EMSL Research and Capability Development Proposals

Modeling-Assisted Growth of New Multiferroics in the $MTiO_3$ (M = Fe, Mn, Ni) Family as Epitaxial Thin Films

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Materials that show simultaneous electric and magnetic order are currently gaining increasing attention due to the fact that such *multiferroics* show promise for the design of new multifunctional devices, and because of the interesting physics exhibited by these materials. A recent theoretical study has predicted that the family of $MTiO_3$ (M = Fe, Mn, Ni) are promising candidate structures (only if *R3c*) where polar lattice distortion can induce weak ferromagnetism (see *Fennie, Phys. Rev. Lett. 100 (2008) 167203*). These materials whose magnetization can be controlled by electric field may enable applications in new magnetic devices such as memories, biosensors, and other multifunctional devices where electric-field switching of magnetization is utilized.
The goal of this proposal is to:

(1) synthesize high-quality epitaxial films of new multiferroic materials in the $MTiO_3$ family by taking advantage of EMSL's oxide heteroepitaxy capabilities;
(2) study the influence of strain, film thickness, and the electronic structure of the transition metal on the crystal structure, electric polarization, and magnetization of $MTiO_3$ phases; with the help of first-principles calculations, optimize the physical properties by tuning the heteroepitaxial strain through varying the lattice mismatch between the film and the substrate, the film thickness, and the $MTiO_3$ composition to achieve coexisting ferroelectricity and ferromagnetism;
(3) demonstrate that the ferroelectric and ferromagnetic orders are <u>coupled</u> in these materials.

Products and Output

In general, beyond making materials whose magnetization can be controlled by electric field, this project represents an example of theory-inspired design, where theory and experiment are closely coupled to elucidate emergent phenomena, and aid rational synthesis of new materials of potential technological importance.
Specifically, our current structural data from x-ray diffraction and x-ray absorption spectroscopy indicate that epitaxial ilmenite-type $NiTiO_3$ films were successfully grown (see Fig. 1, left). From a comparison of the calculated and measured lattice parameters and nearest-neighbor distances, we concluded that the lattice strain exerted by sapphire substrate results in a distorted ilmenite structure

similar to the $LiNbO_3$-type one. Our results indicate a very small difference between the $R\bar{3}$ and *R3c* structures of $NiTiO_3$ (Fig. 1, right) and suggest that a definitive verification of the targeted *R3c* phase may only be possible by physical property (i.e. magnetic susceptibility) measurements (*Varga et al., Thin Solid Films, accepted (2012)*).

