicated a simple tetragonal martensite with a c/a ration of 1.3, the largest hitherto found.

**4:15 PM** U4.3
**Phase Stability and Epitaxial Growth of NiMnAl and NiMn(Ga,Al) Magnetic Shape Memory Thin Films Using MBE Technique.** R. Hassdorf[1], J. Feydt[1], S. Thienhaus[1], T. Buesgen[1], M. Boese[2] and M. Moske[1]; [1]Thin Adaptive Films, Research center caesar, Bonn, Germany; [2]Dept of Chemistry, Univ of Bonn, Bonn, Germany.

Ferromagnetic shape memory alloys such as FePd or FePt as well as the Heusler compounds $Ni_2MnGa$, $Co_2NiGa$ *etc* combine ferromagnetic with ferroelastic properties in a way that makes them promising candidates for magnetically controlled actuator applications. The unusual coexistence of both phenomena basically relies on a strong coupling of the magnetic and structural order parameters mediated via spin-lattice interaction. As a consequence, the field-induced reorientation of twin variants in the martensitic state gives rise to large macroscopic strains, quantitatively of up to ∼10% as observed for single-crystal $Ni_2MnGa$. In a theoretical approach using *ab initio* calculations, we established that in the system Ni-Mn-Al the magnetic ground state close to the Heusler stoichiometry is ferromagnetic ordered [1]. Moreover, as for the lattice dynamics of the system, the cubic $L2_1$ Heusler structure is shown to be unstable against shear displacement along the [110] direction which confirms the tendency to form modulated martensitic structures in this regime. Indeed, such structures, namely 2M and 14M, are found experimentally in coexistence within thin film samples grown by MBE technique, with a composition around $Ni_{50}Mn_{30}Al_{20}$. The structural transition from the disordered B2 to the fully ordered $L2_1$ phase is subject of further investigations. Hereto, NiMn(Ga,Al) alloy thin films were realized by co-deposition of Ni, Mn, and Al on top of single-crystal GaAs at elevated temperatures. As demonstrated from XPS and Auger depth profiling, Ga is incorporated into the film structure almost homogeneously due to its high diffusion mobility. An epitaxial relationship between film and substrate has been confirmed by RHEED. The compositional and microstructural aspects will be discussed. [1] T. Büsgen, J. Feydt, R. Hassdorf, S. Thienhaus, M. Boese, A. Zayak, P. Entel, and M. Moske, Phys. Rev. B 70, 014111 (2004).

**4:30 PM U4.4**
**Shape Memory Effect in Ni-Mn-Ga Thin Films.** Prita Pant and Joost J. Vlassak; Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts.

Single-crystal samples of ferromagnetic shape memory alloys based on the Ni-Mn-Ga Heusler system, have been shown to exhibit large magnetic field induced strains, making them promising materials for use in actuators. However, single crystals are both expensive and difficult to make. Polycrystalline samples (thin-films or bulk), by contrast, can be readily fabricated, but show poor shape-memory behavior due to the limited number of variants associated with the tetragonal martensite observed in these alloys. According to a recent model proposed by Bhattacharya and Shu, this problem can be overcome by using alloys that form martensite with lower crystal symmetry such as orthorhombic or monoclinic. O'Handley and co-workers recently demonstrated that orthorhombic martensite is formed over a limited composition range in the Ni-Mn-Ga ternary system. We have used the model by Bhattacharya and Shu to calculate the recoverable strain for various textures of polycrystalline Ni-Mn-Ga films. We compare these recoverable strains with experimental results obtained for Ni-Mn-Ga films grown by confocal sputter deposition.

**4:45 PM U4.5**
**An Application of Magnetic Shape Memory (MSM) Elements in a Hybrid Microactuator.** Matthias Hahn[1], Emmanouel Pagounis[2] and Hans H. Gatzen[1]; [1]Institute for Mikrotechnology, Garbsen, Germany; [2]AdaptaMat Ltd., Helsinki, Finland.

Introduction Designing a micro actuator, a compromise between the size, travel range and driving force has to be found. One approach to achieve rather great driving forces within a small motor envelop is to take advantage of a material's change in shape as actuator principle. A new class in this category is the magnetic shape memory (MSM) material. Exposed to an external magnetic field, the MSM material changes its length up to 10 %. This paper describes an approach to integrate MSM material into a thin film actuator. MSM Material Magnetically controlled shape memory (MSM) material is a new class of shape memory metals. A representative is Ni-Mn-Ga [1]. The MSM material's crystal structure occurs in "twin variants", i.e. internal areas with different magnetic and crystallographic orientations. When applying a magnetic field, the second type of twin area appears locally. These regions grow with increasing field strength, replacing the first type of twin variants successively. As a result, the length of the material probe increases. This effect is 100 times greater than the effect observed in piezoelectric materials. Experimental Setup For investigating a hybrid design using a discrete piece of MSM material integrated into a thin film micro actuator, a system consisting of two stators and two stripes of MSM material tied together by a connector was fabricated. The arrangement was chosen since in the given configuration the MSM element could only extend, but not contract. Each of the stators consists of nine double-layer thin film micro coils with a total of 50 windings [2]. A single coil's footprint is 2.6 mm x 4 mm. Three coils each are connected to form a coil system with a resistance of 35.4 ohm and each coil system may be excited separately. The stator's total length and width is 24.6 mm and 7.7 mm, respectively. To optimize the system's flux guiding capabilities, a 25 $\mu$m soft magnetic NiFe 81/19 (permalloy) layer was deposited beneath the coils. The dimensions of each MSM stripe are 24 mm x 2.5 mm x 0.5 mm. Each of the two MSM stripes is attached to opposite mounts, both MSM stripes are tied together in the middle by a connector which serves as a traveler yielding the actor motion. Results For initial tests, only one MSM stripe was mounted, allowing to observe the edge of a MSM stripe with an optical microscope containing a video camera. For each elongation test, the current was increased continuously, starting at 50 mA. At 190 mA a significant change in length of the MSM material could be observed. The MSM material's maximal elongation was 1.3 mm, corresponding to 5.47 % of the absolute length, which demonstrates the feasibility of building micro actuators using MSM material. References [1] J. Tellinen, I. Suorsa, A. Jääskeläinen, I. Aaltio, K. Ullakko, Conference Proceedings Actuator 2002, 566 (2002). [2] M. FÖhse, J. Edler, H.-D. StÖlting and H.H. Gatzen, Proceedings of IMECE2003, IMECE2003-41388 (2003).

SESSION U5: Poster Session
Monday Evening, November 28, 2005
8:00 PM
Exhibition Hall D (Hynes)

**U5.1**
**Lattice Effects in Multiferroic $R$Mn$_2$O$_5$ ($R$=Rare Earth).** Makoto Tachibana, Keita Akiyama, Hitoshi Kawaji and Tooru Atake; Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan.

Recently, there has been a resurgence of significant interest in multiferroic materials, where ferroelectricity and magnetism coexist in a single compound. The coupling between these two order parameters is of fundamental interest, and may open up new routes for novel devices. Among the various multiferroic materials reported recently, the rare-earth manganites show particularly interesting phenomena that are associated with the frustration of Mn moments. In perovskite $RMnO_3$ ($R$=rare earth), the Mn-O-Mn bond angle decreases substantially with the decreasing size of the rare-earth ion, and the next-nearest neighbor interaction Mn-O-O-Mn becomes progressively important [1]. As a result, the frustration of ferromagnetic nearest-neighbor and antiferromagnetic next-nearest-neighbor interactions within a $MnO_2$ plane leads to complex magnetic phase diagram with various spin structures as a function of temperature and $R$ [1]. For $R$=Tb and Dy, the modulated magnetic structure is accompanied by a magnetoelastically induced lattice modulation, and a spontaneous polarization that can be switched by the magnetic field appears below the magnetic transition [2]. Similar physical behavior is observed in $RMn_2O_5$ ($R$=rare earth), where competing magnetic interactions, modulated spin structures, and magnetostriction are also believed to play important roles in their extraordinary multiferroic behavior. Especially, $RMn_2O_5$ are notable in possessing extremely large magnetodielectric effect and highly reproducible electric polarization reversal by an applied magnetic field [3]. However, due to the number of different magnetic interactions associated with the complex structure, as well as the difficulty in producing high-quality samples, systematic understating of their behavior as a function of $R$ has not been achieved. In this study, high-quality single crystals of $RMn_2O_5$ ($R$=Sm, Eu, Gd, Tb, Dy, and Y) have been prepared by the flux method, and their structure as well as the sequence of antiferromagnetic, ferroelectric, and incommensurate magnetic transitions have been investigated. Structural refinement of high-resolution synchrotron x-ray powder diffraction data show definitive trend in the structure as a function of $R$, and the bond distances and angles that are relevant to the discussion of magnetic interactions have been determined with high precision. Heat capacity measurements clearly show monotonic change in the antiferromagnetic and ferroelectric transition temperatures as a function of $R$. Lattice effects on the competing magnetic interactions and their implications for the multiferroic behavior in $RMn_2O_5$ are discussed based on the present data. References [1] T. Kimura et al., Phys. Rev. B 68, 060403(R) (2003). [2] T. Kimura et al., Nature 426, 55 (2003); T. Goto et al., Phys. Rev. Lett. 92, 257201 (2004). [3] N. Hur, et al., Nature 429, 392 (2004); Phys. Rev. Lett. 93, 107207(2004).

**U5.2**
**Large Electrostrain by Reversible Domain Switching in Acceptor-doped BaTiO3.** Xiaobing Ren, Materials Physics Group, National Institute for Materials Science, Tsukuba, Ibaraki, Japan.

Ferroelectric crystals are characterized by their asymmetric or polar structures. In electric field, ions undergo asymmetric displacement and result in a small change in crystal dimension, which is proportional to the applied field. Such electric-field induced strain (or piezoelectricity) has found extensive applications in actuators and sensors. However, the effect is generally very small and thus limits its usefulness. Here I show that with a different mechanism, an aged BaTiO3 single crystal can generate a large recoverable non-linear strain of 0.75% at a low field of 200V/mm. At the same field this value is about 40 times higher than piezoelectric PZT ceramics and more than 10 times higher than the high strain PZN-PT single crystals. This giant electro-strain stems from an unusual reversible domain switching in which the restoring force is provided by a general symmetry-conforming property of point defects. This mechanism provides a general method to achieve large electro-strain effect in a wide range of ferroelectric systems and the effect may lead to novel applications in ultra large stroke and non-linear actuators. In this work, I shall present direct evidence for the reversible domain switching process in aged BaTiO3 crystals and show the same mechanism is applicable to polycrystalline ferroelectrics. X. Ren, Nature Materials, 2004; L.X. Zhang, W. Chen and Ren, APL 2004; L.X. Zhang and Ren, PRB 2005.

**U5.3**
**A New Ferroelasticity-Coupled Phase Revealed by Impedance Spectroscopy.** Se-Hun Kim[1], Kyu-Won Lee[1], Cheol-Eui Lee[1], K-S. Lee[2] and S-J. Noh[3]; [1]Physics and Institute for Nano Science, Korea University, Seoul, South Korea; [2]Computer-Aided Science, Inje University, Gimhae, South Korea; [3]Applied Physics, Dankook University, Seoul, South Korea.

The ferroelastic phase in hydrogen-bonded TlH2PO4 was investigated by means of the impedance spectroscopy. The temperature-dependent dielectric susceptibility exhibited a perfect agreement with that expected for a strain-polarization coupling. The high-temperature dielectric susceptibility revealed the corresponding Curie-Weiss temperature to be far above the antiferroelectric phase transition temperature, indicative of a novel mixed phase between the antiferroelectric and ferroelastic phase transitions. Besides, the distinct correlation times below and above the ferroelastic phase transition temperature manifested a coupling between the proton motions and the ferroelasticity in the system.

**U5.4**
**The Elastic Properties of $Gd_5(Si_2Ge_2)$ Studied by the Pulse-Echo Ultrasonic Technique.** Oleksiy Svitelskiy[1], Alexei Suslov[1], Thomas A. Lograsso[2], Deborah L. Schlagel[2], Vitalij K. Pecharsky[2] and Karl A. Gschneidner[2]; [1]National High Magnetic Field Laboratory, Tallahassee, Florida; [2]Ames Laboratory, Iowa State University, Ames, Iowa.

The ternary compound $Gd_5(Si_2Ge_2)$ is a representative of the family of novel Gd-based self-assembled nanolayered multiferroic materials, characterized by colossal magnetostriction (up to 10,000 ppm), substantial magnetoresistance (26%) and uniquely high values of the magnetocaloric effect ($\Delta T/\Delta B \cong 7$ K/2 T). These properties are determined by the first-order magnetic-martensitic structural phase transition that occurs near room temperature and can be triggered thermally, magnetically and/or mechanically. During the transformation, the structure changes from a ferromagnetic orthorhombic state at low temperature to a paramagnetic monoclinic state at high temperature. Small thermal hysteresis (the loop can be as narrow as 2 K) makes $Gd_5(Si_2Ge_2)$ and related alloys promising candidates for a new generation of energy efficient subroom temperature refrigeration based on the magnetocaloric effect. The colossal strain gives this alloy potential for future use in magnetic actuators. However, many of the fundamental properties of these materials have not been investigated yet. In this work, we use the ultrasonic pulse-echo technique to explore the longitudinal and transverse acoustic phonons in single crystals of $Gd_5(Si_2Ge_2)$. The crystals were grown by a tri-arc crystal pulling technique from a stoichiometric mixture of the components in an argon atmosphere under normal pressure using a tungsten rod as the seed material. In particular, for the first time, we have measured the room temperature velocities of all fundamental longitudinal and transverse sound waves, propagated along all three <100>-type and all three <110>-type directions of the crystal (a total 18 velocities). These measurements allowed us to derive the values of all thirteen independent elements of the elastic constant tensor in the high-temperature monoclinic phase (the so-called beta-phase). The excessive number of measured velocities allowed us to perform a self-consistency test of the results using the trace identities obtained from Christoffel equations, as described in [1]. According to this test, the mismatch of our results does not exceed 1.5%. Work at Ames Laboratory is supported by the Office of Basic Energy Sciences, Materials Sciences Division of the United States Department of Energy under contract No. W-7405-ENG-82. Ultrasonic experiments performed at the Tallahassee site of the NHMFL are sponsored by the In-House Research Program, the National Science Foundation under Cooperative Grant DMR - 0084173 and by the State of Florida. [1] A.Deepthy et al., Phys. Rev. B, 62, 8752 (2000).

**U5.5**
**Functional Properties of the CoFe2O4-PbTiO3 Multiferroic Nanostructures.** Jianhua Li[1,2], Virgil Provenzano[2], Igor Levin[2], Julia Slutsker[2], Peter K. Schenck[2] and Alexander L. Roytburd[1,2]; [1]Material Science & Engineering, Univeristy of Maryland, College Park, Maryland; [2]National Institute of Standard and Technology, Gaithersburg, Maryland.

Epitaxial multiferroic thin film nanostructures in the CoFe2O4-PbTiO3 system were grown using Pulsed Laser Deposition (PLD) method on SrTiO3 substrates. The magnetic, and ferroelectric properties of these nanostructures were investigated as a function of film composition and substrate orientation. These two parameters, which determined the morphologies and scale of the resulting nanostructures, were observed to have a strong effect on their functional properties. The measurements of in-plane and out-of-plane magnetization revealed dependence of magnetic anisotropy on the morphology, scale, and internal stresses. The piezoelectric coefficients, measured using a AFM-based set up also exhibited a pronounced dependence on the orientation of the films. The structure-properties relations in these nanostructures, as well as a magnetoelectric coupling, will be discussed. The results of this study indicate that the properties of multiferroic nanostructures in epitaxial films can be controlled by varying film composition, substrate orientation, and film thickness.

