Neutron Diffraction Studies of Reduced Perovskite Iron Oxides

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Why Perovskites?

- Interesting Properties
- Many Applications

Image taken from: http://www.hitechnic.com

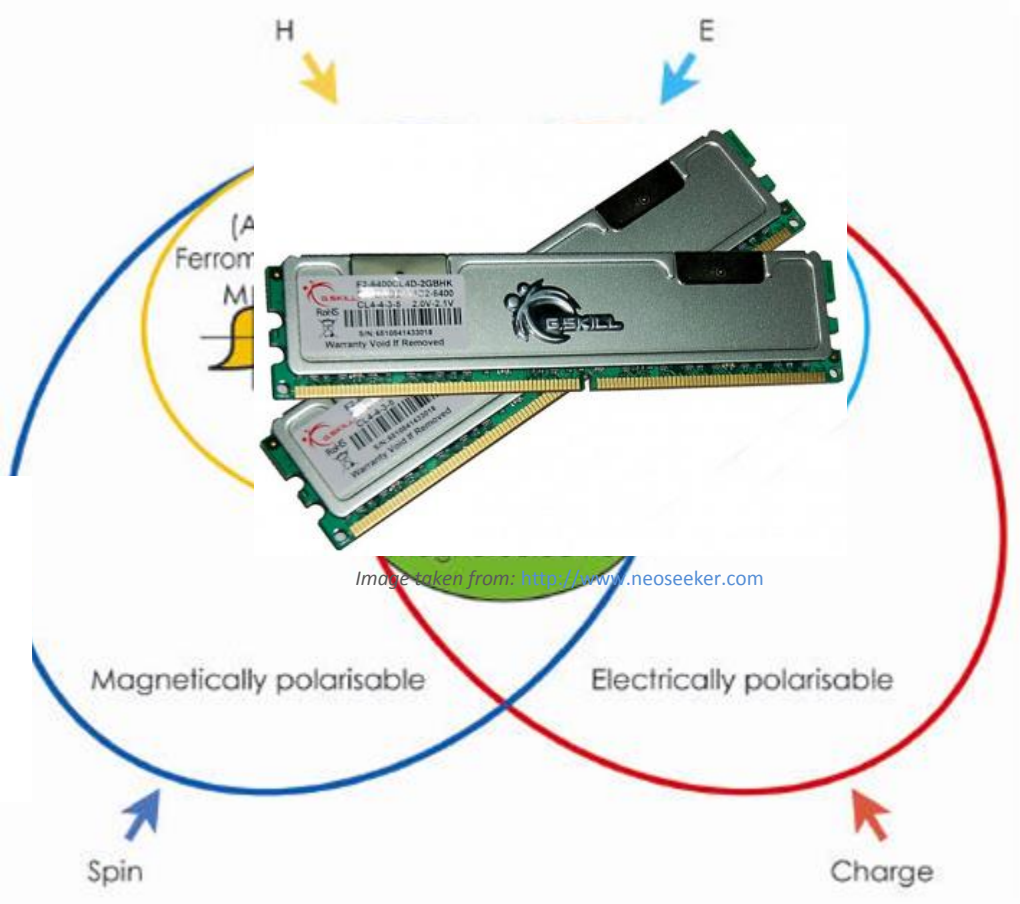
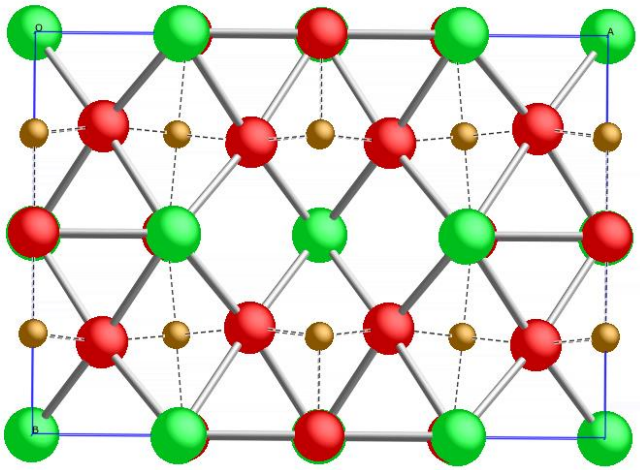


