

Chemistry 483.6 Research Project

Supervisor: Dr. Andrew Grosvenor

The Grosvenor group studies transition-metal/rare-earth oxides, silicates, and pnictides ($Pn = P, As, Sb, Bi$) by X-ray diffraction, X-ray absorption near-edge spectroscopy (XANES), utilizing synchrotron radiation, and electronic structure calculations. To develop these materials for different applications (e.g., catalysts, semiconductor devices, ion conductors, power generation, etc.), it is important to understand the relationship between crystal structure, electronic structure (bonding and charges), and surface reactivity.

Investigation of the site occupancy of substituted Spinel-type oxides ($Zn_{1-x}Fe_xAl_2O_4$) by XANES

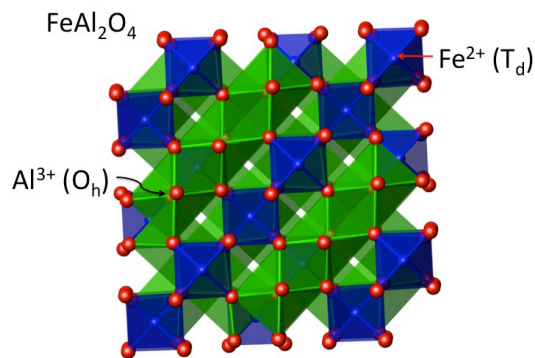


Figure 1: Spinel-type structure of $FeAl_2O_4$.

Spinel-type oxides of the form AB_2O_4 (where the A^{2+} cations lie in a T_d site and the B^{3+} cations lie in O_h sites) can contain a variety of different cations with some materials exhibiting interesting magnetic properties and others being potential catalysts for a large number of reactions. To understand how these properties change with substitution of the constituent elements, it is important to understand into which crystallographic site the cations substitute. In the prototypical spinels, the A^{2+} cations are only found in the tetrahedral site. This is not always the case, as, depending on the A^{2+} cation, it may substitute partially into the octahedral site, which can result in a transformation to the inverse spinel-type structure. X-ray diffraction is normally used to determine metal site-preference, but this is not always possible, requiring the use of other techniques like XANES.

In this project, the preference of Fe^{2+} and Al^{3+} in $Zn_{1-x}Fe_xAl_2O_4$ to lie in either the T_d or O_h sites will be investigated by analysis of Fe K- and Al L-edge XANES spectra. (These spectra are very sensitive to even the slightest change in coordination or oxidation state.) To properly determine the site preference of the Fe and Al atoms, spectra from standard materials, having known Fe and Al coordination environments will also be investigated (FeO , $MgAl_{2-x}Fe_xO_4$, Ca_2AlFeO_5 , $ZnAl_2O_4$, and $MnAl_2O_4$). The student working on this project will synthesize the metal oxides to be examined and investigate their structure by use of powder X-ray diffraction and XANES.

Timeline for project:

Month	Goals
September/ October	<ul style="list-style-type: none">• Learn basic solid-state synthesis skills.• Tour of the CLS/become a user• Start synthesis of materials
November/ December	<ul style="list-style-type: none">• Continue synthesis and confirm product by powder diffraction• Prepare for beamtime at the CLS to collect Al L-edge spectra
January/ February	<ul style="list-style-type: none">• Analyse Al L-edge XANES data• Prepare for beamtime at the CLS to collect Fe K-edge XANES spectra
March/ April	<ul style="list-style-type: none">• Analyse Fe K-edge XANES data• Write / present report