**U5.6**
**Investigating Voltage Induced Magnetic Switching in Multiferroic Materials.** Gavin Lawes[1], Tsuyoshi Kimura[2], A. Brooks Harris[3], Michel Kenzelmann[5], Collin Broholm[5,6], Taner Yildirim[6], Amnon Aharony[7], Ora Entin-Wohlman[7], Robert Cava[8] and Arthur Ramirez[2]; [1]Physics, Wayne State University, Detroit, Michigan; [2]Los Alamos National Laboratory, Los Alamos, New Mexico; [3]University of Pennsylvania, Philadelphia, Pennsylvania; [4]Lucent Technologies, Murray Hill, New Jersey; [5]Johns Hopkins University, Baltimore, Maryland; [6]NIST, Gaithersburg, Maryland; [7]Tel Aviv University, Tel Aviv, Israel; [8]Princeton University, Princeton, New Jersey.

Multiferroic materials, systems which combine long range magnetic and ferroelectric order, are expected to be important for developing novel magnetoelectric devices. Furthermore, investigating the interactions between magnetic and electronic properties in these systems will improve our understanding of how charge and spin can be coupled. In recent years, several new oxides have been identified which develop both magnetic and ferroelectric order at a single temperature. This is significant, because these systems exhibit very strong coupling between charge and spin degrees of freedom. It has been shown that in these materials, the ferroelectric polarization can be switched or even completely suppressed by applying an external magnetic field. However, in order to realize the full potential offered by these multiferroic materials, it is desirable that the magnetic properties be sensitive to an applied electric field. Ni_3V_2O_8 has recently been identified as an example of a multiferroic oxide in which the transition to a ferroelectrically ordered state occurs at the same temperature as incommensurate long range magnetic ordering. Moreover, a mean field model which successfully captures the essential character of the magnetoelectric coupling in this system predicts that this transition should be sensitive to an applied electric field. Recent results concerning the possibility of shifting the magnetic transition by applying an external voltage will be presented. Furthermore, the implications of these results to other multiferroic oxides will be discussed.

**U5.7**
**Improved Insulating Properties in La-doped $BiFeO_3$ Films Fabricated by Chemical Solution Deposition.**
Sushil Kumar Singh and Hiroshi Ishiwara; Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Yokohama, Japan.

Perovskite bismuth ferrite, $BiFeO_3$ (BFO) is a promising candidate for the high density ferroelectric random access memory (FeRAM) because of its large polarization value recently reported in thin films and low crystallization temperature. It belongs to the multiferroics family because it exhibits ferroelectric and antiferromagnetic properties simultaneously. It has ferroelectric properties with high Curie temperature (Tc) of about 1103 K and antiferroelectric behavior with Neel temperature (TN) of about 643 K. The high Curie temperature makes it a suitable candidate to utilize its ferroelectric properties at high temperature. One of the major problems of BFO thin films is low electrical resistivity, which affects the measurement of ferroelectric/ferromagnetic properties at room temperature (RT). The relatively high conductivity of BFO is known to be attributed to valence fluctuation of Fe ions (Fe3+ to Fe2+), creating oxygen vacancies for charge compensation. La-doped bismuth ferrite thin films were formed by chemical solutions deposition on $Pt/Ti/SiO_2/Si(100)$ structures. Through X-ray diffraction patterns, we distinguish the changes in the lattice structure of La-doped and undoped BiFeO3 films. It was found that the small changes in the growth parameters sensitively affected to the orientation of the BFO films as well as the electrical properties. The polycrystalline phase and also small fraction of secondary phase $Bi_2Fe_4O_9$were present in the film deposited on $Pt/Ti/SiO_2/Si(100)$ structures. The leakage current density in La-doped and undoped BiFeO3 films was found to decrease dramatically after optimizing process conditions of stoichemistric BFO and 5% La-doped chemical solution. For the first time, we measured current density in the range of $10^{-8}$A/cm$^2$in BFO thin films, which were 4 orders-of-magnitude lower than typical reported value in pure BiFeO3 films at room temperature, It was confirmed by X-ray photoelectron spectroscopy that the origin of low leakage current was due to the presence of $Fe^{3+}$valance state. In the lower electric field than 0.3 MV/cm, the current densities were lower in undoped BFO films and they were on the order of $10^{-8}$A/cm$^2$, but in the higher electric field than 0.3 MV/cm, La-doped films shows lower leakage current density. The obtained remanent polarization were around 80 $\mu$C/cm2 and 60 $\mu$C/cm2 for undoped and La-doped films measured at 80K. We observed coercive field higher than 0.4 MV/cm for both undoped and La-doped BiFeO3 films.

**U5.8**

**Ferromagnetic relaxor ferroelectrics: New concept for strong spin-lattice coupling.** Tae-Yeong Koo[1], Chan-Ho Yang[2], Bong-Yeol Lee[2] and Yoon-Hee Jeong[2]; [1]Beamline Research Division, Pohang Accelerator Laboratory, POSTECH, Pohang, South Korea; [2]Physics & Electron Spin Science Center, Pohang Univeristy of Science and Technology, Pohang, South Korea.

Various magnetic ferroelectrics have been discovered and studied ever since P. J. Curie proposed in 1894 the possibility of coupling between electric and magnetic degrees of freedom and their potential technological applications. However still an open question is that two ferroic phases from electric and magnetic origins have a big difference in their temperature range of occurrence and there is a rare possibility of having these two phase transitions at the same temperature region. Moreover multiferroic system in a true sense, simultaneous appearance of ferromagnetism and ferroelectricity, with a considerable coupling strength is extremely rare. Here we report the implementation of ferromagnetic relaxor ferroelectrics in a distorted perovskite manganite thin film as a feasible solution to this longstanding problem. A new control parameter, probing frequency through modifying the conventional ferroelectrics into relaxor ferroelectrics can be utilized for regulating the electromagnetic coupling strength effectively. The introduction of relaxation concept for tuning the overlap between two ferroic phases to optimize the coupling constants of their order parameters provides more opportunities for multi-functional device application of multiferroic systems.

**U5.9**

**Electric Field Induced Current Switching and Optically Modulated Conductivity of Charge Ordered $Bi_{0.4}Ca_{0.6}MnO_3$ Thin Films.** S. Chaudhuri and R. C. Budhani; Department of Physics, Indian Institute of Technology Kanpur, Kanpur, India.

Extensive research on transition metal oxides with perovskite related structures over the past few decades have unveiled a host of fascinating properties like High TC superconductivity, colossal magnetoresistance, and coexistence of two or more ferroic features. A promising member of this family of compounds is $Bi_{0.4}Ca_{0.6}MnO_3$ (BCMO). Single crystals of charge ordered BCMO show sub micrometric scale refractive index changes on exposure to visible laser radiation. This feature makes the material promising for creation of photonic bandgap structures [1]. Although bulk $Bi_{(1-x)}Ca_xMnO_3$ is a well studied system, to the best of our knowledge no work on thin films of BCMO has been published. Here we report synthesis of $Bi_{(1-x)}Ca_xMnO_3$ epitaxial films on (100) LaAlO3 substrates using the technique of pulsed laser deposition. We have investigated the crystallographic structure, magnetic ordering, linear and non-linear electrical transport and conductivity changes in these films on illumination with pulses of 355 nm radiation. For the sample deposited at $\sim 750\ ^0$C and $O_2$ base pressure of $\sim$ 300 mTorr, a clear maximum in magnetization and prominent step in resistivity observed at $\sim$ 275 K mark the Charge Ordering temperature ($T_{CO}$). We have measured non linear and linear electronic transport in channels of length varying from 1 mm to 50 mm. Below the charge ordering temperature, we observed Ohmic transport at low bias followed by sharp switching to a conducting state as the bias voltage is increased. The critical switching field goes down as the temperature is raised towards the $T_{CO}$. It is important to mention that while the I-V characteristics are hysteretic, the hysteresis is reproduced on repeated scans at a particular temperature. The photo-conductivity of these narrow channels has been measured using 355 nm pulses ($\sim$ 6 ns) of an Nd-YAG laser at several bias fields. When the system is biased close to but less than the switching field, the photon pulse drives the system to a conducting state. The conductivity transient has a width of $\sim$ 50 ns. Clearly, the channel works as a fast optical switch. Unlike the case of CW laser illumination results of BCMO crystals [1], irradiation with photons in the present case does not lead to a permanent change. Since the CO phase in BCMO is known to have a martensitic character [2], we believe the observed effects are manifestations of the field driven change in the topography of the martensitic phase. Acknowledgement: This research has been supported by a grant from the Indo-French Center for Promotion of Advanced Research. References: [1] I. I. Smolyaninov, et al., Phys. Rev. Lett. 87, 127204 (2001). [2] V. Podzorov, et al., Phys. Rev. B 64, 140406 (2001).

**U5.10**

**Small Signal Dielectric Nonlinearity in [001] and [111] Lead Zinc Niobate - Lead Titanate (4.5% & 8%) Single Crystals.** Bharadwaja S. N. Srowthi[1], Eunki Hong[1], Shujun Zhang[1], Susan Trolier-McKinstry[1] and Dragan Damjanovic[2]; [1]Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania; [2]Ceramic Laboratory, Materials Institute, Faculty of Engineering, Ecole Polytechnique Federale de Lausanne - EPFL, Lausanne, Switzerland.

The orientation dependence of nonlinear dielectric properties in poled and unpoled (1-x) lead zinc niobate - x. lead titanate (PZN-x.PT) (x=4.5% and 8%) single crystals were studied under small ac sinusoidal fields as a function of temperature. The appearance of a second order harmonic in the charge displacement density in ferroelectric relaxors along with the expected odd harmonic components was attributed to internal random fields. The measured temperature and frequency dependent for the second harmonic charge density is 1 to 2 orders smaller than the third harmonic component between 30-250 $^o$C in unpoled [001] and [111] oriented crystals and poled [001] crystals irrespective of composition. However, poled [111] oriented single crystals exhibited larger second harmonic polarization components than [001] PZN-PT single crystals. The nonlinear dielectric properties of unpoled and room temperature poled single crystals were analyzed considering to extract the effective internal random field strengths using the first, second and third harmonic dielectric polarization components.

**U5.11**

**MOCVD Growth of Manganese Oxide-Based Thin Films.** Ruey-Ven Wang[1,2], G.-R. Bai[1], D. D. Fong[1,2] and S. K. Streiffer[1,2]; [1]Materials Science Division, Argonne National Laboratory, Argonne, Illinois; [2]The Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois.

There has been growing interest in the rare-earth manganites ($ReMnO_3$, where Re = Y, Sc, Ho, Er, Tm, Yb, Lu) due to their unique multifunctionality arising from coexistence of ferroelectric and ferromagnetic properties. However, because of the complicated valence behavior of manganese, controlling the Mn oxidation state in such oxide thin films has been a challenging goal. Here we discuss our efforts at synthesizing manganite thin films using metal-organic chemical vapor deposition (MOCVD), a technique that has the potential for producing high-quality uniform oxide thin films over a large sample area. As a first step towards growing the ternary systems, we investigated the growth behavior of the constituent binary oxides. We have performed a systematic study on MOCVD of manganese oxide ($Mn_xO_y$) thin films at various deposition temperatures and oxygen partial pressures. The x-ray diffraction results show that growth on (0001)$Al_2O_3$ forms polycrystalline $Mn_3O_4$ or $Mn_2O_3$, depending on the oxygen partial pressure, while $Mn_3O_4$ grows epitaxially on (111) MgO regardless of the deposition conditions. Further analysis using x-ray photo-electron spectroscopy for identifying the oxidation states will also be presented. Based on our understanding of the conditions for $Mn_xO_y$ growth, we have successfully grown the three-component hexagonal manganites $YMnO_3$ and $ScMnO_3$. The relationships between the surface morphology, crystal orientations and the MOCVD process parameters of the manganite thin films will be discussed.

**U5.12**

**Magneto-electric Coupling in Ferromagnetic Cobalt/Ferroelectric Copolymer Ultrathin Multi-layer Films.** Marcus L. Natta, Mengjun Bai, A. Baruth, Kristin L. Kraemer, Stephen Ducharme and S. Adenwalla; University of Nebraska-Lincoln, Lincoln, Nebraska.

The synthesis of new classes of multiferroic materials has resulted in materials displaying much larger magnetoelectric effects than previously thought possible. Much work has been directed at the development and synthesis of materials that must undergo both magnetic and ferroelectric transitions, as well as showing strong coupling between the two[1]. An alternative approach that relaxes the competing demands and constraints on a single material may be found by using heterostructured materials with separate magnetic (or magnetostrictive) and ferroelectric components. [2] Here we report on the magnetoelectric coupling of a thin multi-layer film sandwich of ferromagnetic (Cobalt)/ferroelectric (PVDF/TrFE)/ ferromagnetic (Cobalt). The metallic layers were sputtered on glass substrates in UHV, with the top (130 Å) and bottom (300 Å) stripe electrodes oriented perpendicular to each other. The polymer ferroelectric films are deposited by the Langmuir-Blodgett technique and are 53 nm thick. The magnetic and ferroelectric layers of the samples have been carefully characterized using the Magnetic Optical Kerr Effect (MOKE) and the pyroelectric effect, respectively. The out-of-plane magnetic hysteresis loops of the cobalt are typical hard-axis loops. The PVDF/TrFE film is saturated and the pyroelectric response, which is proportional to the electrical polarization, measured as a function of perpendicular magnetic field. A large magneto-electric coupling is observed, with the pyroelectric response decreasing by $\sim$30% on application of a 2 kG field. Our observations indicate that polarization change occurs abruptly at the closing of the magnetic hysteresis loop and shows little hysteresis. Possible explanations for this unexpectedly large effect are discussed. [1] T. Kimura1*, T. Goto1, H. Shintani1, K. Ishizaka1, T. Arima2 & Y. Tokura1 Nature 426, 55 ( 2003) [2]P. Murugavel, P. Padhan, and W. Prellier, App. Phys. Lett. 85 , 4992,( 2004).

**U5.13**

**Obtainment of Pb2FeNbO6 Thin Films on Si (111) by RF Sputtering.** Oscar Raymond[1], Reynaldo Font[2,1], Jorge Portelles[2,1], Roberto Machorro[1], Javier Salinas[1] and Jesus M. Siqueiros[1]; [1]Centro de Ciencias de la Materia Condensada, UNAM, Ensenada, Baja California, Mexico; [2]Facultad de Fisica, Universidad de la Habana, La Habana, Ciudad de la Habana, Cuba.

In the development of novel devices and intelligent systems, single phase multifunctional materials such as Pb2FeNbO6 (PFN), where ferroelectric and magnetic order coexist, are very promissing and have great interest from the academic and technological point of view. Here, a report of the best conditions for the obtainment of PFN thin films on Si (111) by RF sputtering in an argon/oxygen atmosphere is presented. Two targets fabricated with powders of pure PFN and plus a ten percent weight of PbO were employed. The crystalline evolution of the samples and the parameter optimization for the deposit processes have been evaluated by X-Ray Diffraction, Scanning Electron Microscopy and Energy Dispersive Spectroscopy. A new cubic pyrochlore phase Pb2FeNbO6.5 (to be reported) was identified during different deposition runs under different conditions; its presence is associated to Pb deficiency in the growth process of the film. The substrate temperature and argon/oxygen/lead partial pressure effects in the pyrochlore and PFN phases formation are discussed using an Optical Field Spectroscopy technique applied in situ to the plasma produced during the sputtering processes. Acknowledgments: This work was partially supported by DGAPA-UNAM (Projects No. IN109305-3 and IN100903) and CONACYT No. 47714-F. The authors thank E. Aparicio, I. Gradilla, P. Casillas, J. Peralta, J. Camacho and J. Hernandez for their technical assistance.