Image taken from: http://www.neoseeker.com

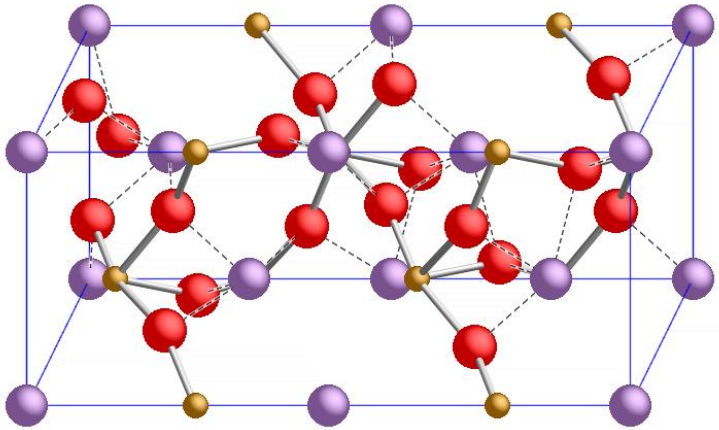
Image taken from:
http://www.esrf.eu/UsersAndScience/Publications/Highlights/2009/elecstrmag

A-FeO_3 Systems

$SrFeO_3$
Cubic Perovskite

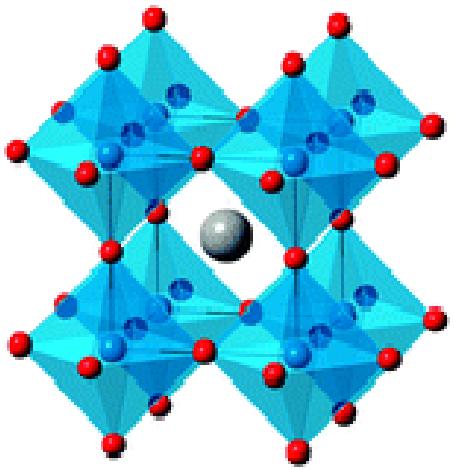


$BiFeO_3$- The novel multiferroic!
Rhombohedral Perovskite



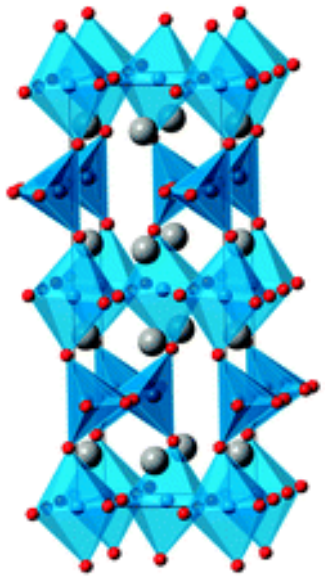
Strontium
Bismuth
Oxygen
Iron

Topotactic Route- Hydride Reduction Reactions



$SrFeO_3$

+ CaH_2 → (280°C, 24 hrs)



