Neutron Diffraction Studies of Reduced Perovskite Iron Oxides

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Why Perovskites?

- Interesting Properties
- Many Applications
A-FeO$_3$ Systems

SrFeO$_3$
Cubic Perovskite

BiFeO$_3$- The novel multiferroic!
Rhombohedral Perovskite

Strontium
Bismuth
Oxygen
Iron
Topotactic Route- Hydride Reduction Reactions

Project Goals

• Reduce BiFeO$_3$ to BiFeO$_{3-\delta}$
• Intercalate between layers of SrFeO$_2$
  – Organics have been intercalated in layered titanates, try to replicate with iron oxides
  – Other inorganic ligands to prepare mixed anion materials
• Change magnetic and chemical properties of starting perovskite iron oxides
Diffraction of Crystals

Braggs Law: \( 2d \sin \theta = n \lambda \)
X-Rays vs Neutrons

- Need less sample
- Cheaper
- Better for initial characterization

- More accurate
- Sensitive to lighter elements
- Magnetic information
Rietveld Refinement

- Lattice Parameters
- Occupancies

BT1 Powder Diffractometer
Solid State Synthesis-SrFeO$_2$

SrCO$_3$ + 0.5 Fe$_2$O$_3$ $\rightarrow$ SrFeO$_3$ + CO$_2$

1200°C
12 hrs

SrFeO$_3$ + CaH$_2$ $\rightarrow$ SrFeO$_2$ + Ca(OH)$_2$

280°C
24 hrs
(Sealed tube rxn)

Wash with 0.15M NH$_4$Cl/ Methanol solution to remove Calcium Hydroxide and excess Calcium Hydride
Solid State Synthesis- BiFeO$_3$

1.06 Bi$_2$O$_3$ + Fe$_2$O$_3$ $\rightarrow$ BiFeO$_3$ + $\alpha$Bi$_{25}$FeO$_{40}$ $\rightarrow$ BiFeO$_3$ + waste

2.5M HNO$_3$

*iron source XRD
Intercalating SrFeO$_2$

Pyridine has been intercalated in layered titanates through vapor reactions.
SrFeO$_2$ Reactions With Various Ligands

$S^{2-}$
SrFeO$_2$ goes to Brownmillerite

DSC/ $\frac{dDSC}{dt}$

Enthalpy (μV/mg)/Temp (°C)

DSC

*μV/mg/min
BiFeO$_3$ Reduction Reactions

- BiFeO$_3$ +CaH$_2$
- BiFeO$_3$ +NaH
- Various temperatures
- Various reaction times

- Stirred/ heated in solution
- Vapor reaction
- Hydrothermal bomb
BiFeO$_3$ + CaH$_2$ 100°C - XRD Results
Conclusions

• Ligands will not readily intercalate in SrFeO$_2$
• SrFeO$_2$ decomposes at relatively low temperatures
• SrFeO$_{2.5}$-like phase can form with oxygen vacancies to change magnetic and chemical properties
• BiFeO$_3$ starts to undergo a structural change at 100°C
Future Directions

- Neutron Diffraction study of reduced BiFeO$_3$
- More neutron diffraction on Brownmillerite–like phase
- Different SrFeO$_2$ ligand reaction routes

Image taken from: [http://www.impactlab.net](http://www.impactlab.net)
Thanks to:

- Dr. Efrain Rodriguez
- Dr. Mark Green
- Dr. Donna Arnold
- Dr. Pawel Zajdel
- Dr. Julie Borchers
- NCNR Staff
- Surf Organizers
And last but not least...

• All the other SURF students!
Thanks For Listening! Questions?