**U5.14**

**Direct Measurement of Triaxial Strain Fields around BiFeO3 Multiferroic Thin Film Domains Using in-situ X-ray Microdiffraction.** Chung Wung Bark[1], Yang Mo Koo[1], Nobumichi Tamura[2], DongEun Lee[1], Hyun Myung Jang[1], Namsu Shin[3] and Kunpyo Hong[4]; [1]Department of Materials Science and Engineering, Pohang University of Science and Technology, Pohang, Kyungsangbuk-Do, South Korea; [2]Lawrence Berkeley National Laboratory, Berkely, California; [3]Pohang Accelerator Laboratory, Pohang, Kyungsangbuk-Do, South Korea; [4]Korea Atomic Energy Research Institute, Daejon, Daejon, South Korea.

There has been recent research interest in a number of prototypical magnetic ferroelectrics including BiMnO3, YMnO3, and etc. However, in any cases of the previously reported compounds, either the PE or the MH curve has been reported at the room temperature. Only BiFeO3 has both ferroelectricity and ferromagnetism simultaneously at room temperature. Recently Santos et al reported simultaneously the PE and MH curves of the thin film and bulk BiMnO3 synthesized under high pressure. And Ramesh et al reported enhancement of polarization and related properties in heteroepitaxially constrained thin films of the ferroelectromagnet, BiFeO3. The formation, movement and interaction of domains have largely effect on behavior of a multiferroic. Therefore, it is crucial that the micromechanics of domains and their effect on internal stresses in multiferroics be understood. In the case of epitaxial PbTiO3 and BaTiO3 films, in-plane compressive stresses lead enhancement of the spontaneous polarization. So, we expect that polarization enhancement of multiferroic material can be similarity understood as direct measurement of triaxial strain fields around BiFeO3 based multiferroic domains by using in-situ scanning X-ray microdiffraction. The materials used BiFeO3 thin film was epitaxial grown in the (001) on STO substrate. The synchrotron radiation source of beam line 7.3.3 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory, was used for the reflection Laue experiment. The samples are mounted on a 0.1?m resolution x-y piezo translation stage, and x-ray microbeam measurements are performed by translating along sample. At each location, in-situ white-beam Laue patterns are taken using a CCD x-ray detector with thermal loading in order to determine orientation and strain of individual grains. In previous MFM experiments, we examined that average domain size of BiFeO3 thin film was 1~2 micron. Due to its small scattering volume, micron sized focused x-ray beam which has high flux is need. We measured directly the local triaxial strain fields around domains in epitaxial grown BiFeO3 thin film with various temperatures. Specifically, strain maps in an interesting region, approximately 20 x 20 um wide, were obtained with 1 um resolution, revealing significant residual strains. Three-dimensional representation of the local distribution of the deviatoric component of the residual strain tensor along the x axis obtained from the two-dimensional scan of the top surface, could show following facts. Especially in-plane strain, at room temperature, strain map had shown that film had mixed domains. As increasing temperature, strain map looked like mono domain-like state. Additionally Strain along in-plane and out-of-plane, some arbitrary directions like xyz, was measured. In next stage, we will measure local strain with E field loading in BiFeO3 based thin film with electrode.

**U5.15**

**Perovskite Bismuth Ferrite Nanopowders Prepared by a Hydrothermal Method.** Chao Chen, Jinrong Cheng, Linjuan Che and Zhongyan Meng; Shanghai University, Sahnghai, China.

Bismuth ferrite (BiFeO3) has attracted much attention due to its simple perovskite structure and the simultaneous coexistence of ferroelectricity and antiferromagnetism. Materials exhibiting above-mentioned properties at room temperature are of much interest to people involved in developing smart materials. However, it is hard to avoid generating impurity phase using the conventional solid-state reaction. In this paper, a hydrothermal method was utilized to synthesize the phase pure BiFeO3 nanopowders. The precursor solution was batched to dissolve Bi(NO3)3-5H2O and Fe(NO3)3-9H2O into H2O solvents using the KOH as the mineralizer. The influence of synthesis conditions on the phase structure and particle size was systematically investigated. Our results indicated that the hydrothermal derived BiFeO3 powders crystallized into the single perovskite structure at 200 oC combining with an optimal chemical environment. The particle size of BiFeO3 powders lies in 10-30 nm according to the X-ray diffraction (XRD) and transmission electron microscopy (TEM) analysis. The differential scanning calorimeter (DSC) measurement reveals a Neel temperature of about 380 oC reflecting the magnetic transformation of BiFeO3 nano-powders.

**U5.16**

**Multiferroic property of epitaxially-grown $BiFe_{1-x}Mn_xO_3$ thin films.** Kouhei Takahashi and Masayoshi Tonouchi; Institute of Laser Engineering, Osaka University, Suita, Osaka, Japan.

A class of materials known as multiferroics has attracted much attention displaying simultaneous ferroelectricity and ferromagnetism in the same phase. Not only the multiferroics exhibit the potential of individual ferromagnets and ferroelectrics, one can expect a great deal of new phenomena arising from the interaction between the magnetic dipole and the electric dipole moment. Perovskite-type $BiFeO_3$ is virtually the most investigated multiferroics owing to its room-temperature multiferroism, i.e. ferroelectric below 1100 K and antiferromagnetic below 640 K. However, due to its antiferromagnetism, the spontaneous magnetization $M_S$ is very weak as well as its electro-magnetic coupling. It has been reported that partial substitution of the Fe ions to Mn ions in $Bi_{0.9}La_{0.1}FeO_3$ powders leads to the enhancement of $M_S$ at low temperature [1]. In the present work, we have fabricated epitaxial $BiFe_{1-x}Mn_xO_3$ thin films on $(LaAlO_3)_{0.3}(Sr_2AlTaO_6)_{0.7}$ substrates by pulsed laser deposition technique and examined the Mn substitution effects on the multiferroic property. Increase of the Mn content resulted in a significant enhancement of $M_S$ at room temperature, accompanied by a deterioration of its ferroelectricity. The optimized composition ratio of the $BiFe_{1-x}Mn_xO_3$ thin film with the best multiferroic property will be demonstrated at the meeting. [1] V. R. Palkar *etal.*, J. Appl. Phys. **93**, 4337 (2003).

**U5.17**

**Synthesis and Characterization of Multiferroic Composites based on Manganate-Type Perovskites.** Gongbao Song and Andrei L. Kholkin; Dept. of Ceramics and Glass Engineering / CICECO, University of Aveiro, Aveiro, Portugal.

Muliferroic composites consist of ferromagnetic (FM) or antiferromagnetic (AFM) components intimately mixed with a ferroelectric (FE) material. High magnetoelectric coupling can be achieved via, e. g., magnetostrictive strain that is expected to modulate the properties of a ferroelectric. The ability to provide this modulation may lead to a variety of future potential devices including magnetic-field-tunable microwave resonators or magnetically switchable ferroelectric memories [1]. The manganate-type perovskites compounds are long time known to crystallize in two structural phases: a cubic phase (or close to it) and a hexagonal phase. This gives a possibility of forming not only a solid solutions but immiscible phase-separated composites. While investigating the doping effect of small Lu ions to $(La,Sr)MnO_3$, Park et al. [2] discovered that a chemical immiscibility exists between FM-metallic $(La,Sr)MnO_3$ (LSMO) and FE $LuMnO_3$ (LMO). In this work, we investigated the effect of immiscibility in solid solutions LSMO and LCMO with LMO. The influence of the processing conditions on grain growth and solid solubility were studied in detail. X-ray, SEM and AFM were used to characterize the crystal structure and microstructure of sintered samples. Selected compositions were tested in terms of their magnetization, dielectric constant and ferroelectric properties at low temperatures. 1. J. Wang, J. B. Neaton, H. Zheng, V. Nagarjan, S. B. Ogale, B. Liu, D. Viehland, V. Vaithyahanadan, D. G. Schlom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wuttig, and R. Ramesh, Science 299, 1719 (2003). 2. S. Park, N. Nur, S. Guha, and S.-W. Cheong, Phys. Rev. Lett. 92, 167206 (2004).

**U5.18**

**Fabrication of Epitaxial SrTiO3/NiO/MgO Thin Film Multilayers For Future THz Negative Index Material.** Steven D. Kirby, Mark Polking and R. B. van Dover; Material Science and Engineering, Cornell University, Ithaca, New York.

Multiferroics have been studied extensively in recent years. The combination of magnetic properties and dielectric properties provides the possibilities of many novel applications. A material with a negative index of refraction might be engineered by combining a material with a negative permeability (and small permittivity) with a material with a negative permittivity (and small permeability). Materials with a magnetic resonance or dielectric resonance can exhibit negative susceptibilities over at least a small range of frequency above the resonance. We propose that antiferromagnetic NiO and dielectric SrTiO3 have resonances that can be tuned to match resulting in a negative index of refraction at approximately 1 THz. Lamellar thin films have been produced using off-axis reactive r.f. sputtering. It is desirable to have high quality epitaxial films to keep the magnetic and dielectric properties from degrading. To achieve this, the depositions are done at an elevated temperature on MgO substrate. Films of NiO/MgO, SrTiO3/MgO, and SrTiO3/NiO/MgO have been produced. Epitaxial quality has been characterized using x-ray diffraction and ion channeling, and electrical and magnetic measurements are underway. Addition of Co to the NiO and/or Ba to the SrTiO3 will be used to tune the resonance frequencies to coincidence. This will be done with composition spreads using off-axis sputtering.

**U5.19**

**Electronic Properties of BiFeO3 Thin Films and Interfaces.** Shawn Michael Walsh[1], Leonard J. Brillson[2,1,3], Fengyuan Yang[1], Min Gao[2], Tong Zhoa[4,5] and R. Ramesh[4,5]; [1]Department of Physics, The Ohio State University, Columbus, Ohio; [2]Department of Electrical & Computer Engineering, The Ohio State University, Columbus, Ohio; [3]Center for Material Research, The Ohio State University, Columbus, Ohio; [4]Department of Materials Science and Engineering, University of California, Berkeley, California; [5]Department of Physics, University of California, Berkeley, California.

Bismuth iron oxide, BFO, has emerged as a leading multiferroic material with combined ferroelectric and ferromagnetic features relevant to high frequency communications and information processing. The growth-dependent localized electronic states within these ultrathin films, at their domain walls, at their free surfaces, and at their metal interfaces can degrade ferroelectric, magnetic, electronic, and optical properties. Yet these properties have until now remained unexplored. Of particular interest are the "bulk" trap states due to native and morphological defects that can degrade frequency response and dielectric loss, but also the tradeoff between thickness-dependent phase formation and the "dead layers" at the outer few nanometers of these films. We have used depth-resolved cathodoluminescence spectroscopy (DRCLS) combined with X-ray diffraction, atomic force microscopy, and susceptibility measurements to measure and compare the band and defect properties of BFO films grown by off-axis plasma sputtering vs. pulsed laser deposition. DRCLS of high quality, sputtered BFO films tens to hundreds of nanometers thick on STO substrates reveal features due to defects and near-surface phase changes. We can dramatically reduce such defects in other metal oxides using remote oxygen plasmas. These results indicate that band gap and defect properties of multiferroic and ferroelectric ultrathin films can now be assessed and correlated with electronic and structural properties vs. growth conditions. We are extending this reduction of native defects by growth and processing techniques to garnets and dielectric composites with high permeability and low loss at 20 GHz for antennas and waveguides now being fabricated at Ohio State.

**U5.20**

**Preparation and Properties of thin Manganite-Titanate Composite-Films.** Kai Gehrke[1], Vasily Moshnyaga[1], Konrad Samwer[1], Joachim Hemberger[2], Andrei Pimenov[2] and Alois Loidl[2]; [1]I. Physikalisches Institut, Universitaet Goettingen, Goettingen, Germany; [2]Experimentalphysik V, Universitaet Augsburg, Augsburg, Germany.

Multiferroic materials with coexistence of ferromagnetism and ferroelectricity are in the focus of modern fundamental and applied research. The coupling of these properties is believed to be very strong in nanocomposite films, containing epitaxial co-grown and elastically coupled Manganite and Titanate phases. The strain induced by the piezo effect of the Titanate phase should alter the magnetization of the CMR-Manganite phase. Thin Manganite-Titanate films were grown on MgO and STO substrates by Metalorganic Aerosol Deposition (MAD) technique. Manganites like La-Mn-O, La-Ca-Mn-O, La-Ce-Mn-O and La-Ba-Mn-O where combined with ferroelectric Barium Titanate. XRD, SEM (EDX) and TEM (EELS) where used to study the microstructure of the samples. Measurements of the temperature-dependence of both conductivity and the magnetic moment unveil a MI- and ferro-paramagnetic phase transition of the Manganite-phase. Dielectric spectroscopy in a wide range of frequencies and temperatures is used to determine the ferroelectric properties also in applied magnetic fields.

**U5.21**

**Growth and Characterization of Multiferroic $Bi_{1-x}La_xFeO_3$ ($0 \leq x \leq 0.2$) Thin Films.** Suprem Ranjan Das[1], Pijush Bhattacharya[1], Ram Naresh Prasad Choudhary[1], Ram Saran Katiyar[1], P. Dutta[2], M. S. Seehra[2] and A. Manivannan[2]; [1]Department of Physics, University of Puerto Rico, San Juan, PR, Puerto Rico; [2]Department of Physics, West Virginia University, Morgantown, West Virginia.

Bismuth iron oxide ($BiFeO_3$) with rhombohedrally-distorted perovskite (R3c) is a novel member of multiferroic family ($BiMnO_3$, $YMnO_3$, $Pb_2(CoW)O_6$ etc) in which three order parameters (i.e., magnetization, spontaneous polarization, and strain) coexist in different magnitudes simultaneously, and hence is useful for multifunctional and spintronics devices. Recently $BiFeO_3$ (BFO) thin films have gained significant importance because of its potential possible applications for next generation multifunctional memory devices. However, the difficulty in synthesizing the film in single phase with high resistance is still debated. Several attempts have been made in different directions including processing technique and suitable substitution by other dopants to solve these problems. In this work, we have made an attempt to prepare $La^{3+}$-modified single-phase high resistant $BiFeO_3$ films with less perovskite distortion. Thin films of $Bi_{1-x}La_xFeO_3$ ($0 \leq x \leq 0.2$) were grown on $Pt/TiO_2/SiO_2/Si$ and $SrTiO_3$ (001) substrates at different temperature (450-650 0C) and $O_2$ pressure (10-200 mTorr) using pulsed laser deposition technique. The single-phase BFO thin films were obtained at 10 mTorr as confirmed by XRD and increase in $O_2$ pressure produced secondary phase. Temperature dependent micro-Raman spectroscopy was carried out to study the effect of La substitution on structural phase transition of BFO. Ferroelectric and ferromagnetic measurements were also carried out on La-modified BFO thin films. Magnetic measurements, M vs. H and M vs. T will be presented for BFO and for different La doping concentrations in the temperature range of 2 to 300 K. The improved multifunctional behavior due to La-substitution in BFO films will be explained on the basis of increased stability and microstructure of the compound.