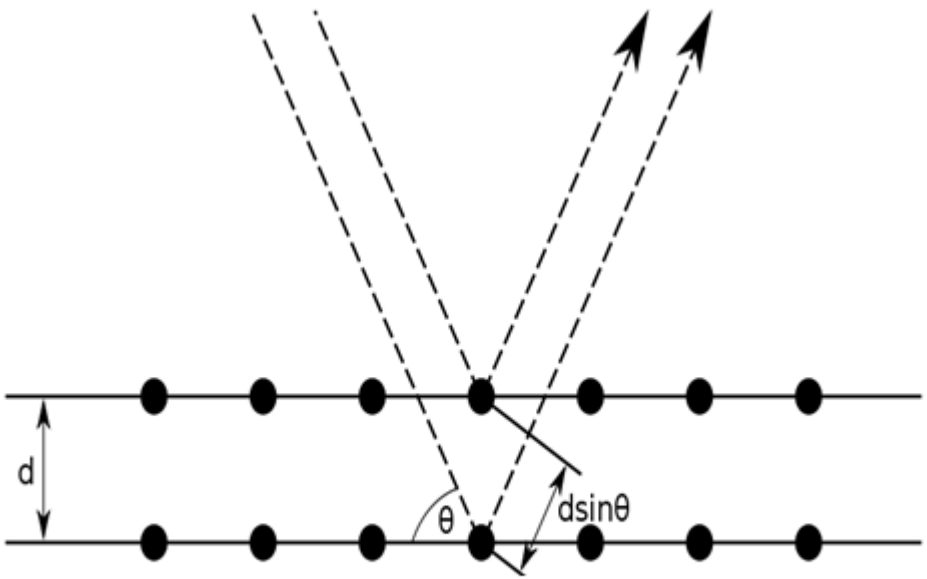
$SrFeO_{2.5}$

Y. Tsujimoto, C. Tassel, N. Hayashi, T. Watanabe, H. Kageyama, *et al*, Nature Letters, **2007**, *450*, 1062-1065

Project Goals

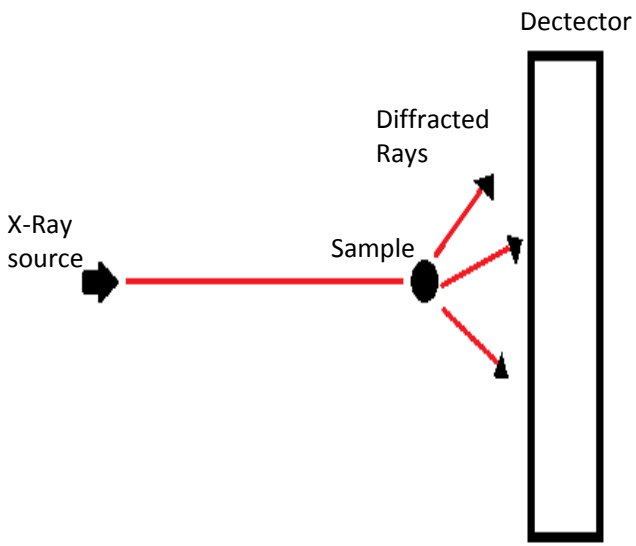
- Reduce $BiFeO_3$ to $BiFeO_{3-\delta}$
- Intercalate between layers of $SrFeO_2$
  - Organics have been intercalated in layered titanates, try to replicate with iron oxides
  - Other inorganic ligands to prepare mixed anion materials
- Change magnetic and chemical properties of starting perovskite iron oxides

