STRUCTURAL STUDIES OF MULTIFERROIC THIN FILMS

Lisa Krayer (UCSD)

Mentor: Daniel Pajerowski (NIST)

Collaborating with:

(University of Florida)

Professor Amlan Biswas

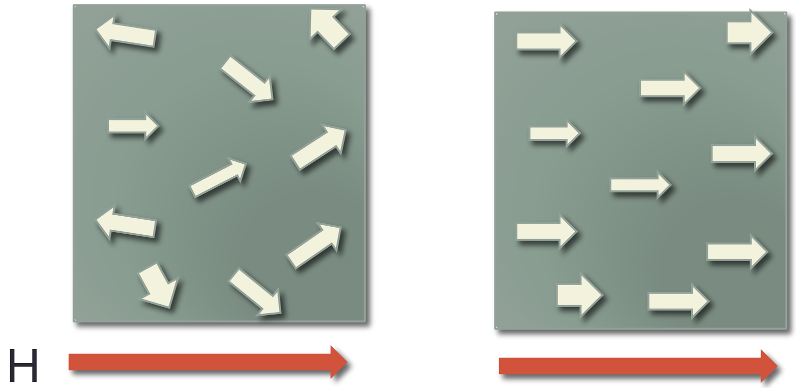
Daniel Grant

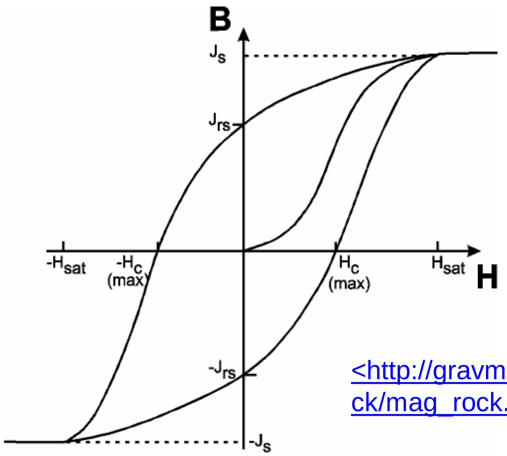
NCNR

<http://www.ncnr.nist.gov/instruments/dcs/>

Ferroicity

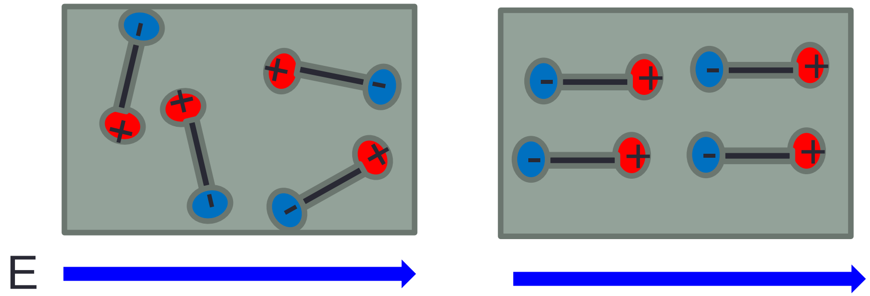
Ferromagnetism

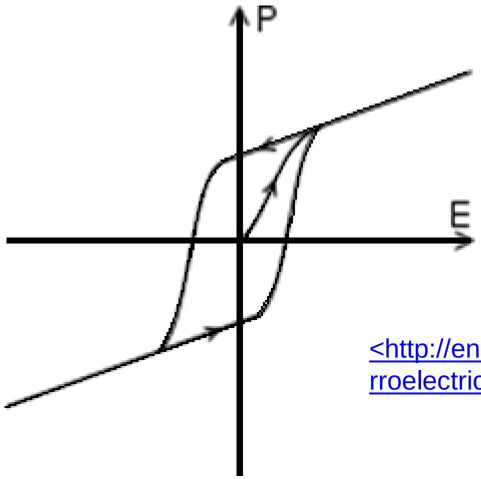




<http://gravmag.ou.edu/mag_rock/mag_rock.html>

Ferroelectricity





<http://en.wikipedia.org/wiki/Ferroelectricity>

Magnetoelectric

$$\alpha_{\eta\xi}/4\pi < (\chi_{\eta\eta}\kappa_{\xi\xi})^{1/2}.$$

$\chi_{\eta\eta}$: Magnetic Susceptibility Tensor

$\kappa_{\xi\xi}$: Electric Susceptibility Tensor

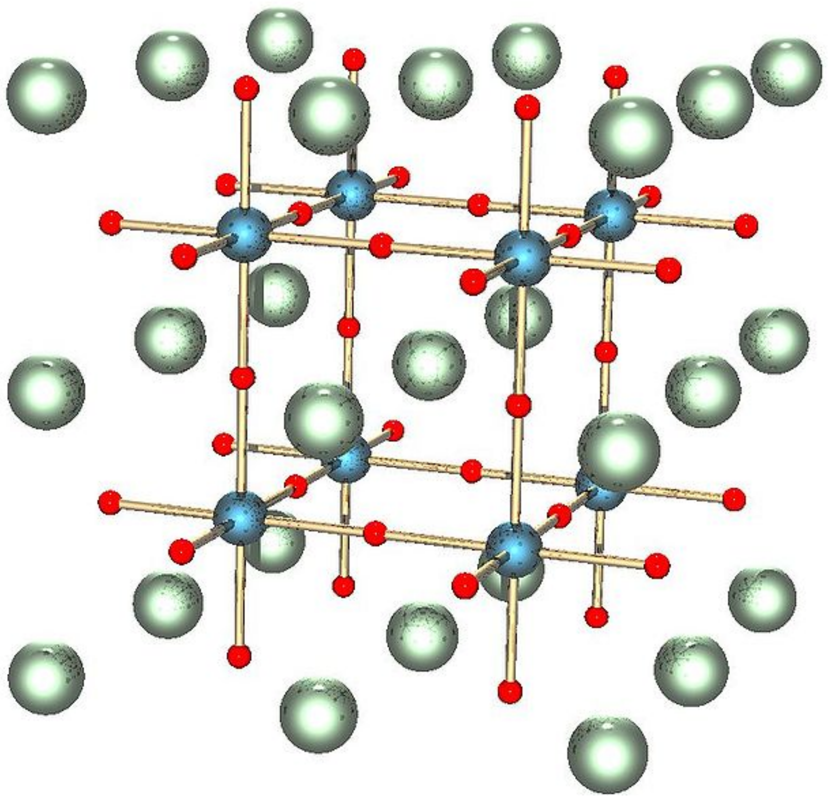
W. F. Brown, Jr., R. M. Hornreich and S. Shtrikman. **Phys. Rev. 168**, 2 (1968) 574-577.

Perovskite Structure (ABO_3)

A-Site Atoms

B-Site Atoms

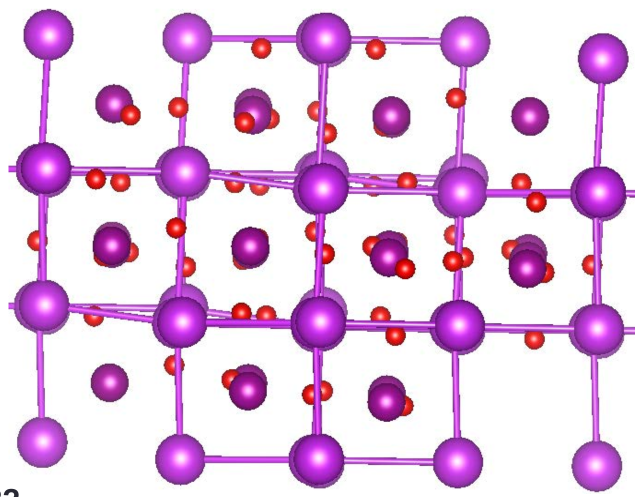
Oxygen Atoms



<http://en.wikipedia.org/wiki/Perovskite_(structure)>

$BiMnO_3$

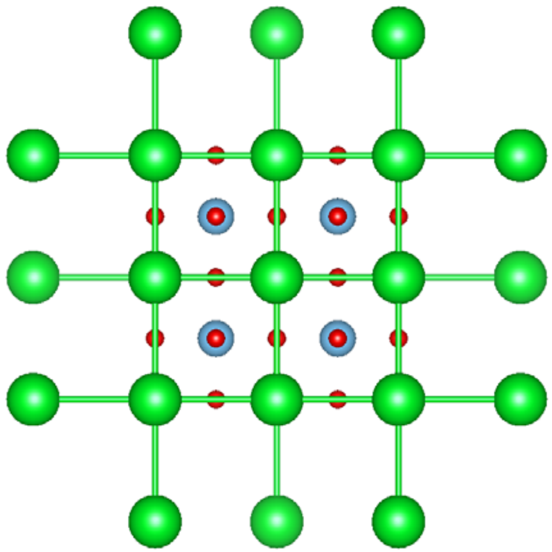
- Distorted perovskite structure.
- Multiferroic (Magnetoelectric).



Boukhvalov, D.W.; Solovyev, I.V. Phys. Rev. Serie 3. B – Cond. Matt. **82**, (2010) 245101-1.

$SrTiO_3$ (Substrate)

- Perovskite structure.

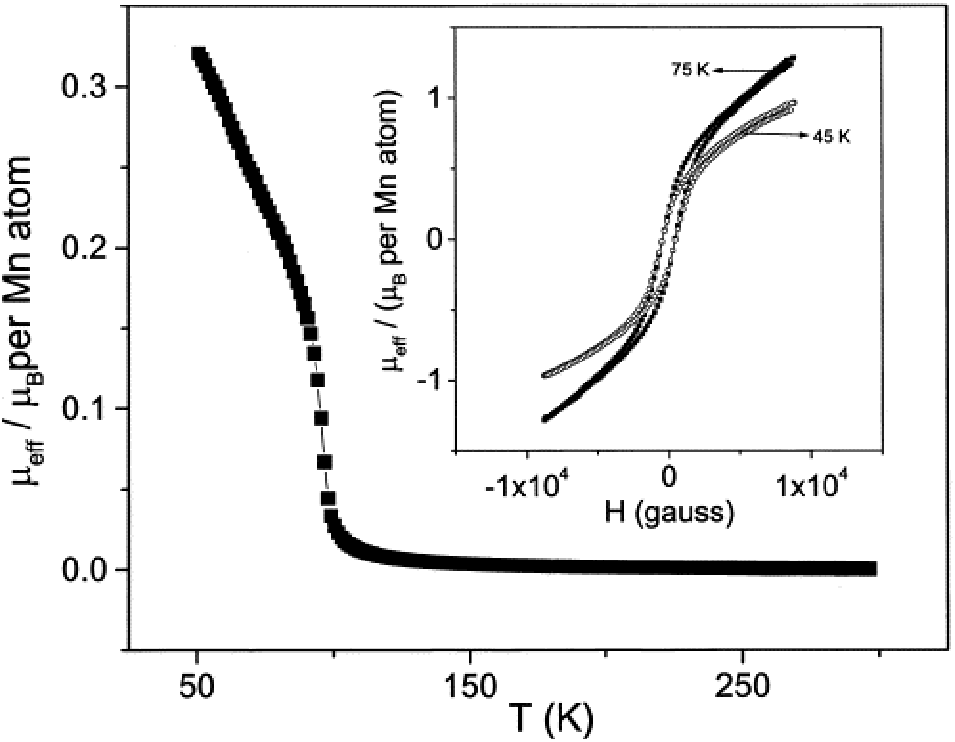


Brous, J.; Fankuchen, I.; Banks, E. **Acta Cryst**. **6**, (1953) 67-70.