**U5.22**

**Kinetic Pathways of Temperature- and Field-Dependent Structural Phase Transitions in PMN-PT and PZN-PT near Morphotropic Phase Boundaries.** Yu U. Wang, Materials Science and Engineering, Virginia Tech, Blacksburg, Virginia.

Thermodynamic analysis and kinetic modeling are developed to explain recent experimental observations of the structural phase transition sequences, phase stabilities, polarization rotations, crystallographic data, and ultrahigh electromechanical responses of PMN-PT and PZN-PT ferroelectric/ferroelastic perovskites. It is shown that the fascinating while puzzling phase behaviors in such multiferroic oxides can be understood from the perspectives of self-accommodation of spontaneous ferroelastic strain and ferroelectric polarization and self-assembling of ferroelastic and ferroelectric domains at nanometer length scale. Extensive experimental data supporting this theory are presented. Ongoing computer simulation effort to gain better quantitative insight into this problem is also discussed.

**U5.23**

**$BiCrO_3$ thin film epitaxy: a candidate for multiferroic properties.** Dae Ho Kim, Hans M. Christen, Ho Nyung Lee, Maria Varela and Douglas H. Lowndes; Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

$BiCrO_3$ (BCO) is expected to exhibit multiferroic properties with ferroelectric and antiferromagnetic ordering. In 1968, Sugawara and Iida synthesized perovskite BCO at high pressure (3.5 to 5.5 GPa) and reported a structural phase transition at 410 K. [1] The magnetic properties were revealed to be antiferromagnetic with a weak ferromagnetic moment below 123 K. However, the understanding of electric properties is rather incomplete compared to that of the magnetic properties, mainly because it is very difficult to synthesize single-phase material. Recently, Hill *etal.* suggested that Bi-induced displacements result in an antiferrodistortive or antiferroelectric distortion. [2] Niitaka *etal.* reported a dielectric anomaly around 440 K in polycrystalline BCO, which may imply a ferroelectric transition. For a clearer understanding of both the electric and the magnetic properties, it is essential to fabricate epitaxial BCO layer and to form thin film capacitors. We have successfully grown such BCO thin films by pulsed laser deposition on single crystalline $LaAlO_3$ substrate, using a polycrstalline target with excess Bi and a KrF excimer laser. Detailed analysis with x-ray diffraction (including $\theta - 2\theta$ scans, pole figures and reciprocal space maps) as well as scanning transmission electron microscope revealed an epitaxial alignment of the films' crystalline axes with those of the substrates. Systematic studies on various substrates with different crystalline orientations revealed that the epitaxial strain induced by a structurally similar crystalline substrate plays an important role in stabilizing the perovskite type structure of BCO. Finally, we present electric and magnetic properties, obtained with a ferroelectric tester and a superconducting quantum interference device, respectively. Research sponsored by the U.S. Department of Energy under contract DE-AC05-00OR22725 with the Oak Ridge National Laboratory, managed by UT-Battelle, LLC, as part of a BES NSET initiative on Nanoscale Cooperative Phenomena. [1] F. Sugawara and S. Iida, *J. Phys. Soc. Japan* **25** (1968) p. 1553. [2] N. A. Hill et al.,*J. Phys. Chem. B* **106** (2002) p. 3383. [3] S. Niitaka et al.,*Solid State Ionics* **172** (2004) p. 557.

### U5.24

**Synthesis and nanoscale characterization of multiferroic Ba(Ti,Zr)O3-YTiO3 thin films.** Carlos Edo Ostos[1,3], Maria Luisa Martinez-Sarrion[3], Eduardo Delgado Marulanda[2], Pedro Prieto Pulido[2] and Lourdes Mestres Vila[3]; [1]Chemistry, Universidad Nacional de Colombia, Bogota, Colombia; [2]Physics, Universidad del Valle, Cali, Colombia; [3]Inorganic Chemistry, Universidad de Barcelona, Barcelona, Spain.

A Ba(Ti,Zr)O3-YTiO3 perovskite-type homogeneous nanoparticles were synthetized by a novel soft chemistry method. The target with a specified stoichiometry was obtained by synthering at 1700 K for two hours under air atmosphere. The single perovskite phase was determined by X-ray diffraction and the stoichiometry was determined by X-ray fluorescence. The thin films were grown by RF-magnetron sputtering with oxygen high pressure on Pt/TiO2/SiO2/Si and SrTiO3.Nb substrates at 873 K. The structural characteristics were determined by XRD and AFM showing a epitaxial growing on (00l) direction and homogeneous surfaces respectively. The electric and magnetic properties were determined by P-E curves and magnetic susceptibility showing a preliminary multiferroic behavior.

### U5.25

**Diluted magnetic ferroelectric films.** Riad Nechache[1], Olivier Gautreau[1], Catalin Harnagea[1], Francois Normandin[2], Teodor Veres[2] and Alain Pignolet[1]; [1]INRS-EMT, INRS / Universite du Quebec, Varennes, Quebec, Canada; [2]Industrial Material Institute, National Research Council Canada, Boucherville, Quebec, Canada.

Multiferroic materials exhibiting simultaneously a spontaneous electric polarization and a spontaneous magnetization are interesting both from the fundamental point of view and for novel applications. For example, in data storage a linear coupling between the polarization and magnetization would allow data to be electrically written and magnetically read or magnetically written and electrically read, possibly solving some problems existing in conventional devices. Moreover, multiferroic materials also have high dielectric permittivity and high magnetic permeability and could therefore be of interest in many devices. However, quite few of these materials have been identified, and the coexistence of ferromagnetism and ferroelectricity is difficult to achieve essentially for structural reasons. Known magnetoelectrics, such as $BiFeO_3$, have been little investigated and thin films of these materials even less. Often one or several of the properties (ferroelectricity, ferromagnetism, insulating properties) are not robust enough at room temperature to be of use. In this work, we propose to study a range of diluted magnetic ferroelectrics obtained by doping PLD-grown ferroelectric oxides with magnetic transition metal ions, thus achieving a magnetic-ferroelectric composite material. First results on the structural, microstructural, ferroelectric and magnetic properties and their coupling will be presented, as well as how they depend on the type of transition element.

SESSION U6: Magnetoelectric Bulk Materials
Chair: Dwight Viehland
Tuesday Morning, November 29, 2005
Republic A (Sheraton)

### 8:00 AM *U6.1

**Multiferroic Composites.** Robert E. Newnham, Materials Research Laboratory, Pennsylvania State University, University Park, Pennsylvania.

Some of the concepts employed in composite multiferroics are reviewed in this talk, and illustrated with transducers, actuators, and sensors. The key ideas can be summarized by "Ten Commandments" as listed in the table. The number of conceivable composite structures boggles the mind, so the best strategy is to concentrate on important applications. A few examples based on thirty years experience will be presented.

### 8:30 AM *U6.2

**From Ferroelectricity to Magnetism: Towards an Understanding of Spin-Lattice Coupling in the Hexagonal Manganites from First Principles.** Craig J. Fennie and Karin M. Rabe; Physics and Astronomy, Rutgers University, Piscataway, New Jersey.

It has been established that to coexist with magnetism, the nature of the ferroelectricity in multiferroics cannot be that found in prototypical perovskite ferroelectrics (FEs) such as $BaTiO_3$. For example, first-principles calculations for the hexagonal manganites ($ReMnO_3$ for Re=Ho-Lu and Y), a class of multiferroic materials that are simultaneously FE and antiferromagnetic (AFM), have shown that the usual indicators of a FE instability (e.g. large Born effective charges) are absent. Polarization on the order of $5\mu$ C/cm$^2$ results primarily from the buckling of the Re-O planes, with no significant off-centering of the Mn cations as would be characteristic of a perovskite FE. As such, the hexagonal manganites have been referred to as "geometric ferroelectrics." Many physically interesting and potentially technologically relevant manifestations of spin-lattice coupling are observed in the hexagonal manganites, and it has been suggested that the ferroelectricity might somehow be responsible for the enhancement of this coupling. With continuing advances in theoretical algorithms and computational power it is now possible to use first-principles methods to study complex oxide systems such as the hexagonal manganites, and to obtain quantitative material-specific information about structural energetics, collinear and non-collinear magnetic order, and the spin-lattice coupling. In this talk I will discuss our first-principles study of $YMnO_3$, a natural first step in the analysis of the rich physics of the hexagonal manganites, as it allows us to separate out the additional effects of magnetism of the Re sublattice, not present for Re=Y. Calculations of the total energy and phonons reveal the mechanism by which the "geometric ferroelectricity" originates. By performing a systematic study of the energy surface around the prototypic PE phase, we find a single instability at the zone boundary which couples strongly to the polarization. This coupling is the mechanism that allows multiferroicity in this class of materials. Further, identifying this zone-boundary mode as the primary order parameter, we argue that there is an improper FE transition in the hexagonal manganites. This leads us to suggest that improper ferroelectric materials should be considered as templates for the design of new multiferroics. Calculations for a range of hypothetical collinear magnetic orderings allow us to draw inferences regarding the paramagnetic FE phase. Finally, we will report on our ongoing first-principles investigation of the coupling of the electronic structure and the FE-phase structural distortions to the noncollinear magnetic order experimentally observed below $T_N$.

### 9:00 AM U6.3

**Designed new ferroelectric, ferromagnetic materials -$Bi_2NiMnO_6$ and $Bi_2CoMnO_6$-.** Kazuhide Takata, Masaki Azuma, Yuichi Shimakawa and Mikio Takano; Institute for Chemical Research, Kyoto University, Uji, Japan.

Single-component multiferroic materials are rare in nature and most of them are antiferromagnets with small response to an external magnetic field. We have succeeded in synthesizing new ferrelectric, ferromagnetic materials $Bi_2MMnO_6$ ($M$ = Ni, Co). The crystal structures of these compounds are a heavily distorted double-perovskite with $M^{2+}$ and $Mn^{4+}$ ions ordered in a rock-salt configuration. The 6s$^2$ lone pair of $Bi^{3+}$ ions and strong covalent character of Bi-O bonds stabilize a noncentrosymmetric-distorted structure with $C2$ symmetry. The structure of $Bi_2NiMnO_6$ crystallizes in monoclinic unit cell of $a = 9.4646(4)\mathring{A}$, $b = 5.4230(2)\mathring{A}$, $c = 9.5431(4)\mathring{A}$, and $\beta = 107.823(2)^\circ$. $Bi_2CoMnO_6$ has also monoclinic unit cell of $a = 9.4886(8)\mathring{A}$, $b = 5.4445(0)\mathring{A}$, $c = 9.5676(1)\mathring{A}$, and $\beta = 107.605(0)^\circ$. This $C2$ symmetry of these compounds allow spontaneous polarization along the $b$ axis. On the other hand, ordering of two kinds of transition metal ions with and without $e_g$ electrons in a rock-salt configuration produces the magnetic exchange paths, -$M^{2+}$-O-$Mn^{4+}$-O-$M^{2+}$-, which lead to ferromagnetism, according to the Kanamori-Goodenough rules. Ferroelectric and ferromagnetic transition temperatures of $Bi_2NiMnO_6$ are at 465 K and 140 K, respectively. Ferroelectric transition temperature of $Bi_2CoMnO_6$ is over 600 K, while ferromagnetic transition temperature is 95 K. We will discuss the difference between the two compounds.

**9:15 AM U6.4**
**Suppression of the Tetragonal Distortion of PbTiO3 and Related Materials by Solid Solution.** Angel Arevalo[1], Susana Garcia-Martin[1] and Miguel Alario-Franco[2,1]; [1]Facultad de Quimica, Universidad Complutense, Madrid, Spain; [2]Facultad de Quimica, Madrid, Spain.

PbTiO3, a well known ferroelectric (FE) perovskite, shows, at room temperature, a large tetragonal distortion, space group P4mm. The presence of a lone 6s2 pair in Pb(II) and covalency effects in the Pb-O bond, as compared with isostructural BaTiO3, which is also tetragonal and, indeed, the archetype of perovskite ferroelectrics, are quoted among the causes of the large tetragonality (c/a = 1.06)(1,2). PbTiO3 becomes cubic, and the material paraelectric (PE) at a critical temperature of 763 K, while in the case of BaTiO3 the FE to PE transition takes place at the much lower Tc of 403 K. On the other hand, PbCrO3, a high pressure Cr(IV) perovskite, is cubic, space group Pm3m and a semiconducting antiferromagnet(3). We have observed that the replacement of Titanium by Chromium progressively destabilises the tetragonal structure of PbTiO3 and the corresponding solid solution Ti1-xCrxO3 becomes cubic for x around 0.4. In the present communication, the evolution with the composition of the structure, microstructure, electric and magnetic properties of this system will be presented and discussed. (1) R.E. Cohen, Nature, (1992), 358, 136 (2). Kuroiva et al, PRL (2001), 87, 217601 (3) B.L. Chamberland and C.W. Moeller, J. Solid State Chemistry (1972), 5, 39.

**9:30 AM U6.5**
**Magnetoelectric Coupling in $\epsilon$-$Fe_2O_3$ Nanoparticles.** Marti Gich[1], Natalia Bellido[2], Carlos Frontera[1], Anna Roig[1], Elies Molins[1], Charles Simon[2] and Josep Fontcuberta[1]; [1]ICMAB-CSIC, Bellaterra, Barcelona, Spain; [2]CRISMAT/ENSI-Caen, CNRS, Caen, Normandie, France.

Among the iron (III) oxides $\epsilon$-$Fe_2O_3$ is one of the rarest and less studied polymorphs due to the difficulty to synthesize it as a single-phase or as a large single crystal. Recently, pure $\epsilon$-$Fe_2O_3$ nanoparticles were prepared by sol-gel synthesis [1]. Interestingly, $\epsilon$-$Fe_2O_3$ has an orthorhombic non-centrosymmetric structure (space group $Pna2_1$) which is isomorphous to that of the piezoelectric, ferromagnetic and magnetoelectric $GaFeO_3$. At room temperature, $\epsilon$-$Fe_2O_3$ is a ferrimagnet with a large coercivity (20 kOe). More remarkably, upon cooling, a strong reduction of the coercivity and the squareness ratio, $M_R/M_S$ is observed at T $\sim$ 100 K which is ascribed to a magnetic transition involving changes in the structural parameters as revealed by neutron diffraction measurements. Here, we will report on the measurements of the dielectric permittivity as a function of temperature, frequency and magnetic field. Relative changes in dielectric constant as large as 30 % have been measured along the temperature range of the magnetic transition evidencing the existence of a magnetoelectric coupling in this material. Indeed, magnetic field dependent measurements at 100 K have revealed an increase of the permittivity by about 0.3 % in 6 T. A ferric oxide such as $\epsilon$-$Fe_2O_3$ would have significant advantages over the Bi or Mn-based biferroic materials, in terms of control of stroichiometry and current leakages due to its more stable chemical composition. Prospective advantages of $\epsilon$-$Fe_2O_3$as a multiferroic material will be discussed. [1] M. Popovici, M. Gich, D. Niznansky, A. Roig, C. Savii, Ll. Casas, E. Molins, K. Zaveta, C. Enache, J. Sort, S. de Brion, G. Chouteau and J. Nogues, Chem. Mater. 16, 5542 (2004).

**9:45 AM U6.6**
**Searching for novel single phase magnetoelectric materials: their magnetic properties.** Jian Yu and Mitsuru Itoh; Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan.