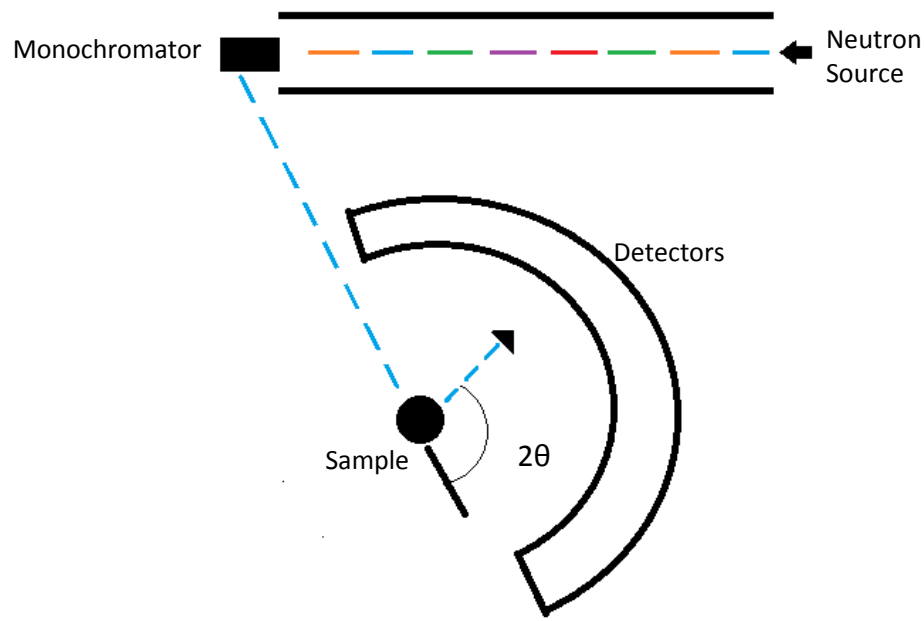
Diffraction of Crystals



Braggs Law: $2d\sin\theta = n\lambda$

X-Rays vs Neutrons





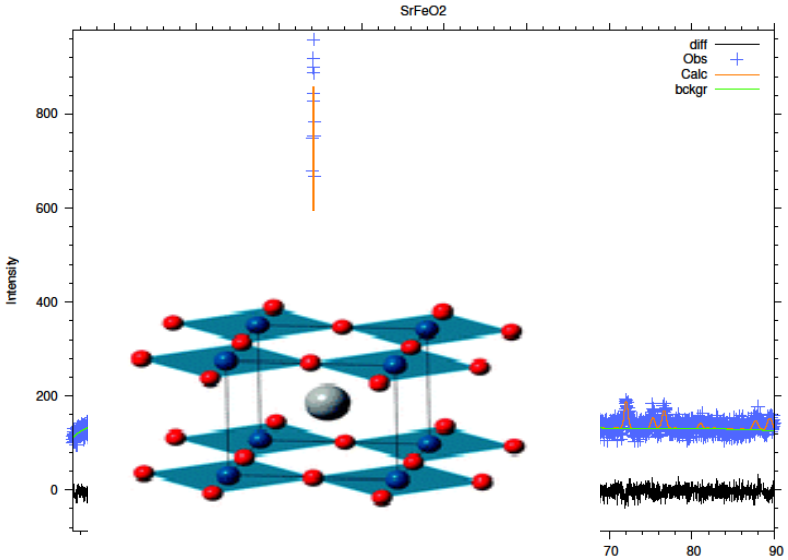
- Need less sample
- Cheaper
- Better for initial characterization

- More accurate
- Sensitive to lighter elements
- Magnetic information

Rietveld Refinement

BT1 Powder Diffractometer

- Lattice Parameters
- Occupancies



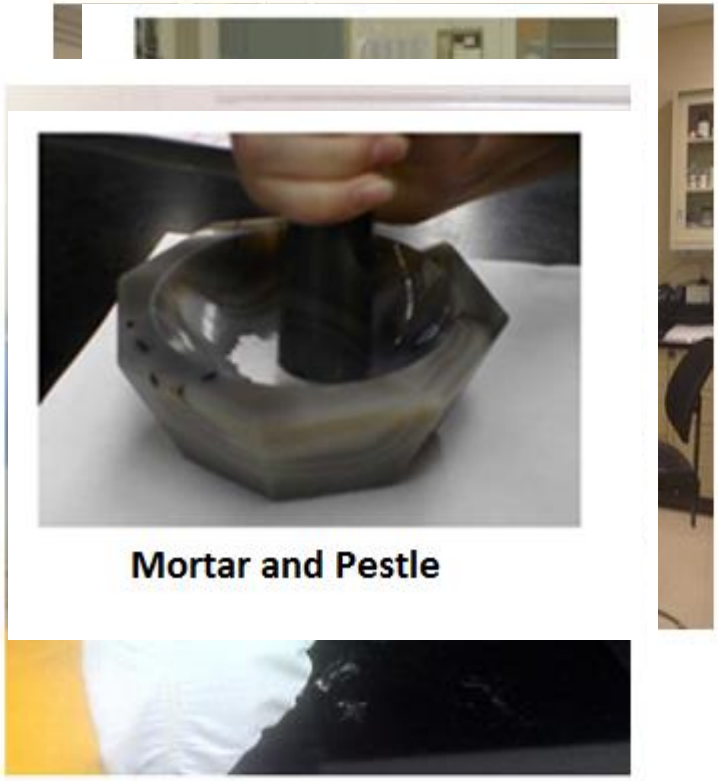
Solid State Synthesis-$SrFeO_2$

$$SrCO_3 + 0.5\ Fe_2O_3 \xrightarrow[\text{12 hrs}]{\text{1200°C}} SrFeO_3 + CO_2$$

$$SrFeO_3 + CaH_2 \xrightarrow[\text{24 hrs}]{\text{280°C}} SrFeO_2 + Ca(OH)_2$$

(Sealed tube rxn)

Wash with 0.15M
NH_4Cl/ Methanol solution
to remove Calcium Hydroxide
and excess Calcium Hydride