K. Momma and F. Izumi, "VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data," *J. Appl. Crystallogr.*, 44, 1272-1276 (2011).

Bulk (Powder) $BiMnO_3$

- 3GPa, 1100K for synthesis.
- Msat = 3.6 μ_B/Mn at 5 K
- Tc = 105 K
- Ps = 62 $\mu C/cm^2$ at 87K



A. Moreira dos Santos, S. Parashar, A.R. Raju, Y.S. Zhao, A.K. Cheetham, C.N.R. Rao, **Solid State Commun. 122**, (2002) 1–2.

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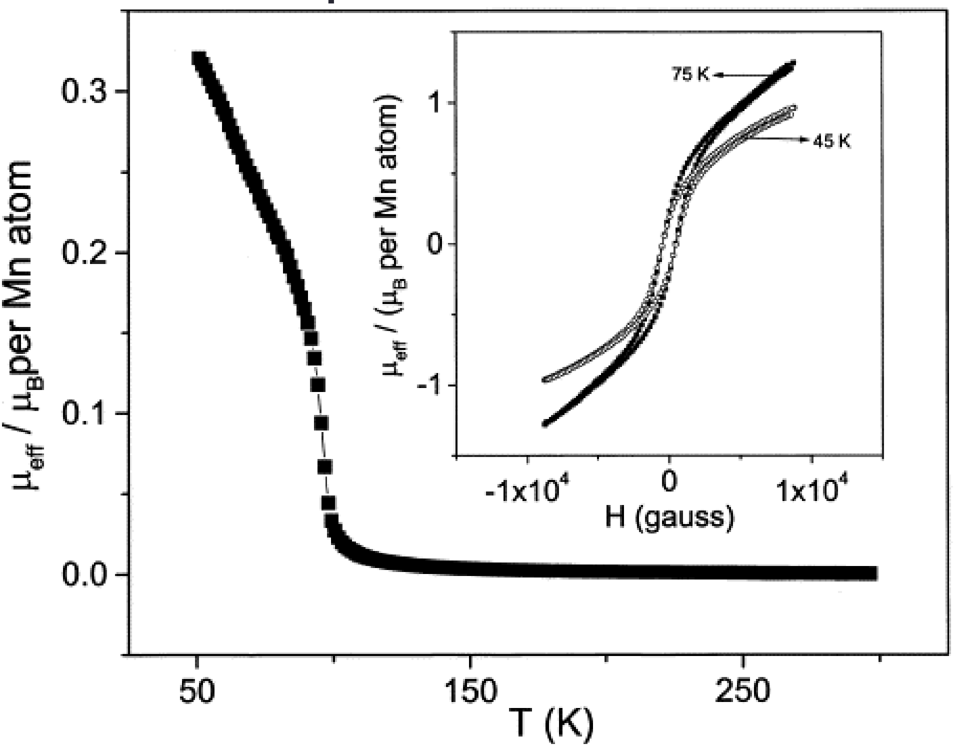
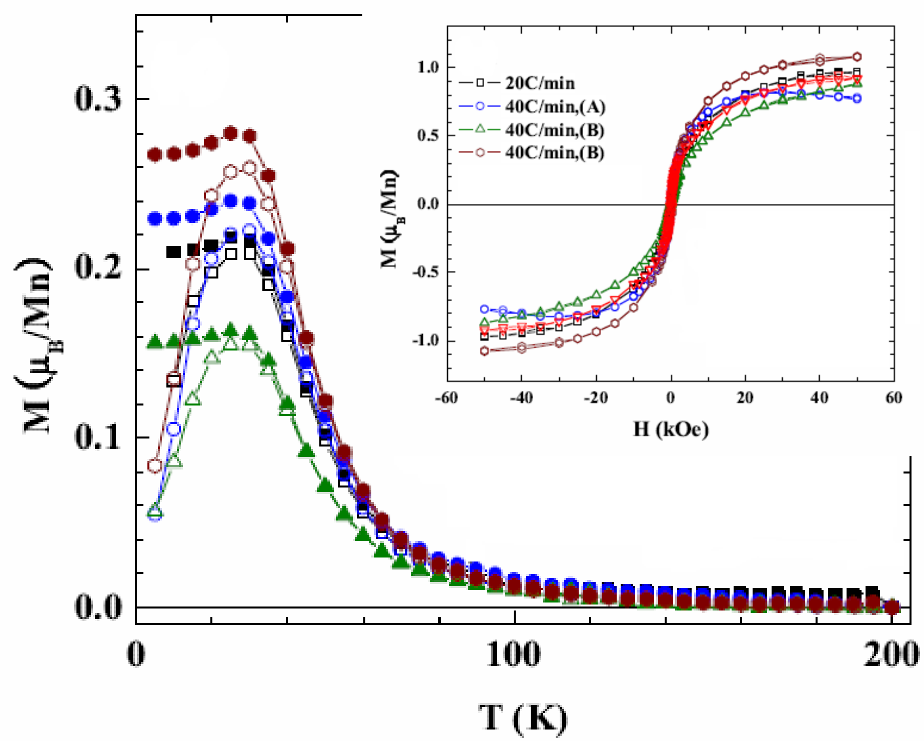


A. Moreira dos Santos, S. Parashar, A.R. Raju, Y.S. Zhao, A.K. Cheetham, C.N.R. Rao. **Solid State Commun. 122**, 1–2, (2002)

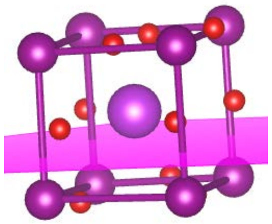
Film $BiMnO_3$

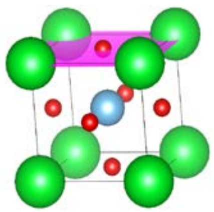
- Pulsed Laser Deposition.
- Msat = 1 μ_B/Mn at 5 K
- Tc = reduced / smeared
- Ps = 16 $\mu C/cm^2$ at 87K



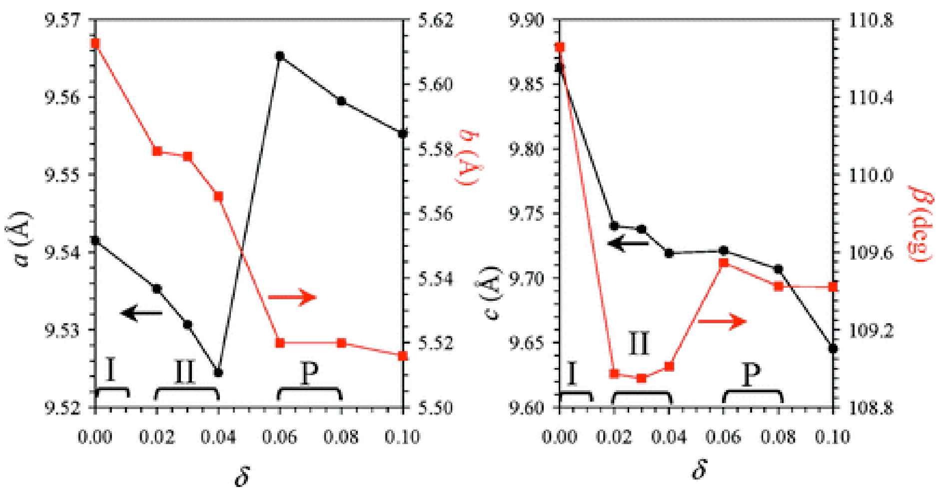
Why is there a difference between the bulk and the film form of $BiMnO_3$?

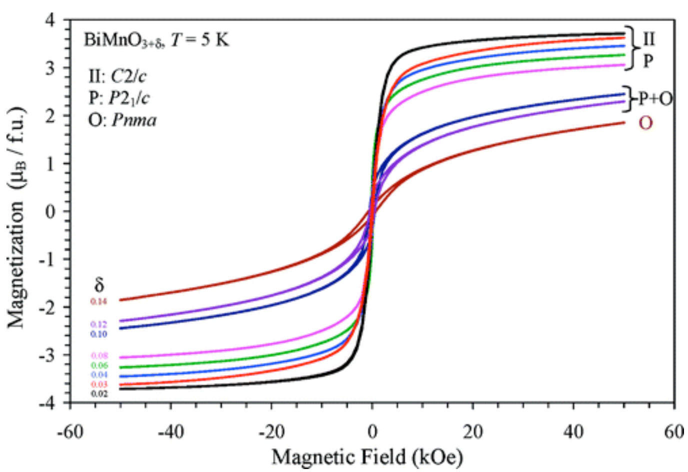
Hypotheses





1. Strain from substrate
   - 1 0 0 $SrTiO_3$ plane binds with 1 1 1 $BiMnO_3$ plane
   - Magnetic moment reduced from change in geometric shape.
2. Unstoichiometric composition
   - Magnetic Properties dependent on stoichiometry ($BiMnO_{3+\delta}$)
     - Magnetic moment is reduced with increased oxygen content.
     - Requires Polarized Neutron Reflectivity to find the magnetic moment as a function of depth.





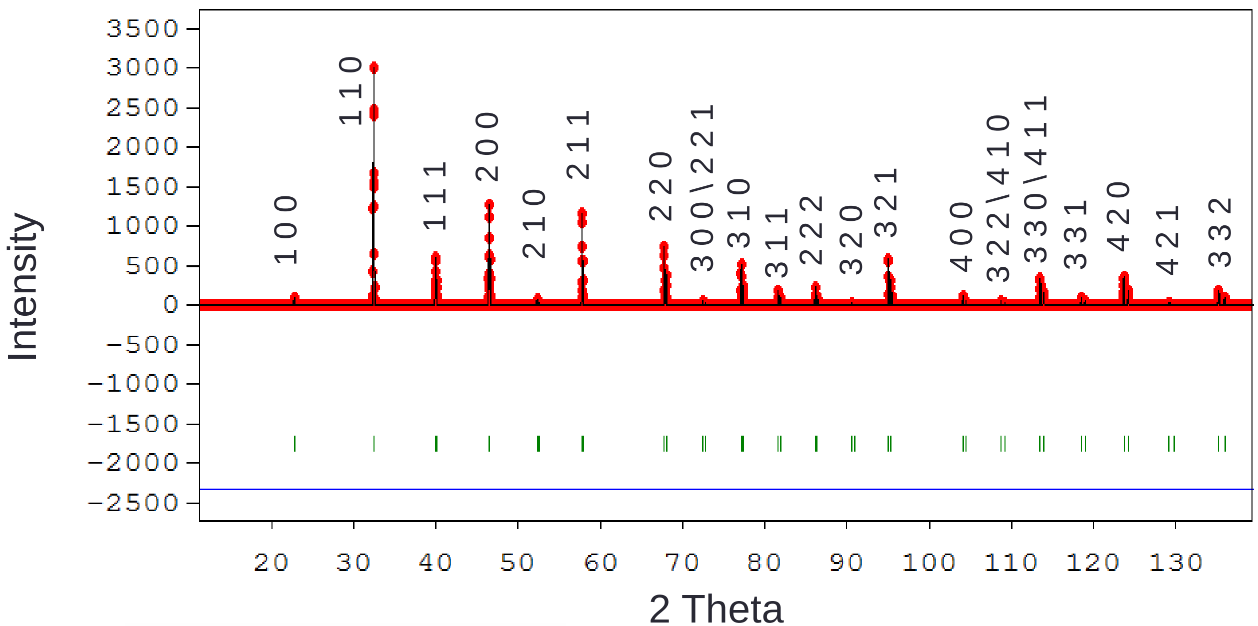
Alexei A. Belik, Katsuaki Kodama, Naoki Igawa, Shin-ichi Shamoto, Kosuke Kosuda and Eiji Takayama-Muromachi**. J. Am. Chem. Soc**. 132, (2010), 8137-8144.