For magnetoelectric effect — induction of magnetization by an electric field or of polarization by a magnetic field, although it was predicted theoretically early in the 1894 and demonstrated in experiments twenty years later, this field develops very much slowly owing to very few systems of magnetic ferroelectrics in nature. [1,2]. In the recent five years, it comes into a revival accompanying the progresses of material sciences. Besides magnetic/ferroelectric composites, many single phase materials with linear magnetoelectric effect were also revealed[2]. In order to obtain excellent high temperature magnetoelectric effect, one of strategies is to make use of solid solution of magnetic and ferroelectric materials. Here, we reported several systems of $BiFeO_3$($LaFeO_3$,$LaCrO_3$)-$Bi_4Ti_3O_{12}$, $Bi_5Fe_2Ti_2O_{15}$, $Bi_3FeTiO_9$, $BiCrO_3$ and $Bi_2FeCrO_6$, which were prepared with various methods, including conventional solid state reaction, sol-gel, coprecipitation, and hydrothermal. X-ray diffraction and magnetic measurements indicated that their homogeneous single phases were obtained successfully. Except the case of $Bi_2FeCrO_6$, they exhibit paramagnetic behavior, and are not good candidates for magnetoelectric materials as expected previously. [3,4,5]. For $Bi_2FeCrO_6$, its paramagnetic Curie temperature was extrapolated as $\sim$220K, and a spin glass state was found below 20K. Our preliminary experiments showed that it is also different from recent theoretical predictions[6,7], which can be attributed to different lattice structure. [1] N. A. Hill, J. Phys. Chem. B 104, 6694 (2000). [2] M. Fiebig, J. Phys. D: Appl. Phys. 38, R123 (2005). [3] R. S. Singh, T. Bhimasankaram, G. S. Kumar, and S. V. Suryanarayana, Solid State Commun. 91, 567 (1994). [4] A. R. James, G. S. Kumar, M. Kumar, S. V. Suryanarayana, and T. Bhimasankaram, Modern Phys. Lett. B 11, 633 (1997). [5] S. T. Zhang, Y. F. Chen, Z. G. Liu, N. B. Ming, J. Wang, and G. X. Cheng, J. Appl. Phys. 97, 104106 (2005). [6] C. Ederer and N. A. Spaldin, Phys. Rev. B 71, 060401 (2005). [7] P. Baettig and N. A. Spaldin, Appl. Phys. Lett. 86, 012505 (2005).

SESSION U7: Multiferroic Nanostructures
Chair: Florin Zavaliche
Tuesday Morning, November 29, 2005
Republic A (Sheraton)

**10:30 AM *U7.1**
**Electric Field-Induced Magnetization Reversal in Epitaxial Multiferroic Nanostructures.** Florin Zavaliche[1,2], H. Zheng[1,2], L. Mohaddes-Ardabili[2], S. Y. Yang[2], Q. Zhan[1,2], P. Shafer[2], S. Crane[2], L. Q. Chen[3], D. G. Schlom[3] and R. Ramesh[1,2]; [1]Department of Materials Science and Engineering, University of California, Berkeley, California; [2]Department of Physics, University of California, Berkeley, California; [3]Department of Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania.

Direct evidence of room temperature magnetization switching induced by an electric field in a fully epitaxial ferroelectric $BiFeO_3$ - ferrimagnetic $CoFe_2O_4$ columnar nanostructures is presented. The coupled piezoelectric-magnetic switching was investigated by using a combination of piezoelectric force microscopy and magnetic force microscopy techniques. Quantitative analyses performed on Pt/$(BiFeO_3)_{0.65}(CoFe_2O_4)_{0.35}$/$SrRuO_3$ test structures give a perpendicular magnetoelectric susceptibility of $\sim 1.0\times10^{-2}$ G cm/V. We explain the observed effect by the onset of a strong elastic coupling between the two ferroic constituents as the result of the three dimensional heteroepitaxy. These nanocomposites with columnar morphology open exciting room-temperature applications for microwave filters, energy conversion, and as a recording medium in probe-based storage devices. This work has been supported in part by the U. of Maryland NSF-MRSEC under grant #DMR 00-80008, by the ONR under a MURI program, and by SRC under a MARCO program.

**11:00 AM U7.2**
**Thin-Film Multiferroic $BiFeO_3$-$NiFe_2O_4$ Nanostructures.** Steven P. Crane[1], H. Zheng[1], F. Zavaliche[1], M. de la Paz[1], Q. Zhan[1], L. Mohaddes-Aribili[1], P. Shafer[1] and R. Ramesh[1,2]; [1]Department of Materials Science and Engineering, University of California-Berkeley, Berkeley, California; [2]Department of Physics, University of California-Berkeley, Berkeley, California.

Multiferroic $BiFeO_3$-$NiFe_2O_4$ thin films are interesting because of the magnetically soft $NiFe_2O_4$, which is critical to creating an electrically and magnetically tunable material based on heteroepitaxial strain coupling between the two phases. We have created nanostructures composed of ferrimagnetic $NiFe_2O_4$ nanopillars embedded in a ferroelectric $BiFeO_3$ matrix. The crystal structure and morphology were probed via x-ray diffraction, cross-sectional and plan-view transmission electron microscopy, and atomic force microscopy. We found that $BiFeO_3$-$NiFe_2O_4$ nanostructures form above a diffusion threshold temperature, and the lateral size of the $NiFe_2O_4$ pillars increases as the deposition temperature increases. The magnetic and ferroelectric properties were studied using magnetic force microscopy, vibrating sample magnetometry, and piezoforce microscopy. The films provide well-behaved ferrimagnetic and ferroelectric behavior in the $NiFe_2O_4$ and $BiFeO_3$ phases, respectively. S.P. Crane is funded by the National Science Foundation through the graduate research fellowship program. This project is funded by an ONR MURI program. The authors acknowledge the support of the staff and facilities at the National Center for Electron Microscopy at Lawrence-Berkeley National Laboratory.

**11:15 AM U7.3**
**Localized Magneto−Electric Measurements of $BaTiO_3$−$CoFe_2O_4$ Nano Composites with a Microwave Microscope.** Yi Qi[1], Steven M. Anlage[2], Haimei Zheng[3], Florin Zavaliche[3] and Ramamoorthy Ramesh[3]; [1]Materials, University of Maryland, College Park, College Park, Maryland; [2]Physics, University of Maryland, College Park, Maryland; [3]Materials Science and Engineering, University of California, Berkeley, California.

We report on local microwave measurements of the magneto-electric (ME) coefficient of ferroelectro-magnetic thin film samples using a novel microwave microscope technique. $BaTiO_3-CoFe_2O_4$ (BTO−CFO) and $BiFeO_3-CoFe_2O_4$(BFO−CFO) nano-composite samples were investigated both with ac electric field and ac magnetic field. The magnetic field produces a non-linear dielectric change in the sample through the ME effect which is equivalent to that produced by an electric field. By measuring the non−linearity of the effective dielectric constant of the material under the electric field and magnetic field, we calculated the ME coefficient. Images of the local ME coefficient can also be obtained. A ME image scanned with micron-scale resolution shows information about ME dependence on composition and nanostructure. The temperature dependence of the ME signal is also measured. The results are compared to other, more macroscopic, measurements of the ME effect.

**11:30 AM U7.4**
**Characterization Of The Multiphase Formation In Bi-Fe-O And Bi-Cr-O Thin Films Grown By Pulsed Laser Deposition.**
Sung Hwan Lim, Makoto Murakami, Shigehiro Fujino, Manfred Wuttig, Ichiro Takeuchi and Lourdes G. Salamanca-Riba; University of Maryland, College Park, Maryland.

Bi based magnetic oxide systems like, Bi-Fe-O and Bi-Cr-O, are being investigated by many research laboratories because of their multiferroic properties. In the bulk, both of these systems form in several phases consisting of different structure and composition which in turn give rise to different electrical and magnetic properties. There are few studies on the control of the desired phase in films of Bi-based magnetic oxides which frequently consist of more than one phase. We report on a systematic study of the multiphase formation in thin film growth of the Bi-Fe-O and Bi-Cr-O systems as a function of deposition temperature and oxygen partial pressure. The Bi-Fe-O and Bi-Cr-O thin films were fabricated on $SrTiO_3$(001) and $NdGaO_3$ (110) substrates by pulsed laser deposition. The oxygen pressure and the substrate temperature during the deposition were varied in the ranges of 2.5 x $10^{-5}$ - 0.1 Torr and 550 - 750°C, respectively. The structural properties of the films were studied using transmission electron microscopy, x-ray diffraction and energy dispersive x-ray spectroscopy. In this study, we found that the dominant phase found in the Bi-based films can be changed from pure $BiFeO_3$ and $BiCrO_3$, which are both ferroelectric at room temperature to a 2nd phase which is ferromagnetic and similar to $Bi_3Fe_5O_{12}$ by controlling the oxygen partial pressure during deposition. Our TEM results show that at low oxygen partial pressures the second phase forms as domains over a layer of $BiFeO_3$. The density and size of these domains increases with decreasing oxygen partial pressure while the thickness of the underlying $BiFeO_3$ phase decreases. This work was supported by NSF MRSEC under account No. DMR-00-80008.

**11:45 AM U7.5**
**Tailoring Epitaxial Multiferroic Self-Assembled Nanostructures: CoFe2O4-PbTiO3 Case Study.**
Jianhua Li[1,2], Igor Levin[2], Peter K. Schenck[2], Virgil Provenzano[2] and Alexander Roytburd[1]; [1]Materials Science and Engineering, University of Maryland, College Park, Maryland; [2]NIST, Gaithersburg, Maryland.

Multiferroic materials which display a co-existence of ferroelectric and ferromagnetic responses attract interest because of their potential for several novel device applications. Self-assembled epitaxial heterophase nanostructures consisting of ferromagnetic (FM) and ferroelectric (FE) phases represent one promising class of multiferroics. The strong magnetoelectric coupling obtained in such self-assembled nanostructures is attributed to highly efficient elastic interactions yielding a strong magnetic response to an electric field (or vice versa) via magnetostriction and piezoelectric effect. The same elastic interactions also control the self-assembling of the component phases so that the architecture of the nanostructures can be predicted and controlled by manipulating the stress state in the film. In this work, we studied the effect of stress conditions on the morphologies of epitaxial, self-assembled nanostructures in PbTiO3-CoFe2O4 thin films. The two-phase nanostructures were grown on single crystal SrTiO3 having (001), (110), and (111) orientations. Our results demonstrate that regardless of substrate orientation, the nanostructures exhibited a 3-D epitaxy and consisted of vertical columns of either ferromagnetic CoFe2O4 dispersed in the ferroelectric PbTiO3 matrix, or vice versa. However, the morphologies of these columns, and their spatial arrangements, exhibited a marked dependence on the substrate orientation. The differences in nanostructure morphologies were concluded to arise from elastic anisotropy of the film. The evolution of internal stresses, developed in the nanostructures upon the cubic-tetragonal transition in PbTiO3, was analyzed using high-temperature X-ray diffraction, and a strong elastic coupling was confirmed. The relations between the nanostructure morphologies, internal stresses, and functional properties will be discussed.

## SESSION U8: Magnetoelectric Thin Films I
Chair: Ichiro Takeuchi
Tuesday Afternoon, November 29, 2005
Republic A (Sheraton)

**1:30 PM *U8.1**
**Magnetoelectric effect and toroidal ordering in multiferroic manganites.**
Manfred Fiebig, Max-Born Institute, 12489 Berlin, Berlin, Germany.

Recently, an enormous interest in multiferroics - compounds which unite two or more different forms of primary ferroic ordering in one phase - is observed. From a practical point of view multiferroics allow one to build devices with multiple or novel functionalities. On the other hand the interplay of different forms of (anti-) ferroic ordering is a rich source for exploring the fundamental science of phase control. Because of the complexity of the interaction in multiply ordered compounds the correlations between the coexisting forms of ordering are in general not well understood and a unifying concept for ferroicity has yet to be developed. In my talk I will discuss various manifestations of multiferroic correlations in the system of hexagonal $RMnO_3$ (R = Sc, Y, In, Ho-Lu). Based on this I will suggest a classification of the different manifestations of ferroic ordering. (i) With ferroelectricity, antiferromagnetic $Mn^{3+}$ ordering, and ferro- or antiferromagnetic ordering at the two $R^{3+}$ sites hexagonal $RMnO_3$ possesses up to four ordered sublattices. It will be shown how *microscopic* magnetoelectric correlations between the sublattices in combination with multiple frustration lead to gigantic manifestations of *macroscopic* magnetoelectric behavior. This leads to magnetic phase control by external electric or magnetic fields or temperature. (ii) Manifestations of *antimagnetoelectric* behavior in the $RMnO_3$ compounds in the form of microscopic magnetoelectric correlations which compensate each other on the macroscopic scale will be discussed. (iii) It will be shown that in addition to ferromagnetism, ferroelectricity, and ferroelasticity as the three widely known forms of primary ferroic ordering ferrotoroidicity - formation of a spontaneous magnetic vortex - must be included as the fourth variety since it puts all ferroic forms of ordering into a particularly simple and fundamental relationship. Toroidic domains can exist and have already been observed in multiferroic $YMnO_3$, but were not recognized as such. However, after introducing toroidic domains as physically independent states the former observation becomes physically sound.

**2:00 PM U8.2**
**Comparison of Magnetoelectric Composites Consisting of Different Magnetostrictive and Piezoelectric Materials.**
Andreas Gerber[1], Simon Stein[1], Eckhard Quandt[1], Liyang Dai[2] and Manfred Wuttig[2]; [1]caesar, Bonn, Germany; [2]Department of Materials Science and Engineering, University of Maryland, College Park, Maryland.

The magnetoelectric (ME) effect is a polarization P response to a magnetic field H (MEH effect) or, vice versa, a magnetization M response to an electric field E (MEE effect). Its occurrence was first observed in BiFeO3 single crystals [1]. A composite ME effect can be achieved as a product property of magnetostriction and piezoelectricity. This was demonstrated in ferrite systems composed of Ni1-xZnxFe2O4/PZT [2] as well as Terfenol-D/PMN-PT bulk composites [3]. The (ME) effect can be used as a magnetic field sensor for small ac-fields. A quantitative measure of the MEH effect, which will be considered in this presentation, is the voltage coefficient . Measurements were carried out by applying superimposed magnetic DC and AC fields generated by a solenoid and Helmholtz coils, respectively. The generated ME voltage across the composite was picked up by a lock-in amplifier tuned to a phase, eliminating induced voltages in the leads to the sample. Thus, only the ME signal in phase with the magnetic AC field was measured. This presentation focuses on approaches to miniaturize these ME composites by using thin films or multilayers [4], melt-spinning ribbons or polymer piezoelectrics. The results will be discussed in view of data obtained with Terfenol-D/PMN-PT composites. Furthermore, the results will be compared in the framework of existing theories. [1] G.A. Smolenskii, V.M. Yudin, E.S. Sher, and Y.E. Stolypin, Sov. Phys. JETP 16 (1963), 622. [2] G. Srinivasan, C.P. DeVreugd, C.S. Flattery, V.M. Laletsin, and N. Paddubnaya, Appl. Phys. Lett. 85 (2004), 2550. [3] S.X. Dong, J.F. Li, and D. Viehland, IEEE Trans. Ultrason. Ferr. 51 (2004), 794. [4] S. Stein, M. Wuttig, D. Viehland, and E. Quandt, J. Appl. Phys. 97, (2005)

**2:15 PM U8.3**
**Multiferroic $Pb(Zr,Ti)O_3/CoFe_2O_4$ Multilayer on Pt-silica substrate using pulsed laser deposition.**
Nora P. Ortega[1], Subhasis B. Majumder[1], Pijush Bhattacharya[1], Ram S. Katiyar[1], P. Dutta[2], M. S. Seehra[2] and A. Manivannan[2]; [1]Physics, University of PUerto Rico, San Juan, Puerto Rico; [2]Physics, West Virginia

University, Morgantown, West Virginia.