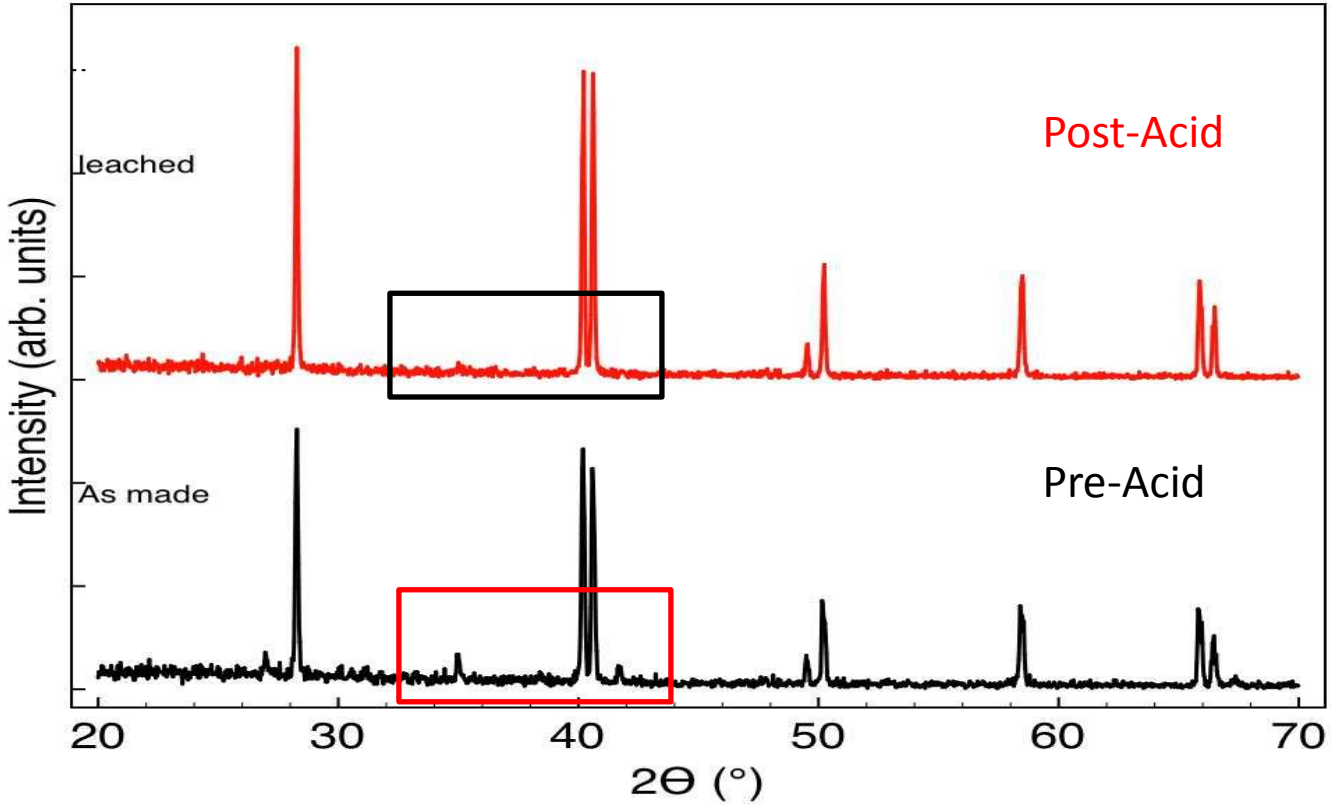
Mortar and Pestle

Flame Torch

Vacuum Line

Solid State Synthesis- $BiFeO_3$

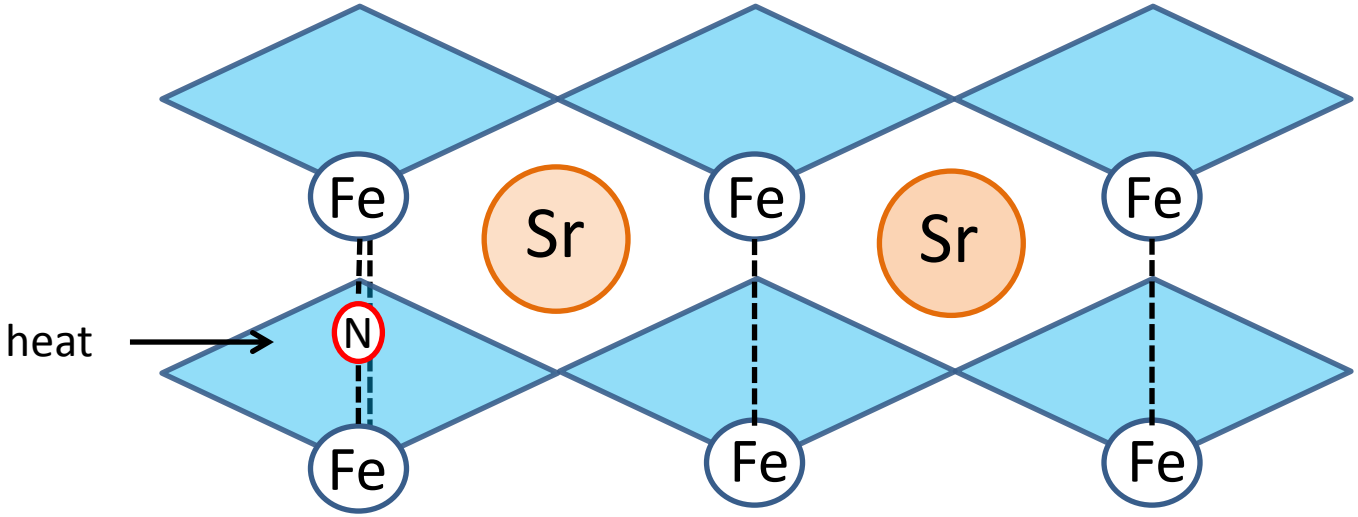
$$1.06\ Bi_2O_3 + Fe_2O_3 \rightarrow BiFeO_3 + \alpha Bi_{25}FeO_{40} \xrightarrow{2.5M\ HNO_3} BiFeO_3 + \text{waste}$$