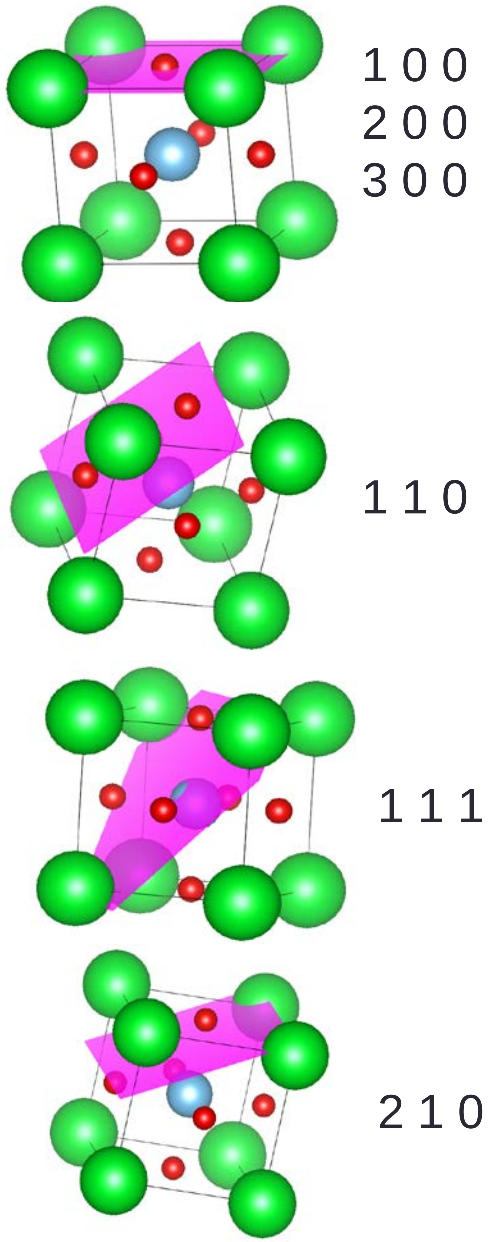
Attacking the Problem

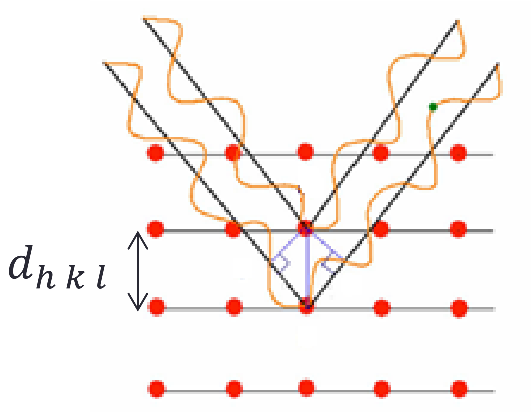
- Diffraction
  - Growth orientation
  - Lattice parameters
- Atomic Force Microscopy
  - Surface roughness
- Reflectometry
  - Roughness
  - Thickness
  - Density as a function of depth.
- X-Ray Photoelectron Spectroscopy
  - Atomic composition as a function of depth

X-Ray Diffraction

Powder Diffraction Peaks of $SrTiO_3$



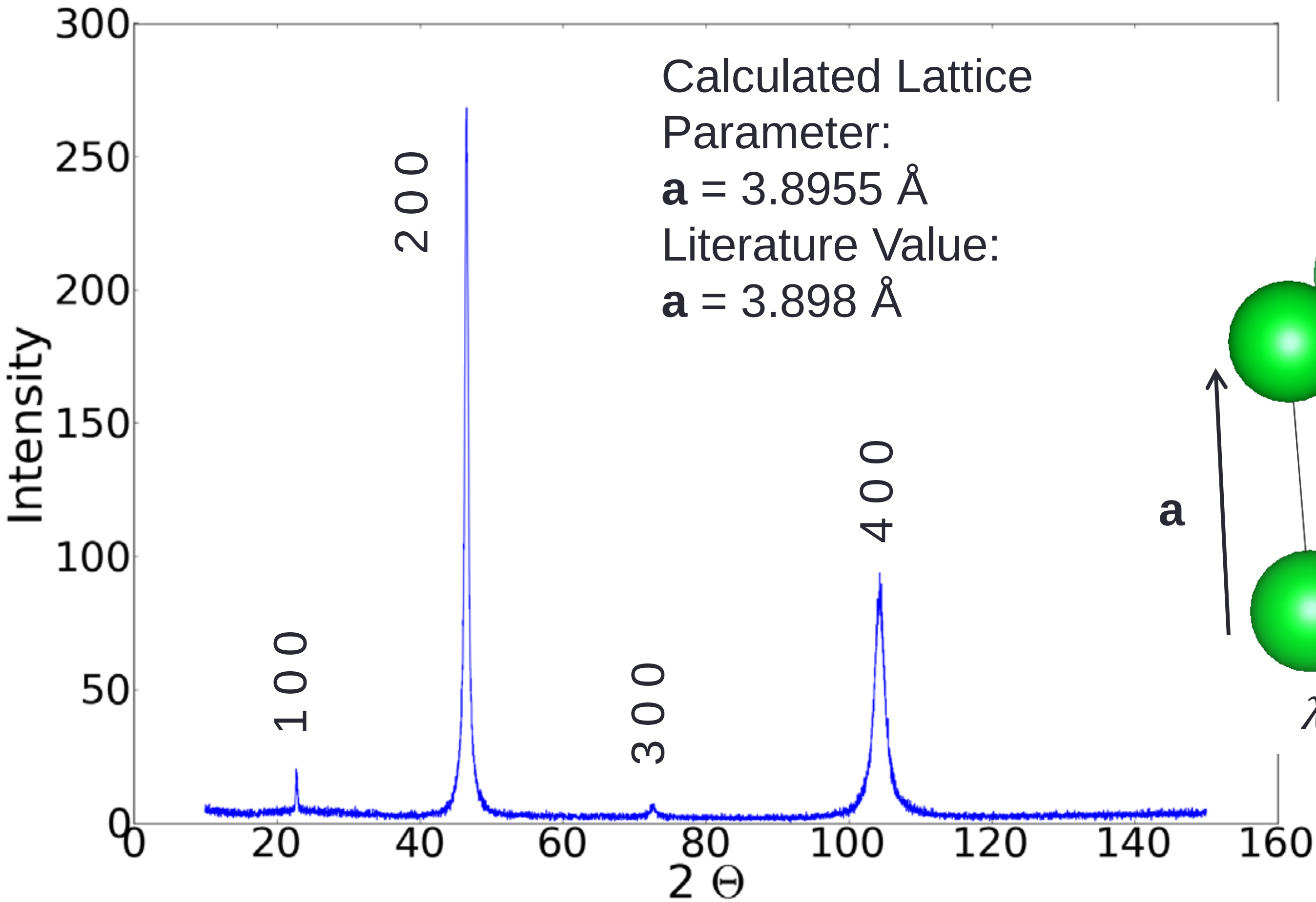




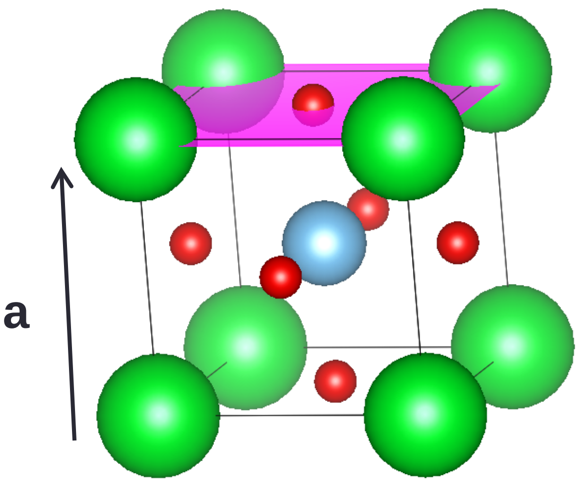
$$\lambda = 2\, d_{h\,k\,l}\, \sin\theta$$

Brous, J.; Fankuchen, I.; Banks, E. **Acta Cryst. 6**, (1953) 67-70.