Magnetoelectric (ME) materials are one class of multiferroics in which change in magnetization is induced by an electric field and change in electric polarization is induced by an applied magnetic field. There are a few materials have been found to exhibit this kind of properties. Recently, synthesis of ME materials that has been gradually drawn towards the fabrication of composite thin film. The composite thin film heterostructures having ME properties are the potential candidate for microsensors, micro electro mechanical systems (MEMS), and high-density information storage applications. In this work, we have fabricated $Pb(Zr,Ti)O_3/CoFe_2O_4$ (PZT/CFO) multilayer thin films using pulsed laser deposition on $Pt/TiO_2/SiO_2/Si$ substrate. Two different ceramic pellets of CFO and PZT prepared by conventional ceramic route were used as targets. The PZT-CFO multilayer films were deposited at 400°C and post annealed at 650 to 750°C using rapid thermal annealing (RTA) for 150 to 300 seconds for crystallization. X-ray diffraction and scanning electron microscopy reveal that the perovskite (PZT) and the spinel CFO grown in two separated phases. The Raman spectra of multilayer films also showed separated peaks for PZT and CFO. The dielectric constant of PZT-CFO multilayer was found to be ~ 350 (100 kHz) lower compared to PZT dielectric constant ~1000 (100 kHz). The loss tangent of PZT-CFO film (0.1 @100 kHz) was also increased compared to PZT value (0.04 @ 100 kHz). The remanent polarization ($P_r$) of the multilayer film was found to be 30 $\mu C/cm^2$, which was lower a PZT (40 $\mu C/cm^2$) thin film and the coercive field ($E_C$) for PZT-CFO film was 60 kV/cm, which was higher than in PZT (30 kV/cm). The detailed magnetic measurements M vs H of multilayers will be carried out.

SESSION U9: Magnetoelectric Thin Films II
Chair: Teruaki Takeuchi
Tuesday Afternoon, November 29, 2005
Republic A (Sheraton)

**3:30 PM U9.1**
**Phase Field Modeling of Self-Assembling Multiferroic Films.**
Julia Slutsker[1] and Andrei Artemev[2]; [1]MSEL, NIST, Gaithersburg, Maryland; [2]Department of Mechanical and Aerospace Engineering, Carleton University, Ottawa, Ontario, Canada.

Multiferroic films consisting of self-assembling ferroelectric and ferromagnetic phases are perspective material for the number of applications because of a large magneto-electric coupling due to enhanced elastic interactions between phases and the substrate. The elastic interactions provide one of the mechanisms of controlling the electric and magnetic responses in such kind of nanostructures and they determine also the nanostructure architecture of multiferroic films. The general phase field model of formation of multiphase nanostuctures in multiferroic films taking into account elastic interactions will be presented. This model is applied to two particular cases (1) formation of multiphase nanostructures with coherent interphase interfaces and (2) formation of nanostructures with relaxed interfaces. The comparison of results of two approaches as well as relevancy of different phase field models to experimental results on morphology of self-assembling multiferroic films will be discussed. The correlation of nanostructure architectures with electric, magnetic as well as with electro-magnetic coupling of multiferroic films will be explored.

**3:45 PM U9.2**
**Interfacial Structure at a Truly Atomic Scale of a New Multiferroic Epitaxial $BiFeO_3$-$NiFe_2O_4$ Film.**
Qian Zhan[1], R. Yu[2], S. Crane[1], H. Zheng[1], C. Kisielowski[3] and R. Ramesh[1]; [1]Department of Materials Science and Engineering and Department of Physics, University of California, Berkeley, Berkeley, California; [2]Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California; [3]National Center for Electron Microscopy, Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California.

Magnetoelectric (ME) materials, in which spontaneous ferromagnetic and ferroelectric orderings coexist and are coupled together, attract considerable research interests due to their fascinated physical properties and potential applications. Recently, we developed a new interesting ME system: three dimensional heteroepitaxial $BiFeO_3$-$NiFe_2O_4$ composite thin film, in which $BiFeO_3$ (BFO) is ferroelectric with large piezoelectricity and $NiFe_2O_4$ (NFO) is ferrimagnetic. The interface between $BiFeO_3$ and $NiFe_2O_4$ is of great importance to understand the interplay among structure, elasticity, electricity and magnetism. Due to the large difference between the involving crystal structures and the large lattice misfit, the structure of the interface is highly complicated. Here we use the electron exit wave reconstruction method to investigate quantitatively the interfacial structure at a truly atomic scale. The films were grown by pulsed laser deposition (PLD) on (001)-$SrTiO_3$ single crystal substrates upon which a ~55 nm thick $SrRuO_3$ bottom electrode was grown by PLD. Microstructural investigations have been carried out using transmission electron microscopes (Philips CM300 FEG, FEI Tecnai F20 STEM and JEOL 3010). The results show that BFO and NFO phases spontaneously separated and self-assembled during heteroepitaxial growth. They exhibit cube-on-cube relationships on (001)-oriented STO substrate. Rectangular NFO nanopillars were distributed homogeneously in the BFO matrix with (110) as their interface. The exit wave was reconstructed from focal series of the BFO-NFO interface. It reveals that BiFeO layer in BFO matrix bonds to the (Ni,Fe)O layer in NFO, giving the atomic configuration of the interface: bulk-O-BiFeO-(Ni,Fe)O-Fe(Ni,Fe)O-bulk. By measuring quantitatively the atomic positions near the interface, the strain distribution is obtained, which provides critical information to understand the mechanical-magnetic-electric coupling. The interplay between the structure and films growth is also discussed.

**4:00 PM U9.3**
**Self-assembled Multiferroic Oxide Nanostructures.**
Haimei Zheng, F. Zavaliche, L. Mohaddes-Ardabili, Q. Zhan, S. P. Crane, L. W. Martin and R. Ramesh; Physics and Materials Sci Eng, University of California, Berkeley, Berkeley, California.

Self-assembled multiferroic BiFeO3-CoFe2O4 nanostructures have been grown by pulsed laser deposition. These nanostructures show both ferroelectric and ferrimagnetic properties corresponding to the two components in the system. In this paper, we report results of systematic studies of the deposition temperature on the nanostructure morphology and its magnetic/ferroelectric properties. The coupling between the two order parameters has also been demonstrated using both microscopic measurement by MFM and macroscopic SQUID magnetometry. The effect of lateral patterning on the nanostructure assembly has also been investigated. This project is funded by an ONR MURI program under contract No. E-21-6RU-G4.

**4:15 PM U9.4**
**Microstructure and magnetic property control in bismuth iron oxide thin films.**
Shigehiro Fujino[1], Makoto Murakami[1], Sung Hwan Lim[1], Ichiro Takeuchi[1], Manfred Wuttig[1], Lourdes G. Salamka-Riba[1], Samuel E. Lofland[2], Tetsuya Hasegawa[4] and Hidetaka Sugaya[3]; [1]Materials Science and Engineering, University of Maryland, college park, Maryland; [2]Physics and Astronomy, Rowan University, Glassboro, New Jersey; [3]Frontier Collaborative Research Center, Tokyo Institute of Technology, Tokyo, Japan; [4]Chemistry, University of Tokyo, Tokyo, Japan.

$BiFeO_3$ and its room temperature properties have attracted much attention because of its multiferroic properties. There have been a number of reports on $BiFeO_3$ thin films, but their magnetic properties have not been unambiguously established. In this study, we report on the controlled multiphase thin film growth of the Bi-Fe-O system. We have fabricated the Bi-Fe-O thin films on $SrTiO_3$ (001) substrates by pulsed laser deposition. The oxygen pressure and the substrate temperature during the deposition were varied in the ranges from 2.5 x $10^{-5}$ to 0.1 Torr and 550-750 °C, respectively. We found that by varying the deposition oxygen pressure, the dominant phase found in the film can be changed continuously from $BiFeO_3$ which is ferroelectric to $Bi_3Fe_5O_{12}$ which is ferromagnetic. The structural properties of the films were studied using x-ray diffraction and transmission electron microscopy. Magnetization of the films increases as the deposition oxygen pressure decreases and is attributed to the $Bi_3Fe_5O_{12}$phase. We found that epitaxial multiferroic nanocomposite films consisting of $BiFeO_3$ and $Bi_3Fe_5O_{12}$ phases can be formed by controlling the deposition pressure. To systematically study the previously reported stress enhanced magnetization effect in $BiFeO_3$ films, we have made a thickness gradient $BiFeO_3$ film. A continuous change in the out-of-plane lattice constant was observed as the thickness of the film was decreased from 5 to 300 nm, but no enhancement of ferromagnetism was observed. This work was supported by NSF MRSEC under account No. DMR-00-80008.

**4:30 PM U9.5**
**Synthesis and characterization of multiferroic $Bi(Fe,Cr,Mn)O_3$ thin films.**
Makoto Murakami[1], Shigehiro Fujino[1], Sung Hwan Lim[1], Lourdes G. Salamanca-Riba[1], Samuel E. Lofland[2], Hidetaka Sugaya[3], Tetsuya Hasegawa[4], Manfred Wuttig[1] and Ichiro Takeuchi[1]; [1]University of Maryland, College Park, Maryland; [2]Rowan University, Glassboro, New Jersey; [3]Tokyo Institute of Technology, Yokohama, Japan; [4]The University of Tokyo, Tokyo, Japan.

Bi based magnetic oxide systems, such as $BiFeO_3$ and $BiMnO_3$, show magnetism, and they also display ferroelectricity due to hybridization between the Bi $6p$ and O $2p$ electrons. In this study, we will present systematic investigation of multiferroic properties of $Bi(Fe,Mn,Cr)O_3$ thin films. The films are fabricated by pulsed laser deposition under varying deposition conditions. We have found that by changing the

oxygen pressure, a variety of phases can be obtained. At optimized conditions, we have succeeded in obtaining single phase epitaxial thin films of $BiFeO_3$, $BiCrO_3$, and $BiMnO_3$. In particular, $BiCrO_3$ was found to be ferroelectric at room temperature and displays ferromagnetism with Tc = 150 K. We have synthesized pseudo-binary epitaxial thin film composition spreads of $BiFe_{1-x}Cr_xO_3$ and $BiFe_{1-x}Mn_xO_3$ using the combinatorial pulsed laser deposition technique in order to investigate their changing multiferroic properties as a function of composition. Their properties mapped using low temperature scanning SQUID microscopy and microwave microscopy will be discussed. This work was supported by NSF MRSEC under account No. DMR-00-80008.

**4:45 PM U9.6**
**Ferroelectric and Magnetic Properties of Rare-Earth Doped $BiFeO_3$ Thin Films.** Rasmi R. Das[1], Dong-Min Kim[1], Seung Hyub Baek[1], Florin Zavaliche[2], Seungyeul Yang[2], Xianglin Ke[3], Stephen K. Streiffer[4], Mark S. Rzchowski[3], R. Ramesh[2] and Chang-Beom Eom[1]; [1]Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin; [2]Department of Materials Science and Engineering, University of California, Berkeley, California; [3]Department of Physics, University of Wisconsin-Madison, Madison, Wisconsin; [4]Materials Science Division, Argonne National Laboratory, Argonne, Illinois.

There is an increasing interest on the physical properties of multifunctional oxides for various oxide electronic devices. The possibility of multiferroic behavior of hetroepitaxial $BiFeO_3$ thin films opens an avenue to study and search for optimal electrical and magnetic properties in the same material system by tuning the composition and strain in the lattice. Recently, we have reported the ferroelectric and magnetic properties of sputtered (001) $BiFeO_3$ films which show a higher value of remnant polarization (~70 $\mu C/cm^2$) due to smooth surface and high crystalline quality. Four-circle x-ray diffraction shows the $BiFeO_3$ thin films have high crystalline quality and rhombohedral crystal structure irrespective of the film thicknesses. Stripe ferroelectric domains oriented perpendicular to the substrate miscut direction are mapped in $BiFeO_3$ films on (001) $SrTiO_3$. Films grown on (101), and (111) $SrTiO_3$ exhibited remnant polarization of 86 and 100 $\mu C/cm^2$, respectively. $BiFeO_3$ films with (001) orientation showed a magnetization of ~5 emu/cc found to be independent of film thickness. However, thinner $BiFeO_3$ films (60 nm) with (101) and (111) orientations show relatively high magnetization values of 15 and 65 emu/cc, respectively. The high coercive field (~150 kV/cm), higher leakage current density is a limiting factor for the practical device application of $BiFeO_3$. In order to suppress the coercive field and leakage current, we have also investigated epitaxial $BiFeO_3$ thin films with rare-earth (La, Nd, Dy, Gd) doping at Bi-site. The influence of rare earth doping on crystal structure, coercive field, remnant polarization and magnetic properties of epitaxial $BiFeO_3$ thin films will be discussed.

SESSION U10: Oxide Multiferroics I
Chair: Mas Subramanian
Wednesday Morning, November 30, 2005
Republic A (Sheraton)

**8:00 AM *U10.1**
**Piezoelectrically induced strain effects in ferromagnetic manganite films.** K. Dorr[1,2], C. Thiele[1,2], S. Fahler[1,2], R. B. Gangineni[1,2], D. C. Meyer[3], A. A. Levin[3] and L. Schultz[1,2]; [1]Institute for Metallic Materials, IFW Dresden, Dresden, Germany; [2]Institute for Solid State Physics, Dresden University of Technology, Dresden, Germany; [3]Institute of Structure Physics, Dresden University of Technology, Dresden, Germany.

Magnetic transition metal oxides with a lattice constant of 3.8 - 4 Å can be combined with ferroelectric titanates like $Pb(Zr,Ti)O_3$ showing a pronounced piezoelectric effect in epitaxially grown film structures. This approach may offer effective access to electric control of magnetic properties via induced elastic strain. Ferromagnetic perovskite manganites $(R,A)MnO_3$ (R = rare earth element or La, Y, Bi; A = non-trivalent element) have been predicted to be extremely sensitive to distortions of the crystal lattice due to strong electron-phonon coupling [1]. This has been verified by experiments on biaxially strained films grown epitaxially on monocrystalline substrates with slightly mismatching lattice constant (like $LaAlO_3$, $SrTiO_3$, $NdGaO_3$). In most cases (as in [2], with certain exceptions [3]), an in-plane epitaxial strain of the order of 1 % reduces the ferromagnetic Curie temperature $T_C$ by several 10 K. On the other hand, active electric control of in-plane strain in thin films on a piezoelectric substrate or buffer layer is very promising, since it avoids additional effects of changing microstructure and would allow direct recording of strain dependent properties. In earlier work, Lee et al. and Dale et al. have chosen $BaTiO_3$ crystals for this purpose [4]. In this contribution, the effect of a piezoelectrically induced in-plane strain in $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) films (i) in an epitaxially grown field effect transistor (FET) structure of $PbZr_{0.52}Ti_{0.48}O_3$ (PZT) / LSMO / $SrTiO_3$(100) [5] and (ii) on a piezoelectric substrate is analysed. In the FET devices, a small but not negligible strain-induced modulation of the manganite channel resistance has been identified from the butterfly-like hysteresis loops [5]. This was possible due to the low field effect of the LSMO channels. In general, a superposition of strain and field induced resistance modulations is found in such multiferroic FETs with manganite channels. For the films on the piezoelectric substrate, in-plane lattice constants have been reversibly varied by up to 0.06 % via application of an electrical voltage (< 500 V) to the substrate. This modest strain variation nevertheless has a strong impact on the resistive and magnetic behavior of the studied $La_{0.7}Sr_{0.3}MnO_3$ films. For instance, the resistance at 300 K shows a strain-dependent hysteresis with an amplitude of several % and $T_C$ increases by several degrees due to release of in-plane tensile strain. This work is supported by Deutsche Forschungsgemeinschaft, FOR 520 "Ferroic Functional Elements". [1] A. J. Millis et al., J. Appl. Phys. 83 1588 (1998); A.J. Millis, Nature 392 147 (1998). [2] M. Angeloni et al., J. Appl. Phys. 96, 6387 (2004). [3] T. Kanki et al., Phys. Rev. B 64, 224418 (2001). [4] M. K. Lee et al., Appl. Phys. Lett. 77 3547 (2000); D. Dale et al., Appl. Phys. Lett. 82 3725 (2003). [5] C. Thiele et al., Appl. Phys. Lett. (submitted).

