Cation Site Occupancy and Valence in Non-Equilibrium Spinel Oxide Thin Films.

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Magnetic thin films can exhibit properties markedly different from the bulk due to the effects of surfaces or interfaces, strain state and non-equilibrium synthesis. This is particularly true in magnetic spinel oxide thin films, where the magnetic properties are determined by the ferrimagnetic interaction among the transition metal cations with octahedral and tetrahedral coordination. A departure from equilibrium cation valences and site occupancies can cause a dramatic change in the magnetic properties. We have investigated epitaxial thin films of the ferrimagnetic spinels $NiMn_2O_4$ (NMO) and $NiFe_2O_4$ (NFO) that both exhibit anomalous magnetic behavior in thin film form. While NMO exhibits two magnetic transitions in the bulk (a collinear moment configuration below 100K and a canted moment configuration below 60K), epitaxial thin films grown on $SrTiO_3$ and $MgAl_2O_4$ substrates exhibit a single magnetic transition at 60K. Resonant X-ray diffraction (RXS), X-ray absorption spectroscopy (XAS), and X-ray magnetic circular dichroism (XMCD) have been used to investigate both the chemical and magnetic structure of NMO thin films. RXS indicates that the cation site occupancy does not differ markedly from bulk samples, but both RXS and XAS show that differences in the relative amounts of Mn^{2+}, Mn^{3+} and Mn^{4+} may play a role in the difference in magnetic properties. The NFO films also show a departure from bulk magnetic properties, exhibiting a significant increase above bulk magnetization values with decreasing film thickness. Ultrathin NFO films with enhanced magnetization have been characterized by both XMCD and RXS methods in order to investigate if any changes in cation valence and site occupancy are the cause of such properties when compared to thicker films. Preliminary data shows Ni and Fe XMCD lineshapes similar to that of bulk NFO, but with different relative peak intensities.