$SrTiO_3$ X-ray Diffraction (XRD) Data

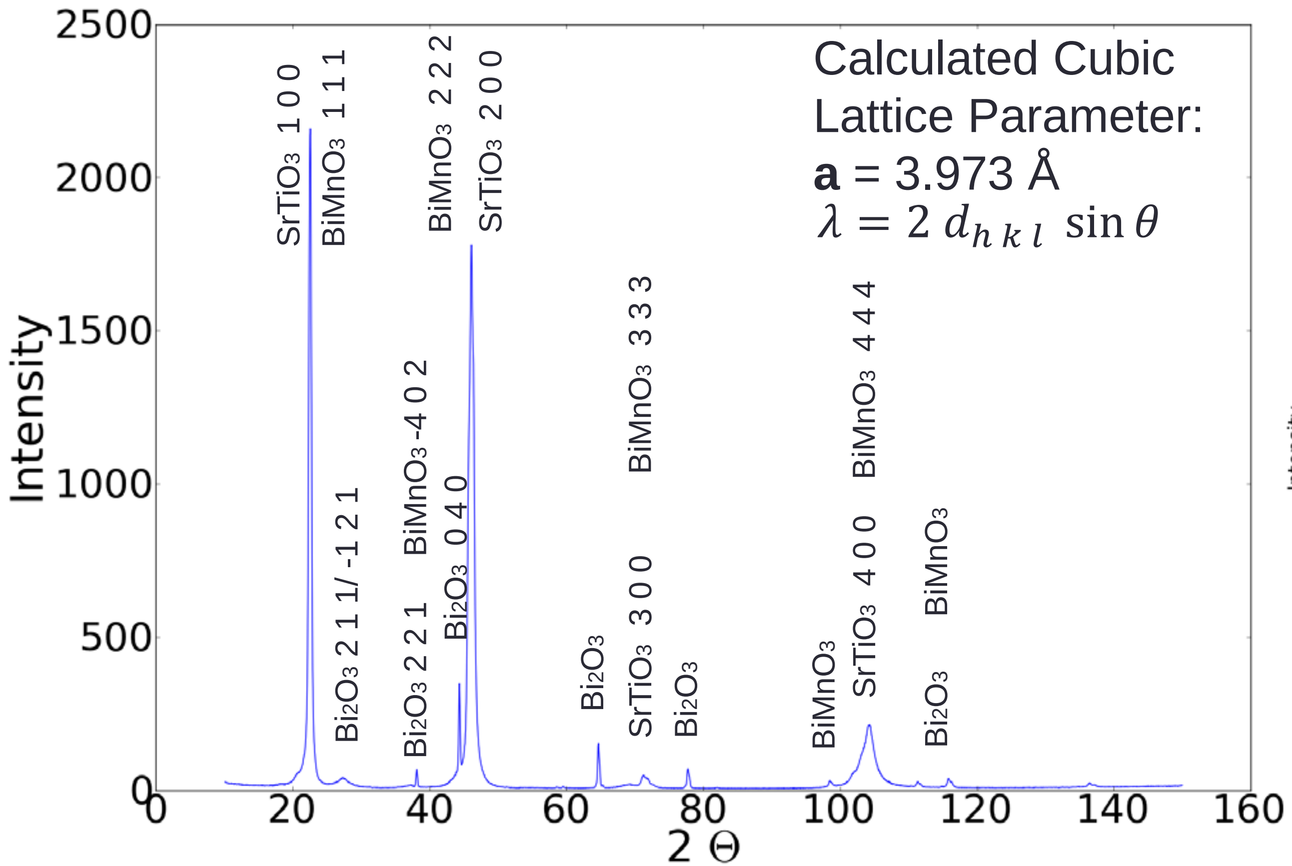


Calculated Lattice Parameter:
a = 3.8955 Å
Literature Value:
a = 3.898 Å



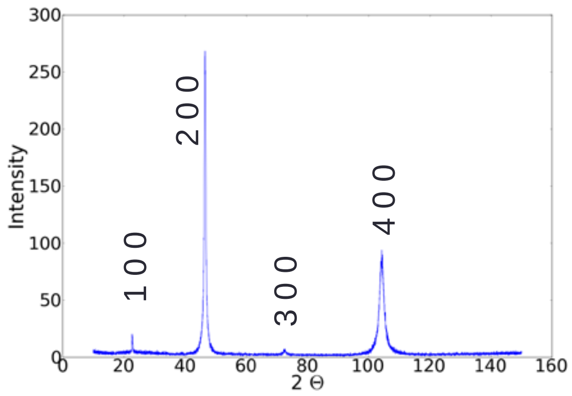
$$\lambda = 2\,a\sin\theta$$

BiMnO$_3$ X-ray Diffraction Data

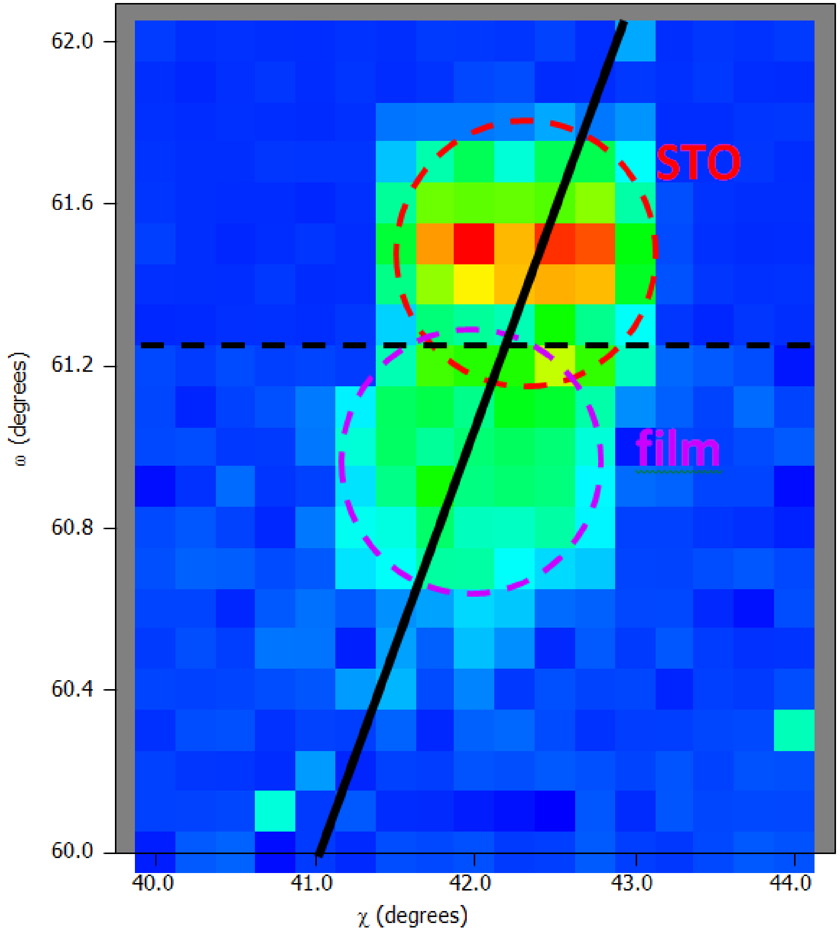


$$\lambda = 2\, d_{h\,k\,l}\, \sin\theta$$

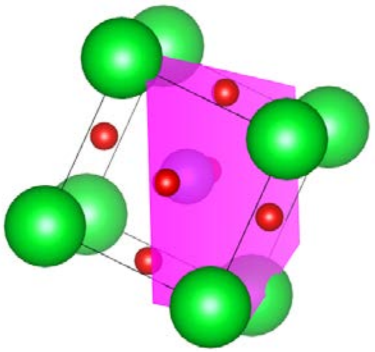
SrTiO$_3$ XRD Data



X-Ray Diffraction Mesh Scan



- {2 1 1} $SrTiO_3$ Plane



- Rocking Curves:

$$\lambda = 2\, d_{h\,k\,l}\, \sin\theta$$

  - a_{SrTiO_3} = 3.898 Å (literature)
  - a_{BiMnO_3} = 3.946 Å in plane (calculated)
    - Elongated out of plane.
- Epitaxial Growth.

Atomic Force Microscopy

Roughness Analysis

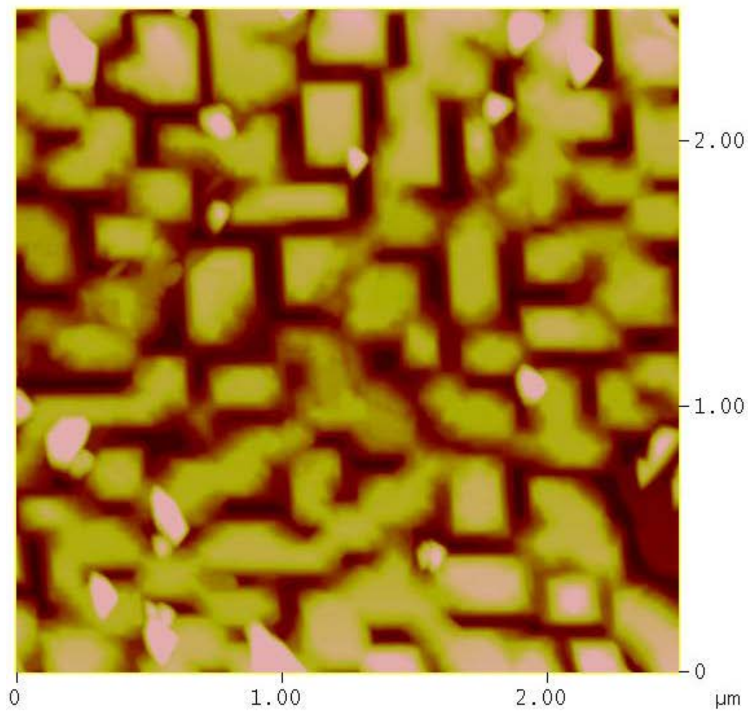
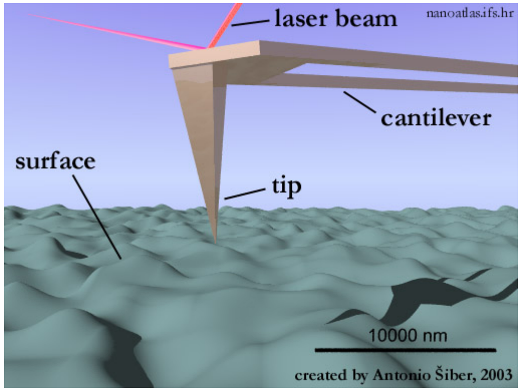


Image Statistics

Img. Z range	163.19 nm
Img. Rms (Rq)	12.894 nm

Box Statistics

Rms (Rq)



<http://www.nanotech-now.com/Art_Gallery/antonio-siber.htm>

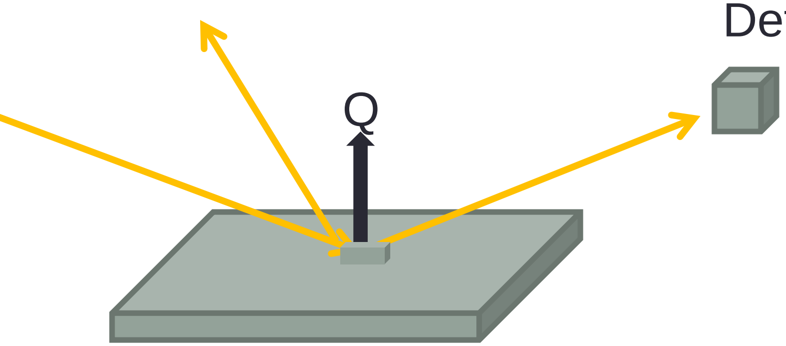
Crevices are calculated to make up 20% of the sample.

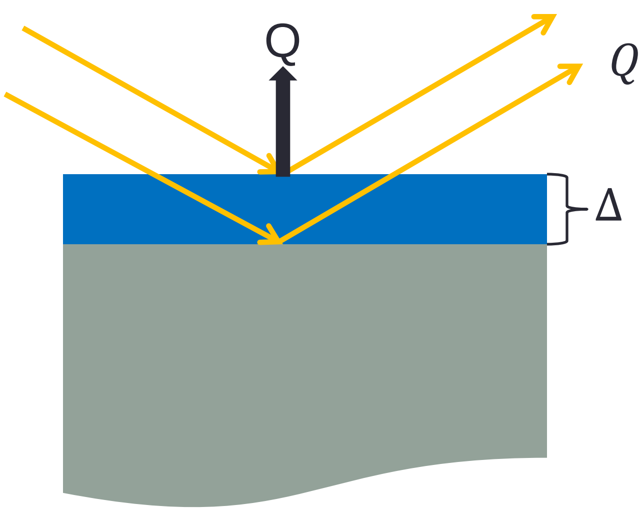
Refectometry

$$\rho = \frac{\sum_{i=1}^{n} b_c}{V_m}$$

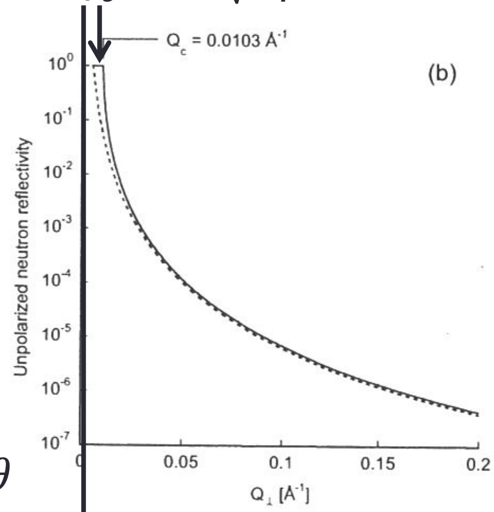
$$\rho = \frac{\sum_{i=1}^{n} Z\, r_e}{V_m}$$