**8:30 AM *U10.2**
**Designing Ferromagnetic Insulators for Emerging Magnetoelectronics.** Mas A. Subramanian, DuPont Central Research and Development, Wilmington, Delaware.

Materials that show various responses to multiple external stimuli enable novel device applications. The behavior of systems with strong coupling between magnetic and electronic degrees of freedom provide both challenges for solid state theory as well as novel phenomena for applications in magnetoelectronics. Similarly, a strong coupling between magnetism and dielectric properties in magnetic insulators or semiconductors should lead to devices based on magnetodielectric effect, where the dielectric properties can be controlled by a magnetic field. Large magnetic field-induced changes in the resistivity and/or dielectric properties are found in ferromagnetic perovskite oxides, $La_2NiMnO_6$ and $MCuO_3$ (M = Se, Te) at temperatures as high as 280 K. This is a much higher temperature than previously observed for such a coupling between the magnetic, electric and dielectric properties in a ferromagnetic insulator. The ferromagnetism in the above oxides was confirmed through neutron diffraction studies. The ever growing proficiencies in crystal engineering of solid state materials in complex inorganic structures leading to applications in emerging electronics will be highlighted.

**9:00 AM U10.3**
**Giant dielectric permittivity and colossal magnetocapacitance effect in complex manganites.** Rinat F. Mamin[1,2], Takeshi Egami[1,3], Zsolt Marton[1] and Stanislav A. Migachev[2]; [1]University of Tennessee, Knoxville, Tennessee; [2]Kazan Physical-Technical Institute, Kazan, Russian Federation; [3]Oak Ridge National Laboratory, Oak Ridge, Tennessee.

The temperature dependences of the dielectric properties and conductivity of the $La_{0.875}Sr_{0.125}MnO_3$ single crystals are investigated in a wide temperature range. In order to understand the origin of the charge and phase separation behavior and to clarify the phase diagram of manganites, we carried out the studies of low-frequency dielectric properties and of the magnetic field effect on these properties. The measurements were carried out on a high-quality right-angled-parallelepiped $La_{0.875}Sr_{0.125}MnO_3$ single crystal with the sizes of 5.13-5.13-7.50 $mm^3$ and with the $c$-axis parallel to the bigger rib. The complex dielectric permittivity was measured by the four-electrode method on a precision impedance analyzer Agilent 4294A. We have shown that the giant dielectric permittivity of up to $10^9$ is displayed in this single crystal. The giant dielectric permittivity occurs by jump, in that time when other parameters of the system change rather smoothly. The certain limited area of the existence of this effect testifies that this effect is intrinsic effect. We believe that this effect occurs due to the pre-percolation regime of the dynamic charge separation. The nature of the giant dielectric permittivity is connected with the fact that in the pre-percolation regime of charge separation there are very thin areas of the insulated phase between metallic areas with big surfaces. Thus, the series of the capacitances with the dynamic system of electrodes (metallic areas) occur. The thickness of the insulated areas can been estimate as 1÷20 nm. Each of these areas have the certain magnetic ordering. Therefore thee external magnetic field strongly affects the charge separation contrast and the colossal magnetocapacitance effect of up to 50000% is observed. The maximal values of the magnetocapacitance effect are observed at the temperatures 140 K and 180 K. These results are one more evidences of the existence of the charge and phase separation in manganites. Two of the authors (R.F.M. and S.A.M) are grateful for financial support to the Russian

Foundation for Basic Research (grant No. 05-02-17182).

**9:15 AM U10.4**

**Spin filtering through ferromagnetic $BiMnO_3$ tunnel barriers.**

Martin Gajek[1], Manuel Bibes[2], Agnes Barthelemy[1], Gervasi Herranz[1], Karim Bouzehouane[1], Stephane Fusil[3], Jean-Marc Triscone[5], Patrycja Paruch[5], M. Dawber[5], Manuel Varela[6], Josep Fontcuberta[4] and Albert Fert[1]; [1]UMP CNRS/Thales, Palaiseau, France; [2]Institut d'Electronique Fondamentale, Universite Paris-Sud, Orsay, France; [3]Universite d'Evry, Evry, France; [4]ICMAB-CSIC, Bellaterra, Spain; [5]Condensed Matter Physics Department, University of Geneva, Geneva, Switzerland; [6]Dept. de Fisica Aplicada i Optica, Universitat de Barcelona, Barcelona, Spain.

Multiferroics belong to a class of compounds which show simultaneous electric and magnetic orders. Much attention has been recently focused on this family of materials because of the potential applications in electronic devices resulting from both the ferroelectric and ferromagnetic degrees of freedom and additional functionalities resulting from the coupling between these two orders displayed in multiferroics. We will show experimental results on the use of $La_xBi_{1-x}MnO_3$ (LBMO) ($x \leq 0.1$) as tunnel barriers [1,2]. Indeed, these materials are ferromagnetic insulators and, therefore, offer the possibility to filter the spin by an active barrier. Such a structure, known as a "spin filter", presents a spin-dependent barrier height for tunneling electrons resulting in highly spin-polarized currents. Moreover, some memory effects can be expected from the ferroelectric nature of these barriers. LBMO compounds are insulating and ferromagnetic perovskite oxides, having a Curie temperature ($T_C$) of about 105 K and a magnetic moment of 3.6 $\mu$B/formula unit (in bulk). They are highly insulating compounds with a robust insulating state. Exchange splitting is estimated to be 0.5 - 1.6 eV depending on theoretical calculations. To demonstrate spin filtering through these ferromagnetic barriers, we have analyzed the spin polarization of the current tunnelling from a nonmagnetic electrode (Au) with a half-metallic ferromagnetic oxide counter-electrode ($La_{2/3}Sr_{1/3}MnO_3$ (LSMO)) through an ultrathin barrier layers (1 - 3.5 nm). At 3 K we have found a 170% change of the tunnel resistances according to whether the magnetizations of LBMO(x = 0) and LSMO are parallel or opposite. This effect corresponds to a spin filtering efficiency of up to 50%. The tunnel magnetoresistance decreases rapidly and symmetrically as a function of the bias voltage, which may be the signature of magnon excitations inside the magnetic barrier. Our results suggest that LBMO could be used for spin-injection in spintronic devices. We will also show piezoresponse images evidencing the ferroelectric nature of our LBMO layers and discuss the influence on the spin-dependent tunneling process of the ferroelectric polarization switching in the LBMO barrier. [1] M. Gajek et al, JAP 97, 103909 (2005) [2] M. Gajek et al, to be published in PRB Rapid Comm, available at arXiv.org/cond-mat/0504667

**9:30 AM U10.5**

**Modulation of Anisotropic Magnetoresistance in the Colossal Magnetoresistive Oxides Using the Ferroelectric Field Effect.**

Xia Hong[1], Jeng-Bang Yau[1], Charles H. Ahn[1], Yosi Bason[2] and Lior Klein[2]; [1]Department of Applied Physics, Yale University, New Haven, Connecticut; [2]Physics Department, Bar-Ilan University, Ramat-Gan, Israel.

We have investigated the roles of charge density and chemical disorder/distortion in the anisotropic magnetoresistance (AMR) of the colossal magnetoresistive (CMR) oxides by electrostatically modulating the carrier density of ultrathin (3-4 nm) manganite films using the ferroelectric field effect. Epitaxial ferroelectric $Pb(Zr_{0.2}Ti_{0.8})O_3$/CMR heterostructures were fabricated using off-axis magnetron sputtering, with high quality crystalline structure and atomically smooth surface having been obtained. This electric field doping changes the carrier concentration, inducing a 25 K shift in the magnetic Curie temperature ($T_C$), while leaving the AMR ratio ($\triangle\rho_{AMR}/\rho 0$) unchanged. This result is in striking contrast to what is obtained using chemical doping, where for similar changes in carrier concentration, the AMR ratio decreases by 30%. The electric field scaling of the AMR ratio has been observed in a variety of heterostructures, independent of doping level and dopant, suggesting that changes in lattice disorder and/or distortion induced by chemical doping are important in understanding the magnetocrystalline anisotropy of these materials.

**9:45 AM U10.6**

**Combining Half-Metals and Multiferroics for Spintronics.**

Helene Bea[1], Manuel Bibes[2], Gervasi Herranz[1], Agnes Barthelemy[1], Karim Bouzehouane[1], Eric Jacquet[1], A. Khodan[1], Jean-Pierre Contour[1], Jean-Marc Triscone[3], Patrycja Paruch[3], M. Dawber[3], Stephane Fusil[4], Frederic Wyczisk[5], A. Forget[6], D. Lebeugle[6], D. Colson[6] and Michel Viret[6]; [1]UMP CNRS/Thales, Palaiseau, France; [2]Institut d'Electronique Fondamentale, Universite Paris-Sud, Orsay, France; [3]Condensed Matter Physics Department, University of Geneva, Geneva, Switzerland; [4]Universite d'Evry, Batiment des Sciences, Evry, France; [5]Thales Research and Technology, Orsay, France; [6]Service de Physique de l Etat Condense, DSM/DRECAM/SPEC, CEA Saclay, Gif-sur-Yvette, France.

Multiferroic materials possessing simultaneously ferroelectric and ferro- or antiferromagnetic orders are nowadays subject of an intense research. The coupling between the two order parameters is very interesting from the point of view of fundamental physics, and could also lead to applications in spintronics and other fields. A first step towards fabrication of magnetoelectric functional devices is to grow these materials as thin films. One of the best candidates is $BiFeO_3$ (BFO) which shows ordered states at high temperatures (it is antiferromagnetic at $T \leq T_N = 647$ K and ferroelectric at $T \leq T_C = 1043$ K). Its perovskite crystallographic structure makes it compatible with many other functional oxide compounds. One of the main issues is to find out the optimal growth parameters which stabilize single-phase pure BFO samples without parasitic phases and to study the impact of possible parasitic phases on the film properties. With this purpose in mind, we have explored the influence of deposition pressure and temperature on the growth of BFO thin films by pulsed laser deposition onto (001)-oriented $SrTiO_3$ substrates. We found that single-phase BFO films are obtained in a region close to $10^{-2}$ mbar and 580C. In non-optimal conditions, X-ray diffraction reveals the presence of Fe oxides ($\gamma$-$Fe_2O_3$ or $Fe_3O_4$ ) or of $Bi_2O_3$ [1]. We have addressed the issue of the influence of these parasitic phases on functional properties. We show that the magnetic properties are extremely sensitive to the presence of Fe oxides. Indeed, large ferromagnetic signals are measured for films showing sizable amounts of $\gamma$-$Fe_2O_3$ detected by X-ray diffraction and confirmed in Auger spectroscopy measurements. In strong contrast with this observation, we found very small magnetic moment, similar to the one measured in bulk single-crystal specimens, for the BFO single-phase films grown at optimal conditions. Also the presence of $Bi_2O_3$ modifies the functional properties of the samples. At non-optimal growth conditions $Bi_2O_3$ overgrowths are observed on the surface. Conductive-tip atomic force microscopy mappings indicate that these overgrowths are conductive and create shortcuts through the BFO films, thus preventing their practical use as ferroelectric elements in functional heterostructures. We show also the preliminary experimental tests of the ferroelectric properties of BFO thin films grown at optimal conditions by means of both piezoelectric atomic force microscopy and ferroelectric hysteresis loops. As a first step towards implementation of BFO in integrated devices, we have characterized the structural and functional properties of $La_{2/3}Sr_{1/3}MnO_3$ (LSMO)/BFO bilayers. We show that these samples have smooth surface morphologies and the BFO layer has a homogeneous resistive state suitable to be used as tunnel barrier. This would open a way to combine the half-metal properties of LSMO with the multiferroic properties of BFO. [1] H. Bea et al., to be published in App. Phys. Lett.

SESSION U11: Oxide Multiferroics II
Chair: Wilfried Prellier
Wednesday Morning, November 30, 2005
Republic A (Sheraton)

**10:30 AM *U11.1**

**Oxide Multiferroic Thin Films: Design, Structure and Properties.**

Wilfrid Prellier[1], Singh Mangala[1], Bernard Mercey[1], Charles Simon[1], Benard Raveau[1] and Laurence Mechin[2]; [1]Laboratoire CRISMAT, UMR 6508, ENSICAEN/CNRS, Caen, France; [2]Laboratoire GREYC, UMR 6072, ENSICAEN/CNRS, Caen, France.

Multiferroics are materials which possess simultaneously ferroelectricity and ferromagnetism and a coupling between them (1). These materials are potential candidates in various devices, such as storage devices and sensors. However, the realization of these devices and understating the mechanism responsible for multiferroism are difficult due to scarcity of the materials. An alternative approach to synthesize the new oxide multiferroics will be demonstrated (2). The materials, synthesized in the form of the thin films by the pulsed laser deposition technique on SrTiO3 substrates, are made by alternatively staking in a superlattice a manganite perovskite, typically La0.7Ca0.3MnO3 and a ferroelectric perovskite typically Ba1-xSrxTiO3. A series of artificially grown multilayers have thusly been grown by changing the nature of the layer and its number of unit cells. The structural (X-ray diffraction, transmission electron microscopy) and magnetoelectric properties (resistive, capacitance and magnetization) have been examined and a clear correlation between structure/properties can be established. Several superlattices display ferromagnetic and ferroelectric behaviours and a clear coupling between them. Our results show that it is possible to achieve multiferroism in a single phase by manipulating the ferroelectric do-cations and ferromagnetic dn-cations in perovskite oxides. At the end, the existence of magnetoelectric effect will be discussed and a

comparison between our results and the published literature will also be presented. This work is supported by the European Network of Excellence FAME (FP6-500159-1) and the Centre National de la Recherche Scientifique (CNRS). (1) H. Schmid, Ferroelectrics 221 (1999) 9. (2) P. Murugavel et al., Appl. Phys. Lett. 85 (2004) 4424.

### 11:00 AM U11.2

**Electronic Configuration at $LaMnO_3/SrTiO_3$ Interfaces and in Related Heterostructures.** Hans Christen[1], Maria Varela[1], Claudia Cantoni[1], Dae Ho Kim[1], Matthew F. Chisholm[1], Ho Nyung Lee[1], David P. Norton[2] and Douglas H. Lowndes[1]; [1]Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; [2]Department of Materials Science and Engineering, University of Florida, Gainesville, Florida.