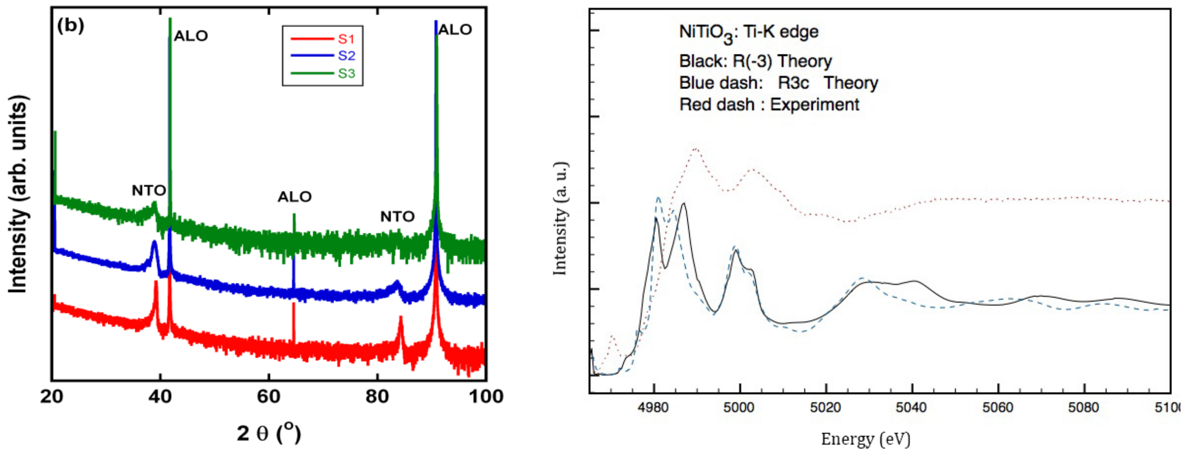

Fig. 1: *Left:* High-resolution 2*θ*-*θ* XRD scans of $NiTiO_3$ films grown on (001) sapphire showing only (006) and (0012) peaks; *Right*: Ti K-edge XANES spectra calculated for $R\bar{3}$ (solid line) and *R3c* (blue dashed line) $NiTiO_3$. Our experimental data (red dotted line) are more consistent with spectral features of the calculated spectrum for *R3c* $NiTiO_3$.

Our most recent physical property results show that our epitaxial $NiTiO_3$ film deposited on sapphire exhibits a Neel transition shifted to higher temperature relative to ilmenite-$NiTiO_3$ as predicted by the theory (Fig. 2, left). Furthermore, our epitaxial $NiTiO_3$ film deposited on a hematite (Fe_2O_3) interlayer on sapphire shows clear second harmonic generation (SHG) signal indicative of lattice polarization (Fig. 2, right), a necessary condition for ferroelectricity (and thus an R3c structure as the $R\bar{3}$ phase would be nonpolar).

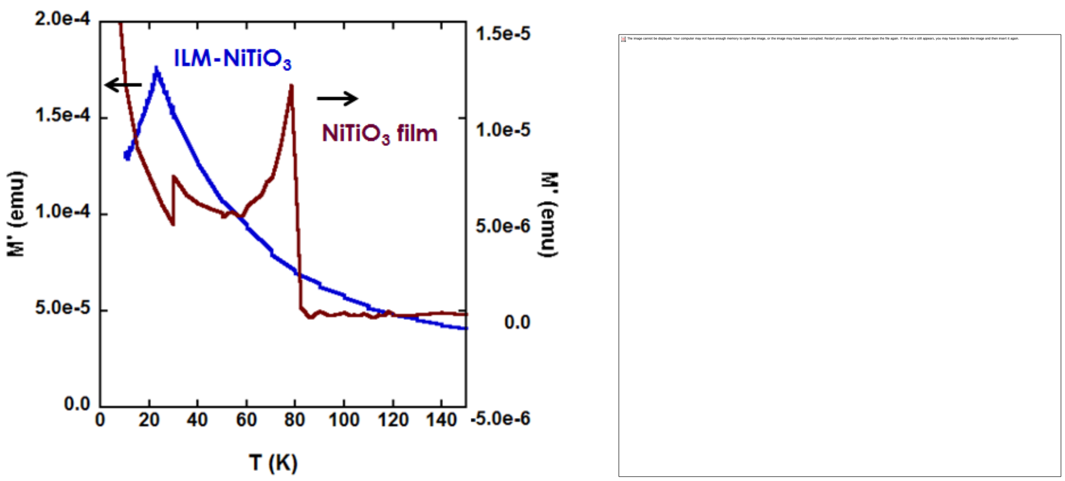

Fig. 2: *Left:* Magnetic (AC) susceptibility of bulk $R\bar{3}$ and epitaxial $NiTiO_3$ film on Al_2O_3. *Right*: Optical SHG image of an $NiTiO_3/Fe_2O_3/Al_2O_3$ film showing SHG signal for the film only (collected by a Zeiss LSM 710 multiphoton microscope with an 40X air objective).

Publications

T. Varga, T. C. Droubay, M. E. Bowden, S.A. Chambers, B. C. Kabius, W. A. Shelton, P. Nachimuthu, and V. Shutthanandan. 2011. "Promise of new multiferroics: Synthesis and characterization of epitaxial $NiTiO_3$ films." Presented at the APS March Meeting 2012, Boston, MA.

T. Varga, T. C. Droubay, M. E. Bowden, P. Nachimuthu, V. Shutthanandan, T. B. Bolin, W. A. Shelton, and S. A. Chambers. "Epitaxial growth of $NiTiO_3$ with a distorted ilmenite structure", accepted, *Thin Solid Films*, 2012