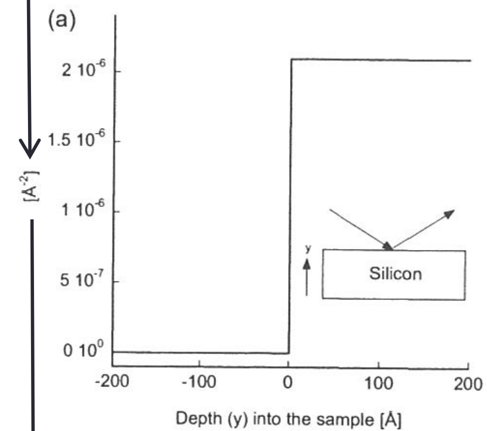
$$Q_c = 4\sqrt{\pi\rho}$$

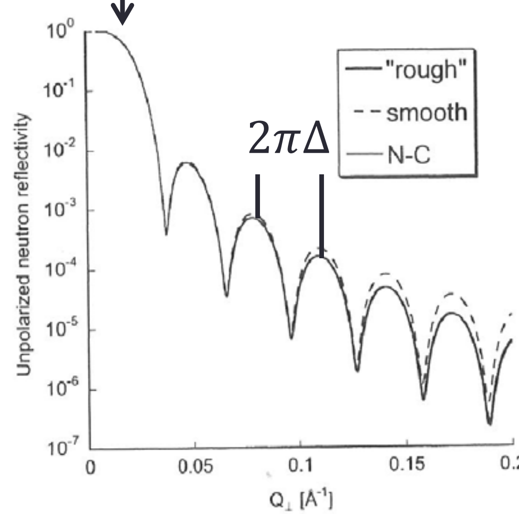


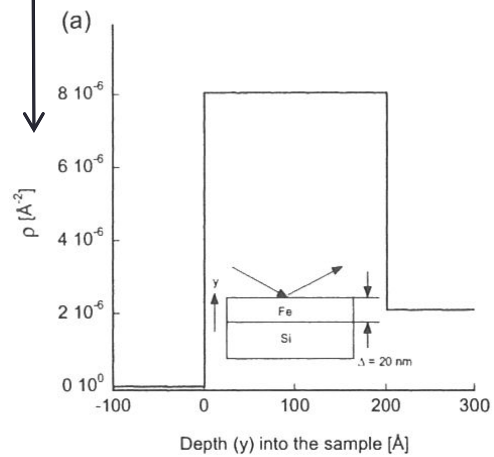


$$Q = \frac{4\,\pi}{\lambda}\sin\theta$$



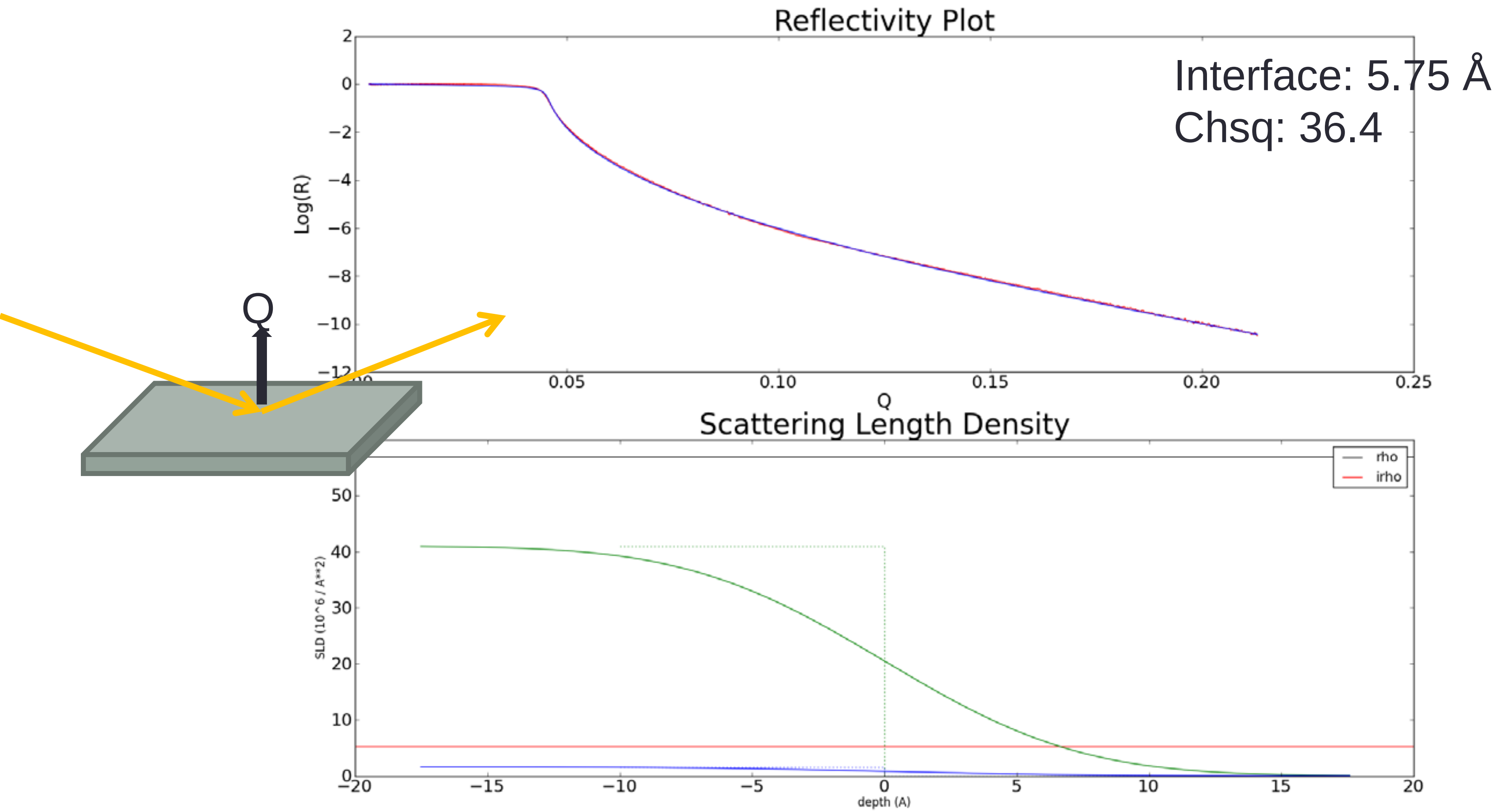




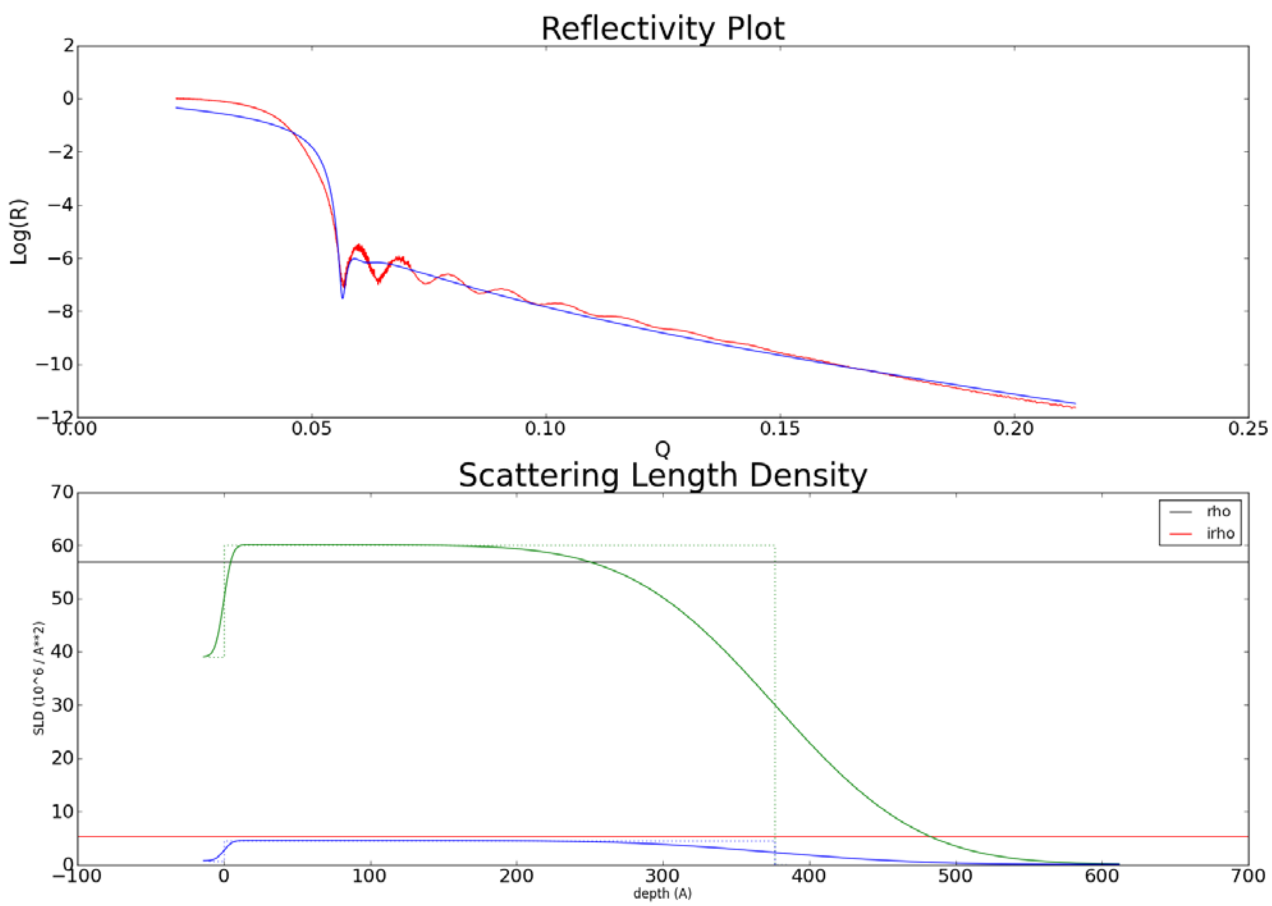


"Modern Techniques for Characterizing Magnetic Materials." Ed. By Yimei Zhu. Kluwer Acad. Publishers (2005).