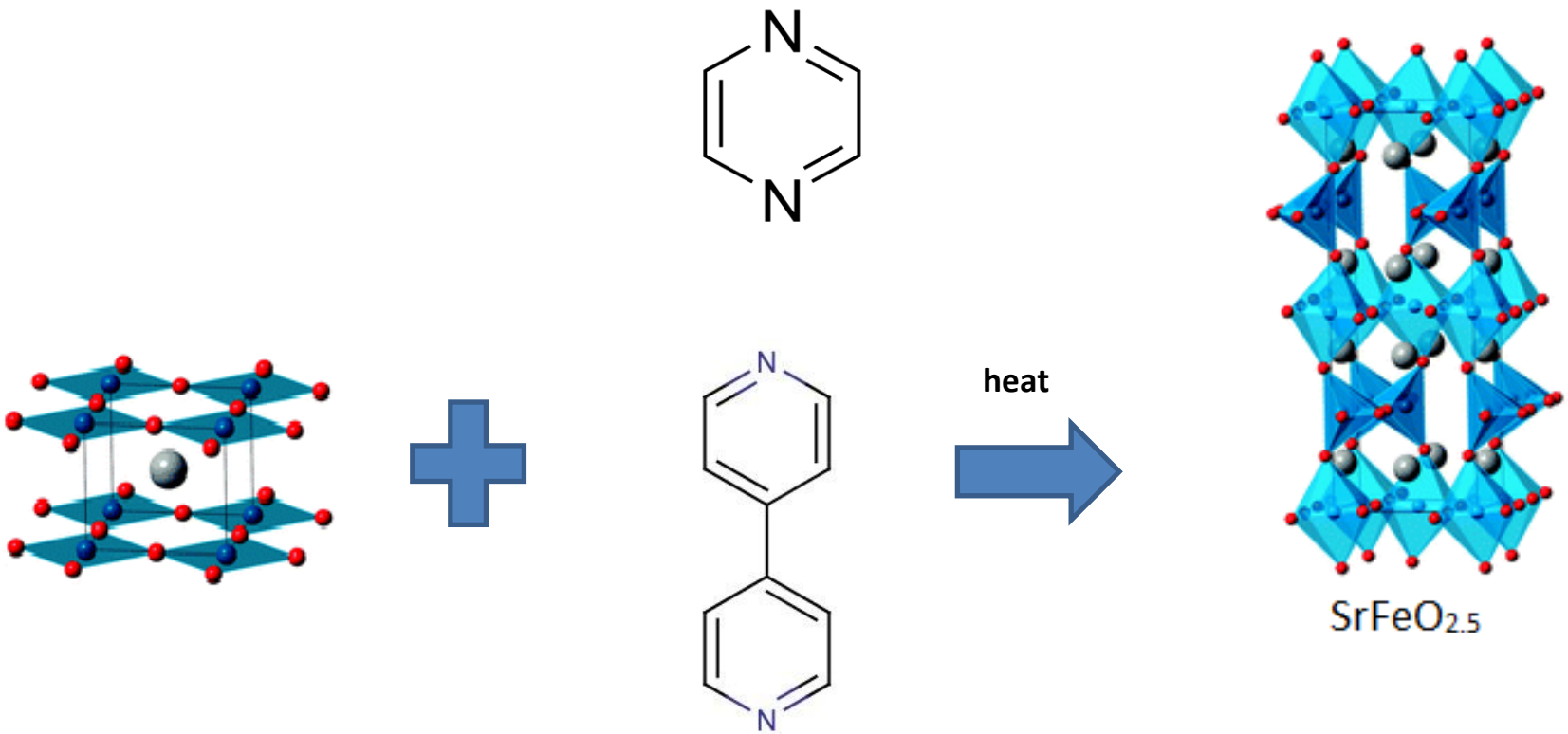
*iron source XRD

Intercalating $SrFeO_2$

Pyridine has been intercalated in layered titanates through vapor reactions

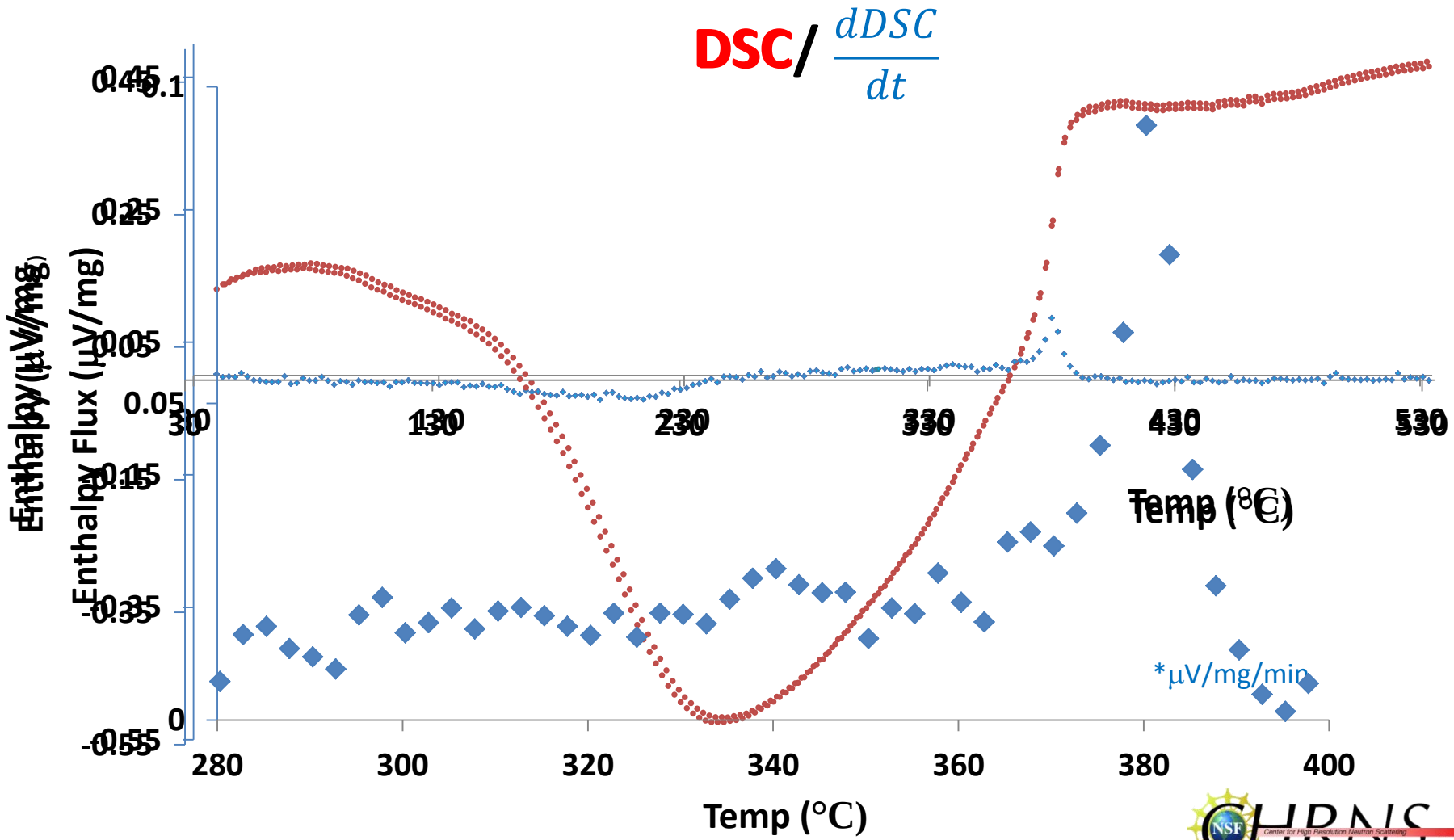


$SrFeO_2$ Reactions With Various Ligands