The construction of "artificial multiferroics" by the integration of magnetic and ferroelectric components in close proximity relies on the constituents' properties near each interface. Epitaxial perovskite heterostructures provide an ideal platform to investigate well-controlled, atomically abrupt compositional discontinuities. As has been reported earlier, the contact between two perovskites – even if both are insulating – can exhibit surprising and fascinating electronic properties. Charge imbalances and charge transfer change the local electronic configuration and thus influence each material's electronic conductivity and magnetic behavior. Here we use the local electron energy loss spectroscopy (EELS) capability of a scanning transmission electron microscope to probe the electronic configuration in $LaMnO_3$ films as a function of the distance from various types of interfaces. The heterostructures were grown by pulsed laser deposition, paying close attention to oxygen stoichiometry. EELS measurements show a drastic change in the occupation of the Mn 3d bands as we approach the interface. These results are compared to similarly obtained measurements on $LaTiO_3/SrTiO_3$ interfaces. In both cases we observe strong asymmetries in the degree to which the B-site 3d occupancy changes on either side of the interface. By studying these changes as a function of distance from the compositional discontinuity we gain an understanding of the relevant length scales and the driving forces responsible for charge transfer and for electronic localization. Our findings allow us to construct superlattice structures with properties that are defined by these local effects and by the strong coupling between dissimilar materials. Research sponsored by the U.S. Department of Energy under contract DE-AC05-00OR22725 with the Oak Ridge National Laboratory, managed by UT-Battelle, LLC

### 11:15 AM U11.3

**Field effect in epitaxial bilayers of ferromagnetic (La,A)MnO3 and ferroelectric Pb(Zr,Ti)O3.** C. Thiele[1,2], K. Dorr[1,2], K. Nenkov[1], W.-M. Lin[3] and L. Schultz[1,2]; [1]Institute for Metallic Materials, IFW Dresden, Dresden, Germany; [2]Institute for Solid State Physics, Dresden University of Technology, Dresden, Germany; [3]Institute for Solid State Electronics, Dresden University of Technology, Dresden, Germany.

Magnetic transition metal oxides with a lattice constant of 3.8 - 4 Å can be combined with ferroelectric titanates like $Pb(Zr,Ti)O_3$ in epitaxially grown multilayer films and may offer effective access to the electric control of magnetic properties. Magnetoelectric phenomena in such composites may appear at room temperature and have the benefit of large magnitude of the electric and magnetic polarization, according to the properties of the chosen magnetic and ferroelectric components. In this work, ferromagnetic manganites $(La,A)MnO_3$ (A = Sr; Ca; Ce) with colossal magnetoresistance were selected for the magnetic part. Epitaxial bilayer films of $PbZr_{0.52}Ti_{0.48}O_3$ (PZT) / $(La,A)MnO_3$ have been grown on $SrTiO_3(100)$ and $LaAlO_3(100)$ substrates by off-axis pulsed laser deposition. It has been shown earlier that manganites are sensitive to an electric field applied via a dielectric [1] or ferroelectric [2,3] gate electrode. Some field effect transistor (FET) structures with a manganite channel and a PZT gate show electrical modulation of the channel resistance proportional to the PZT electric polarization loop [3,4], including remanent states. This is attributed to charge density modulation in the interface-near region of the manganite. On the other hand, Tabata et al. had proposed an effect of elastic strain from the inverse piezoelectric response of the PZT layer [2]. Strain in films clamped to a rigid substrate is small; however, recording complete resistance hysteresis loops in dependence on an applied gate voltage in $PZT/La_{0.7}Sr_{0.3}MnO_3$ FETs has given evidence for butterfly-like hysteresis being typical for in-plane strain modulation in the manganite layer [5]. Hence, in order to study the electric field effect, a possible contribution from strain variation has been checked and separated on the basis of measured channel resistance hysteresis loops. A FET structure with epitaxial bilayers of $PZT/(La,A)MnO_3$ has been prepared using a shadow mask technique and Pt top contacts to the PZT [5,6]. X-ray diffraction and Atomic Force Microscopy have been employed for structural characterization. For $La_{0.8}Ca_{0.2}MnO_3$ channels, the field effect has been found to dominate over the strain effect. In contrast, $La_{0.7}Sr_{0.3}MnO_3$ channels show a very small response to an applied gate voltage, dominated by varied in-plane strain for a channel width below 10 nm [5]. The different behavior of these manganites seems related to their position in the bulk magnetic phase diagram. We discuss the dependence of recorded resistance modulations on channel width and temperature. This work is supported by Deutsche Forschungsgemeinschaft, FOR 520 "Ferroic Functional Elements". [1] B. Ogale et al., PRL 77 1159 (1996). [2] H. Tabata et al., IEICE Trans. Electron. E80-C (1997) 918. [3] S. Mathews et al., Science 276 238 (1997). [4] T. Kanki et al., APL 83 4860 (2003). [5] C. Thiele et al., APL (submitted). [6] C. Thiele et al., Sensors and Actuators A (in press).

### 11:30 AM U11.4

**Leakage Free Multiferroic BiFeO3 - BaTiO3 Thin Films Grown by the Pulsed-Laser Deposition.** P. Murugavel[1], J. H. Lee[1], K. H. Jang[2], J. G. Park[2] and T. W. Noh[1]; [1]ReCOE, School of Physics, Seoul National University, Seoul 151 742, South Korea; [2]School of Physics, Sungkyunkwan Unversity, Suwon 440 746, South Korea.

In recent years, there has been growing interest in tailoring the material with coexistence of ferroelectric and ferromagnetic properties. The coupling between their properties gives an additional degree of freedom in designing of devices, such as transducers, actuators, and information storage etc. Recently, bismuth iron oxide with the perovskite structure has attracted much attention, since it shows simultaneous magnetic and ferroelectric ordering [1]. Wang et al prepared epitaxial BiFeO3 thin films with tetragonal-like crystal structure on single-crystal SrTiO3 substrate by the pulsed-laser deposition. They reported twice the remnant polarization (2Pr) value as approximately 110 $\mu$C/cm2 and the coercive field (2Ec) value as 300 kV/cm. However, a serious problem with BiFeO3 is that it has very high values of leakage current due to deviation from oxygen stoichiometry and defects. This poses a challenging and serious problem for successful development of this material for practical applications, especially in thin film form. One way to overcome this problem is to make solid solution with highly insulating perovskite materials which eventually reduces the leakage current [2]. For this purpose, we have focused on the solid solution of BiFeO3 with perovskite BaTiO3. In the present work we have successfully prepared BiFeO3-BaTiO3 solid solution thin films on the conducting Nb-SrTiO3 (100) and Pt/TiO2/SiO2/Si substrates by pulsed-laser deposition technique. The epitaxial and single phase nature of the film on Nb-SrTiO3 substrate and the polycrystalline film on platinum substrate were confirmed by high resolution x-ray diffractometer. The coexistence of simultaneous ferroelectric and ferromagnetic properties at room temperature was confirmed by TF analyzer and Quantum design magnetic property measurement system, respectively. At room temperature, the epitaxial (Bi0.5Ba0.5)(Fe0.5Ti0.5)O3 film was showing a leakage free, fully saturated ferroelectric hysteresis loop with 52 $\mu$C/cm2 as 2Pr and 480 kV/cm as 2Ec. The thickness dependent multiferroic properties were also analyzed in terms of strain. Though the Pr of our film is lower than the parent BiFeO3 film, it is an order of magnitude higher than the reported value on similar such solid solution film [2]. Single phase, leakage free, as high as 52 $\mu$C/cm2 remnant polarization of our film makes it one of the potential multiferroic materials for device applications. Reference [1] J. Wang, et. al., Science 299, 1719 (2003). [2] K.Ueda, H. Tabata, and T. Kawai, Appl. Phys. Lett., 75, 555 (1999).

## SESSION U12: Magnetoelectric Theory

Chair: Claude Ederer
Wednesday Afternoon, November 30, 2005
Republic A (Sheraton)

### 1:30 PM *U12.1

**Theory of Multiferroic Heterostructures.** Alexander Roytburd[1] and Julia Slutsker[2]; [1]Materials Science and Engineering Department, University of Maryland, College Park, Maryland; [2]Materials Science and Engineering Laboratory, NIST, Gaithersburg, Maryland.

We present the thermodynamic theory of the formation and performance of heterostructures consisting of a ferroelectric phase and ferro(ferri) magnetic (including ferromagnetic shape-memory) or ferroelastic phases. Two types of heterostructures will be considered. The first type of heterostructures includes ferroelectric or ferromagnetic film on ferroelastic substrate as well as ferroelectric/ferromagnetic multilayers. The second type is self-assembled transversely modulated two-phase heterostructure on single crystalline substrate. In both cases the multiphase nano-scale systems with coherent or partial coherent interfaces are formed with strong elastic interactions between the heterostructure components. The elastic interactions determine nanostructure architecture: phase and domain arrangement as well as their scale. On the other hand, the elastic interactions provide one of the mechanisms of controlling the electric and magnetic responses in such kind of nanostructures. It will be shown that by using ferroelastic substrate, piezoresponce of ferroelectric films or magnetostriction of ferromagnetic films can be dramatically enhanced. The different mechanisms of electro-magnetic coupling of self-assembled multiferroic films will be discussed. Supported by NSF-MRSEC grant # DMR008008

**2:00 PM U12.2**
**Strain engineering of multiferroic $DyMnO_3$thin film.**
Jung-hyuk Lee[1], Pettukanu Murugavel[1], Seung-Chul Chae[1], Ji-Young Jo[1], Kwang-Hyun Jang[2], Jae-Gun Park[2] and Tae-Won Noh[1]; [1]Physics, Seoul National University, Seoul, Seoul, South Korea; [2]School of Physics, Sungkyunkwan University, Suwon, Kyung-gi, South Korea.

Orthorhombic dysprosium manganese oxide ($DyMnO_3$) attracts lots of interests due to its unique multiferroic properties (switching of polarization by applying magnetic field).[1] However, its low Curie temperature and small remnant polarization (Pr) hinder it from actual applications. Because of large in-plane lattice mismatch(9.52%), it is even more difficult to make as a thin film form with the single crystal-like properties. However, the hexagonal $RMnO_3$ (R=Ho,Y) shows enhanced multiferroic properties at higher temperature[2]. It is well known that the bulk $AMnO_3$ (A= rare earth ion) crystallizes in orthorhombic and hexagonal forms depending on the ionic radius of A. On the other hand, in thin film form it is possible to control their crystal structure by means of strain-inducing stablization. By selecting suitable substrates with proper epitaxial strain, we have successfully prepared $DyMnO_3$ thin films both in orthorhombic and hexagonal crystalline phases by the pulsed laser deposition (PLD) method. The good crystalline quality and epitaxial nature of the films was confirmed by high-resolution x-ray diffractometer (XRD). The XRD phi scan performed to verify the epitaxial growths of the orthorhombic and hexagonal phases of the films. The low temperature ferroelectric polarization vs. electric field (P - E) hysteresis loop measurements clearly show ferroelectric properties even up to 150 K. The remnant polarization and the coercive field of the hexagonal $DyMnO_3$ thin films at 15 K are 1.5 $\mu C/cm^2$ and 620 kV/cm, respectively. The magnetization with temperature measurement on the $DyMnO_3$ in its hexagonal phase shows an antiferromagnetic behavior with a clear Neel temperature at 75 K. Comparing with the corresponding values of the bulk orthorhombic phase, the values of remnant polarization and the Neel temperature can be enhanced by fabricating thin DyMnO3 films of the hexagonal phase using strain engineering. Reference [1] T. Goto, et. al.,PRL 92, 257201 (2004) [2] T. Lottermoser, et. al. Nature 430, 541 (2004)

**2:15 PM U12.3**
**The Orbital and Magnetic Properties of Multiferroic $BiMnO_3$ Thin Film.**
Chan-Ho Yang[1], Tae Yeong Koo[2] and Yoon Hee Jeong[1]; [1]Physics, Pohang Insititute of Science and Technology, Pohang, South Korea; [2]Pohang Accelerator Laboratory, Pohang, South Korea.

$BiMnO_3$ is known for a true multiferroelectric, ferromagnetic ferroelectrics. In this presentation, we paid attention to the orbital order in $BiMnO_3$, which is responsible for the magnetic state according to the superexchange rule and simultaneously related to the ferroelectric owing to the strong orbital lattice coupling. We observed a resonant peak at the expected reciprocal position using X-ray scattering technique. The dependence on the photon energy, azimuthal angle, temperature of the integrated peak intensity are fully investigated. These are well matched with the calculated prediction and previous structural information. Besides the uniaxial strain can induce larger magnetic frustration which could be explained using variable relative strength(—$J_{AF}$—/$J_F$) of exchange interaction according to the pseudotetragonality.

SESSION U13: Ferromagnetic Shape Memory Alloys II
Chair: Eckhard Quandt
Wednesday Afternoon, November 30, 2005
Republic A (Sheraton)

**3:30 PM *U13.1**
**Structure, Magnetic Shape Memory Effect and Magnetization Changes In Ni-Mn-Ga Alloys.**
Y. Ge, S.-P. Hannula, O. Heczko, V. K. Lindroos, L. Straka and O. Soderberg; Laboratory of Materials Science, Helsinki University of Technology, Espoo, Finland.

The detailed studies of structural, magnetic and magnetoelastic properties of three kinds of Ni-Mn-Ga martensites (five-layered tetragonal (5M), seven-layered orthorhombic (7M) and non-modulated tetragonal) are reviewed. Magnetic shape memory effect (MSME) due to the redistribution of martensite twin variants can be observed in the 5M and 7M martensites. The basic conditions for the MSME are the high mobility of the martensite twin boundaries and high magnetocrystalline anisotropy. There are two complementary magnetic-field-assisted strain effects, in the conventional case the strain occurs as a function of magnetic field under constant external stress and in the second case the reversible stress-induced strain occurs in a constant magnetic field. The conditions for the fully reversible behavior are presented. The unique simultaneous experimental determination of the magnetization M = M (H, $\sigma$ —*tauup*—) and the magnetic-field-induced strain $\epsilon = \epsilon$ (H, $\sigma$ —*tauup*—) as a function of magnetic field, H, external stress, $\sigma$, and temperature T gives the full macroscopic description of the MSME and the direct relation between M and $\epsilon$. The observed structures and magnetic domain arrangements observed by SEM and optical microscopy are correlated to the magnetization process. The detailed knowledge of the magnetization processes is a prerequisite for realistic modeling of the MSM effect. The observed temperature and stress dependence of the MSME can be interpreted and predicted using a simple energy model. The measured non-uniform strain response of similar alloys and samples is noted and the consequence of this for the practical utilization of the MSM alloys discussed.

**4:00 PM U13.2**
**Requirements for Magnetoelastic Behaviour in Ni50Mn30Ga20.**
Uwe Gaitzsch, Stefan Roth, Bernd Rellinghaus and Ludwig Schultz; Inst metal mater, IFW Dresden, Dresden, Germany.

Since 1996, NiMnGa alloys are known to exhibit large magnetic-field-induced strains (MFIS) of up to 10 % due to the motion of twin boundaries in a magnetic field. The mobility of the twin boundaries as well as the magnetocrystalline anisotropy energy depend on the structure of the martensite. The upper limit of the operating temperature is the martensitic transformation temperature, therefore alloys with high Tmart, such as Ni50Mn30Ga20 are of special interest. Thus, the martensite structure of these high-Tmart alloys has to be adjusted in order to obtain high MFIS. This can be achieved by appropriate thermal treatment to select between a tetragonal non-modulated, so-called NM structure (c/a = 1.2) and a pseudo-orthorhombic (c/a = 0.9), actually a 7fold modulated monoclinic structure (7M). Furthermore it could be shown, that powderization leads to structural changes caused by an intermartensitic transformation from 7M to NM. The results were obtained using standard XRD and DSC equipment. The magnetic anisotropy field was measured to calculate the maximum obtainable stress caused by an external magnetic field.