$SrTiO_3$ X-ray Reflectometry Data



BiMnO$_3$ X-ray Reflectometry Data

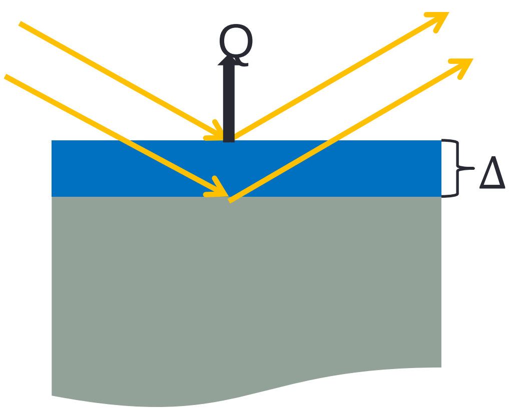


1 Layer of BiMnO$_3$

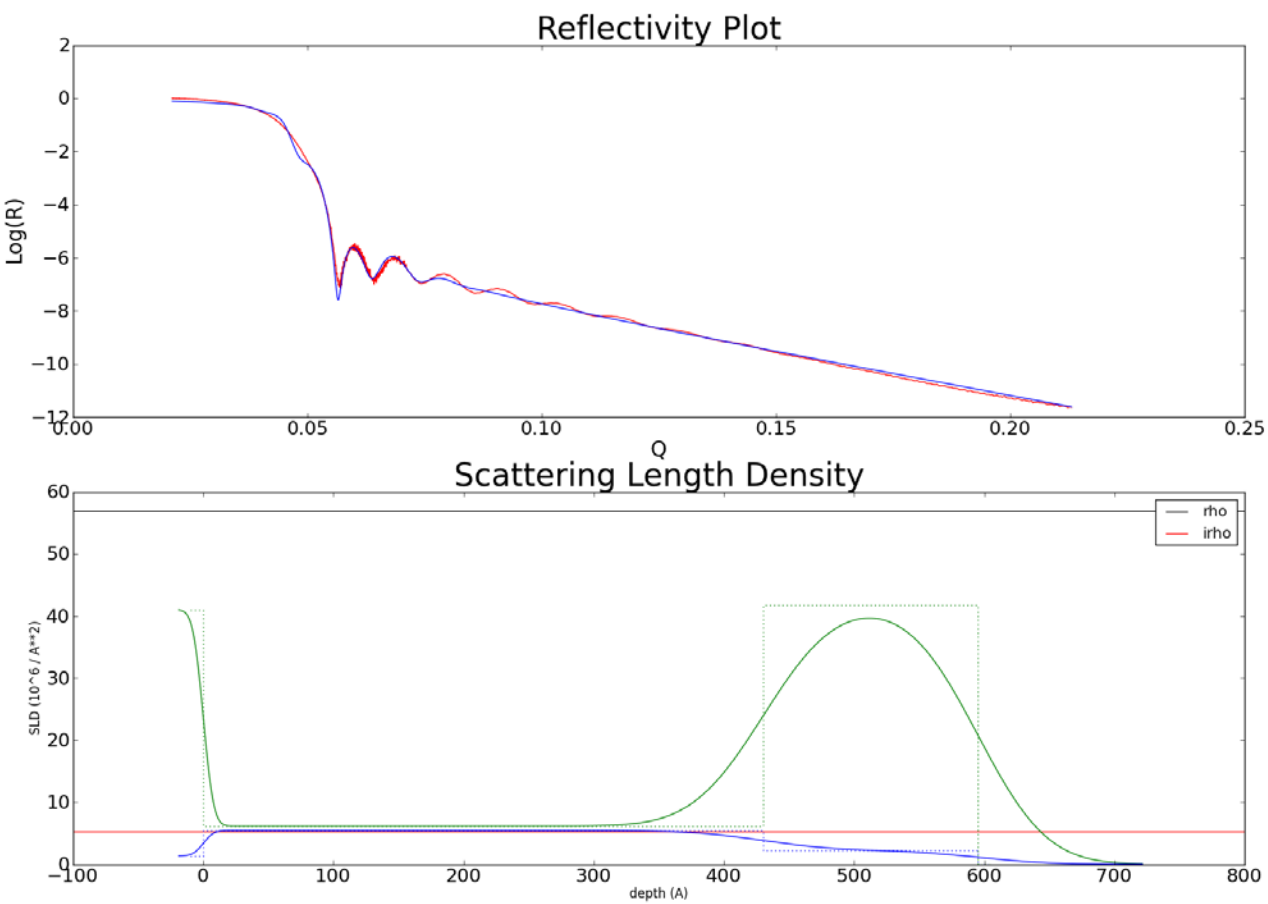
Chsq: 271.5

Thickness: 376 Å

Interface: 78.4 Å



BiMnO$_3$ X-ray Reflectometry Data



2 Layers of BiMnO$_3$

Chsq: 181.3

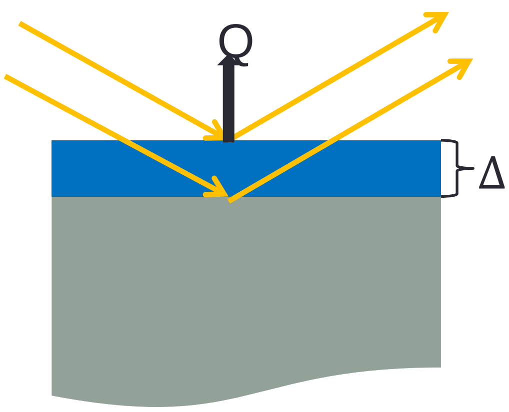
Total thickness: 594.6 Å

1st Layer thickness: 430 Å

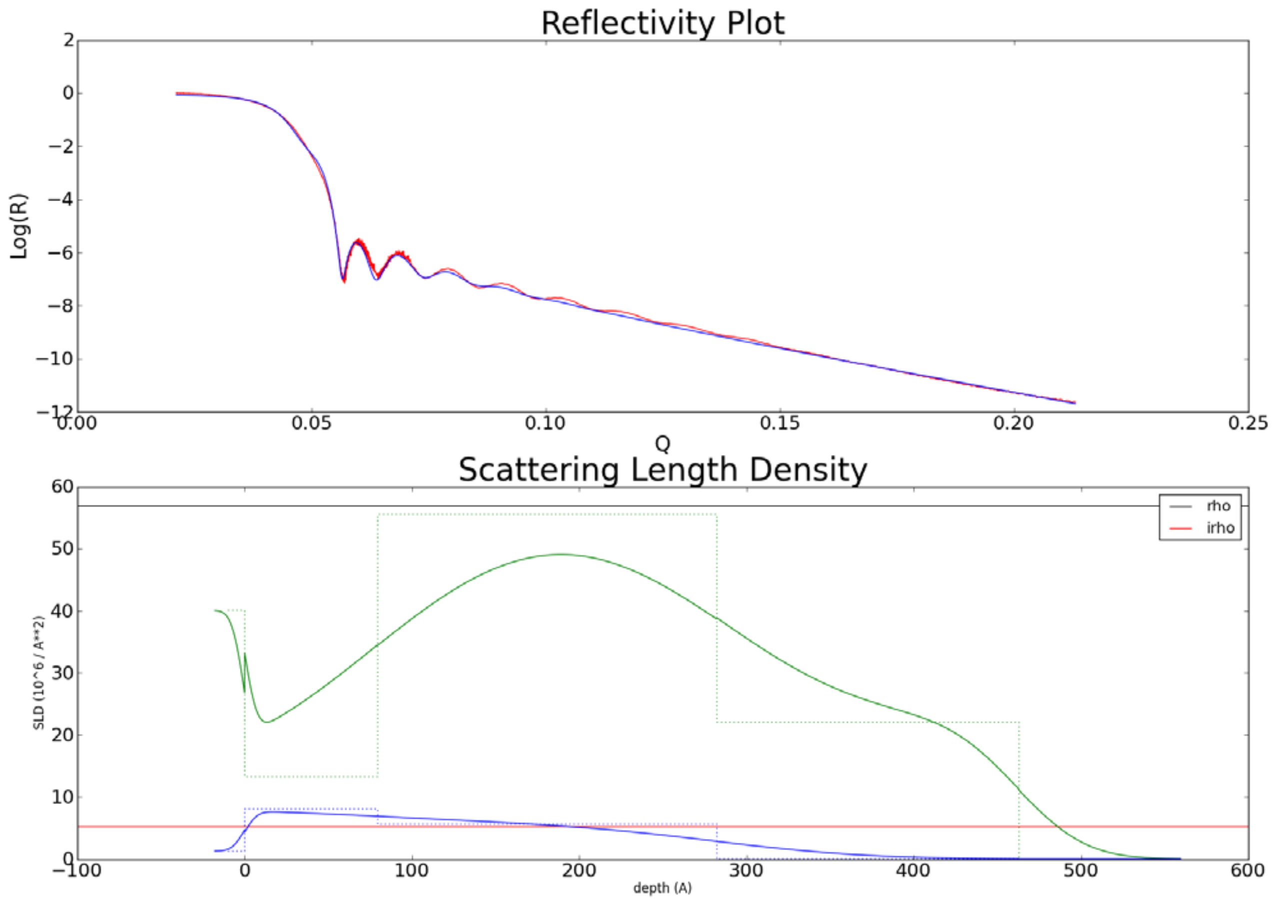
1st Layer interface: 43.4 Å

2nd Layer thickness: 164.6 Å

2nd Layer interface: 42.2 Å



$BiMnO_3$ X-ray Reflectometry Data



3 Layers of $BiMnO_3$

Chsq: 85.9

Total thickness: 594.6 Å

1st Layer thickness: 79.7 Å

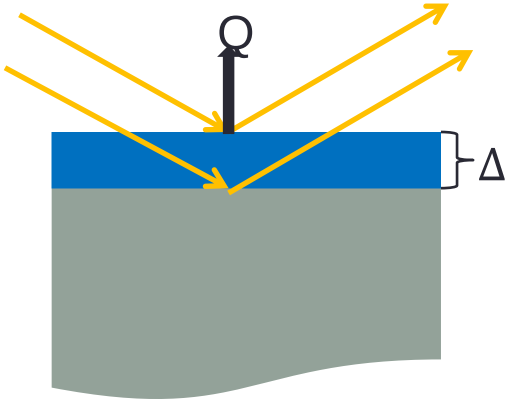
1st Layer interface: 77.5 Å

2nd Layer thickness: 202.2 Å

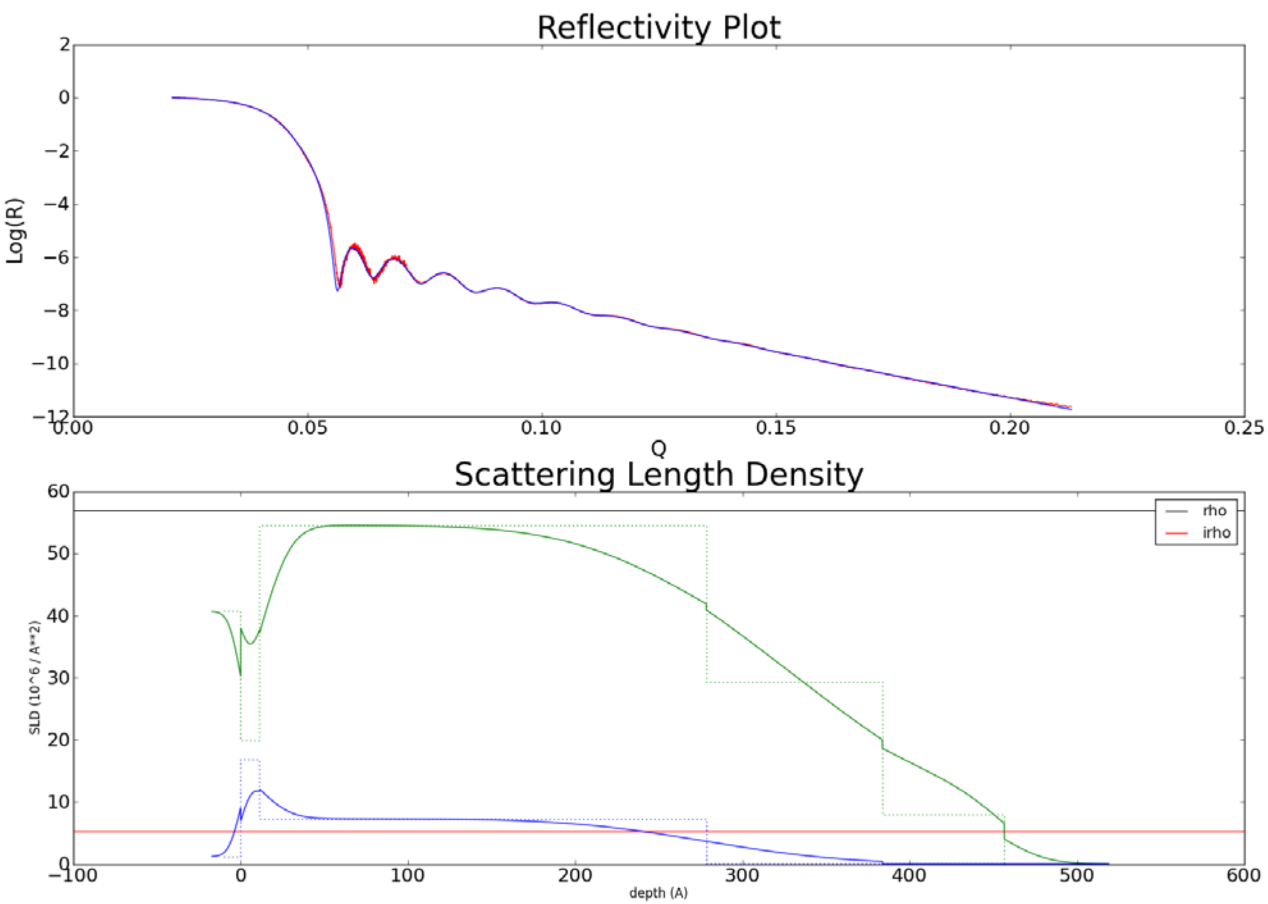
2nd Layer interface: 71.4 Å

3rd Layer thickness: 180.7 Å

3rd Layer interface: 32.2 Å



$BiMnO_3$ X-ray Reflectometry Data



4 Layers of $BiMnO_3$

Chsq: 36.4

Total thickness: 456.14 Å

1st Layer thickness: 11.14 Å

1st Layer interface: 15.04 Å

2nd Layer thickness: 266.6 Å

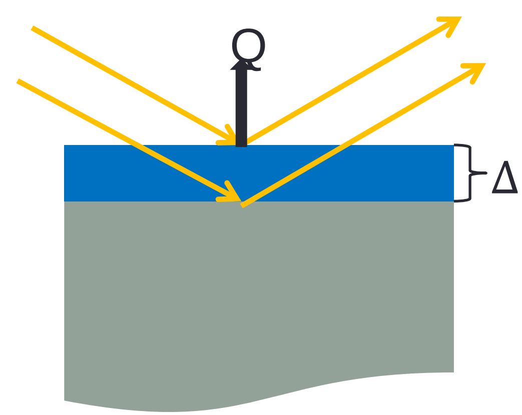
2nd Layer interface: 66.4 Å

3rd Layer thickness: 102.8 Å