S^{2-}

$SrFeO_2$ goes to Brownmillerite



$BiFeO_3$ Reduction Reactions

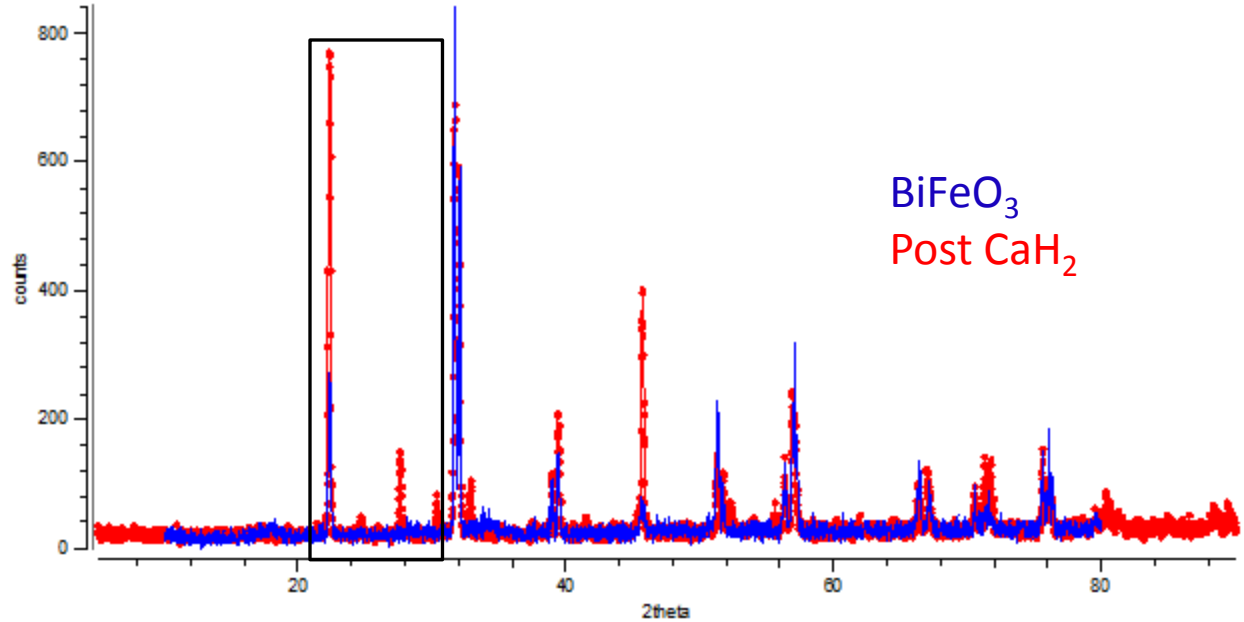
- $BiFeO_3$ +CaH_2
- $BiFeO_3$ +NaH
- Various temperatures
- Various reaction times

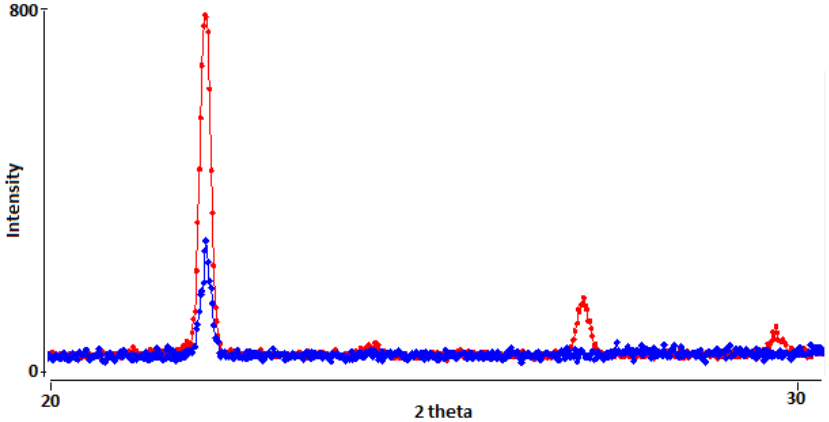
Stirred/ heated in solution

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

Thanks to:

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- 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?