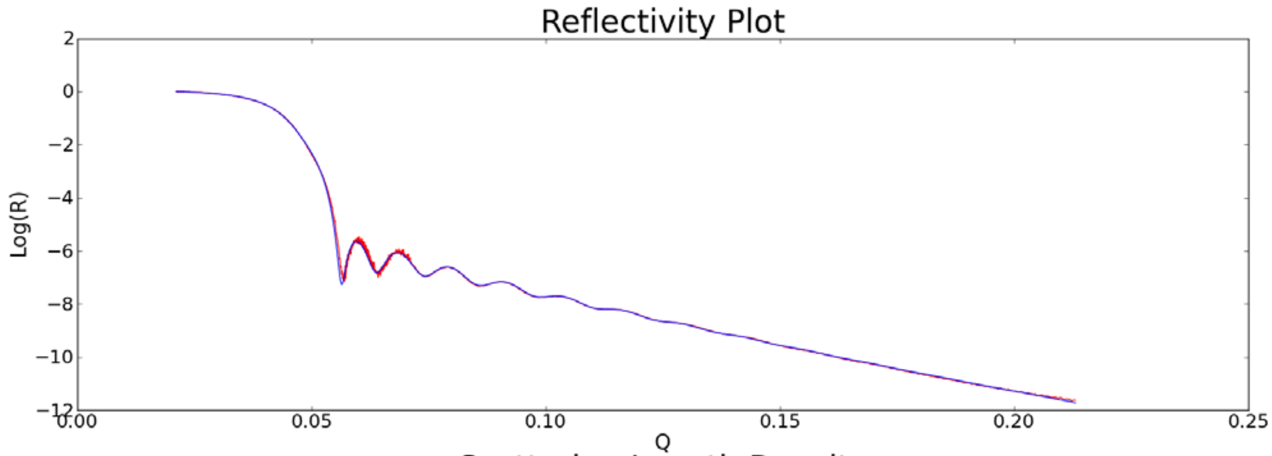
3rd Layer interface: 61.7 Å

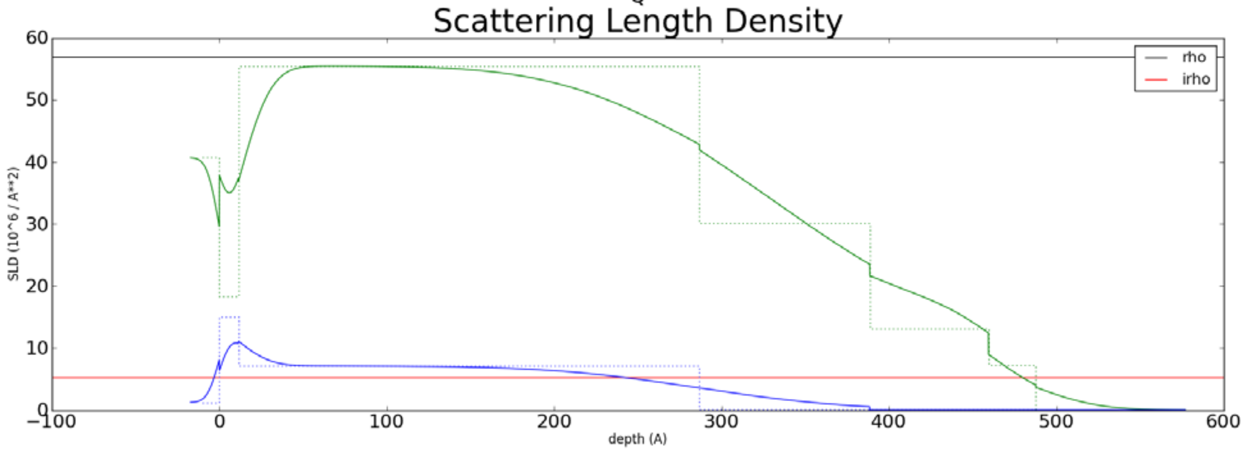
4th Layer thickness: 75.6 Å

4th Layer interface: 21.0 Å



$BiMnO_3$ X-ray Reflectometry Data





5 Layers of $BiMnO_3$

Chsq: 35.00

Total thickness: 487.67 Å

1st Layer thickness: 11.44 Å

1st Layer interface: 15.15 Å

2nd Layer thickness: 275.32 Å

2nd Layer interface: 70.13 Å

3rd Layer thickness: 101.74 Å

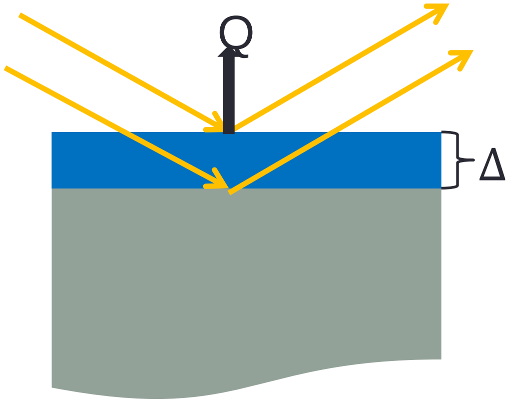
3rd Layer interface: 36.4 Å

4th Layer thickness: 70.91 Å

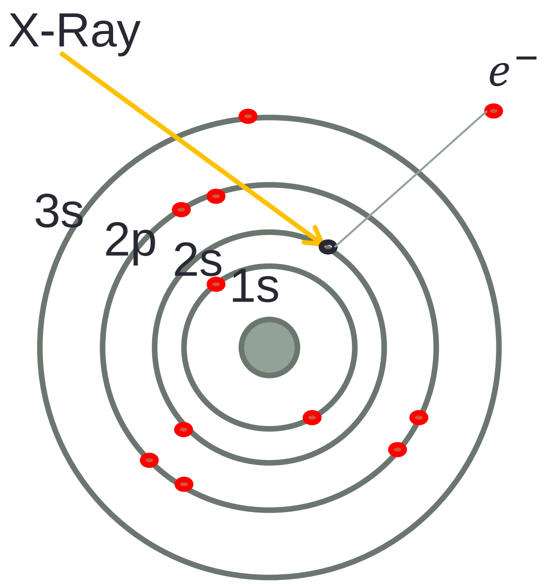
4th Layer interface: 18.9 Å

5th Layer thickness: 28.26 Å

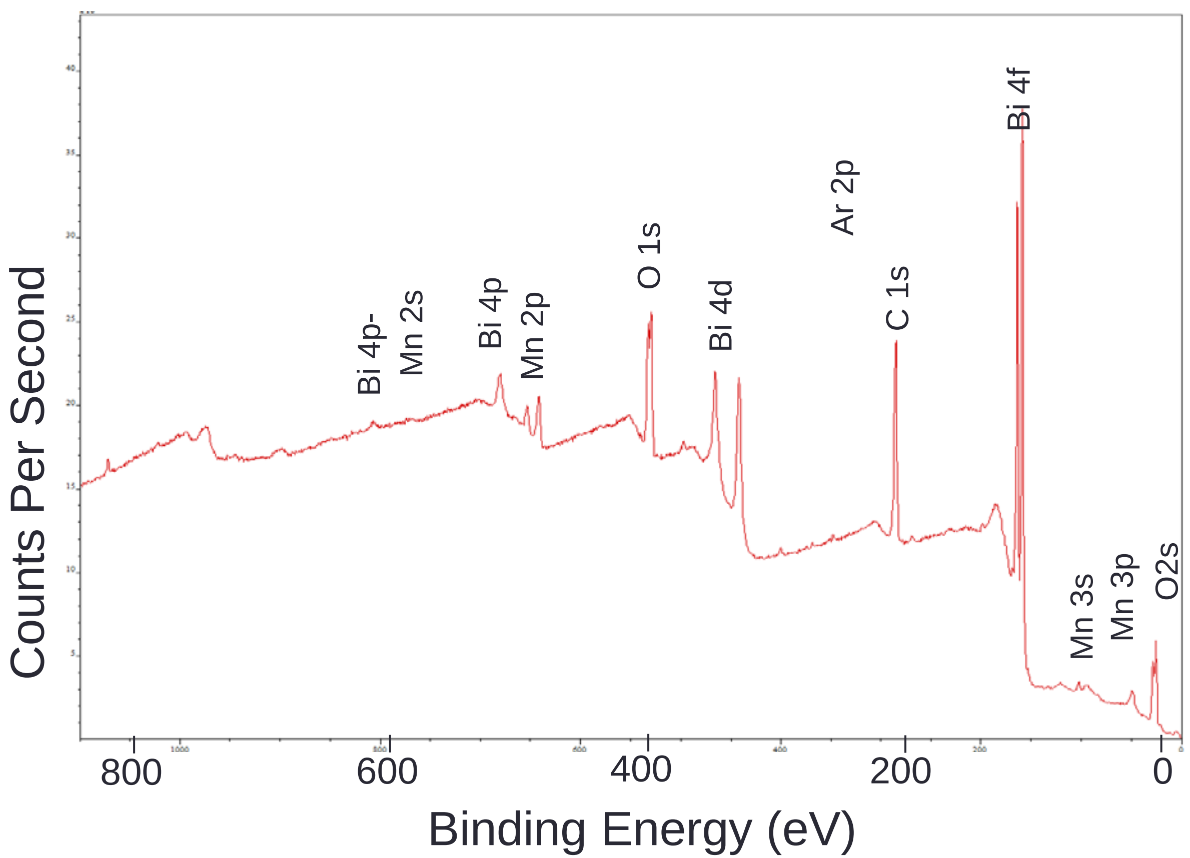
5th Layer interface: 29.76 Å



X-Ray Photoelectron Spectroscopy



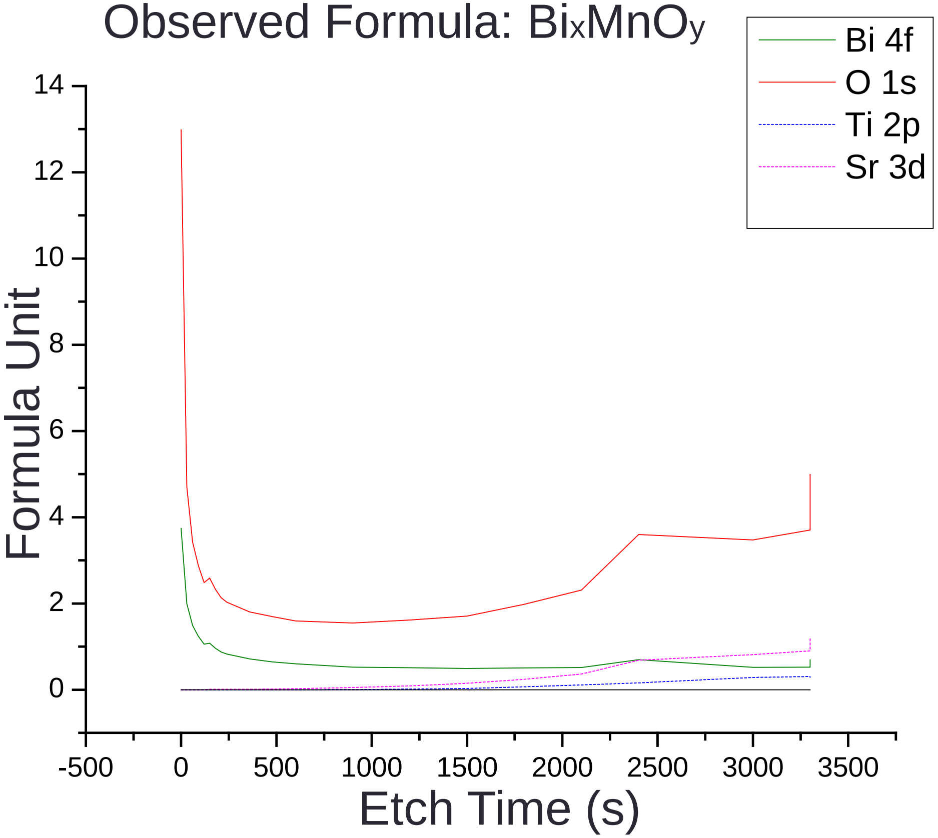
$$KE = h\nu - Binding\ Energy$$

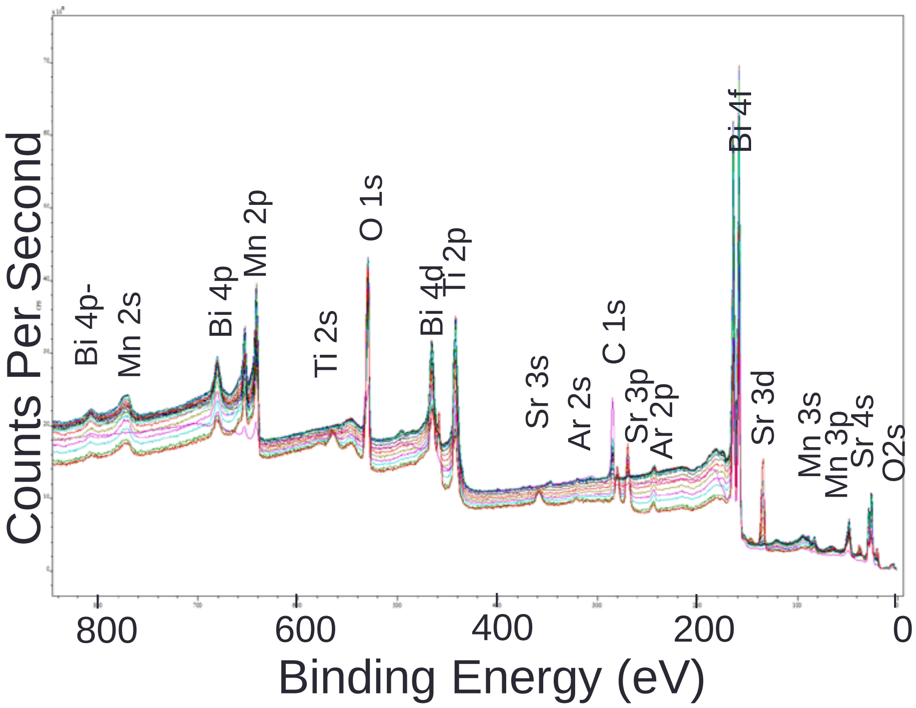


X-Ray Photoelectron Spectroscopy

Expect $BiMnO_3$

Observed Formula: Bi_xMnO_y





Conclusions

- Data suggests unstoichiometric composition of $BiMnO_3$.
  - Diffraction: extra peaks show
  - Atomic Force Microscopy: 20% of the surface has voids.
  - Reflectometry: Reduced scattering length density on the surface and at the interface with the $SrTiO_3$.
  - Spectroscopy: May have an increase in oxygen content at the substrate. Large concentration of Bismuth and Oxygen at surface.

On Going (Over the next 4 weeks):

- Neutron Reflectometry Data
  - Scattering Length Densities
    - X-Rays (electron density): Bi ~ 83, Mn ~ 25, O ~ 8 (atomic number)
    - Neutrons (nuclear constrast): Bi ~ 8.5, Mn ~ -3.73, O ~ 5.803 (bound coherent scattering lengths)
  - Gives additional information on the chemical formula.
- Polarized Neutron Reflectometry:
  - Calculate magnetic moment as a function of depth.

Acknowledgments

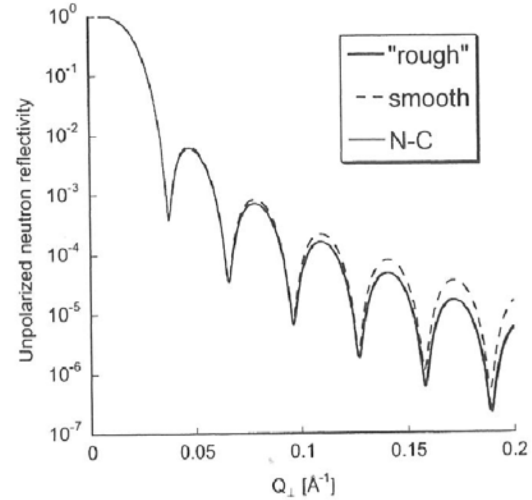
NIST/CHRNS. Julie A. Borchers, Robert D. Shull, and Terrell A. Vanderah (Directors, MML/NCNR Materials Science SURF Program).

Dan Neumann, Rob Dimeo.

Daniel Pajerowski, Professor Biswas and Daniel Grant.

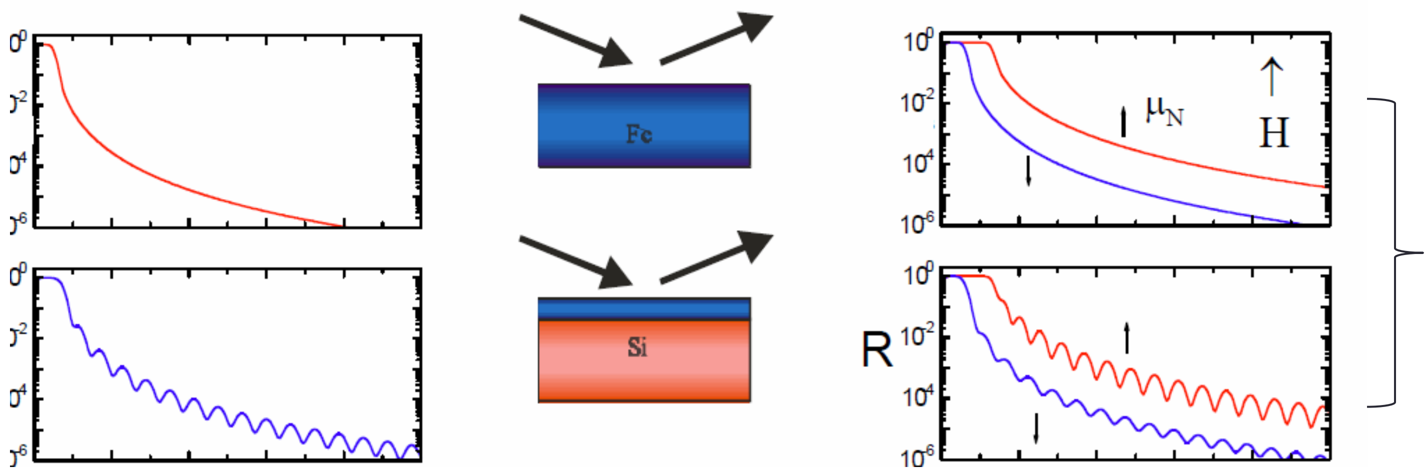
Neutron Reflectometry

- Nuclear and magnetic scattering.



Polarized Neutron Reflectometry

- Separates spin up and spin down.



Red- Spin up
Blue – Spin down

Roger Pynn. Neutron Reflectometry. Indiana U. and Spallation Neutron Source. <http://www.che.udel.edu/cns/pdf/Reflectometry.pdf>