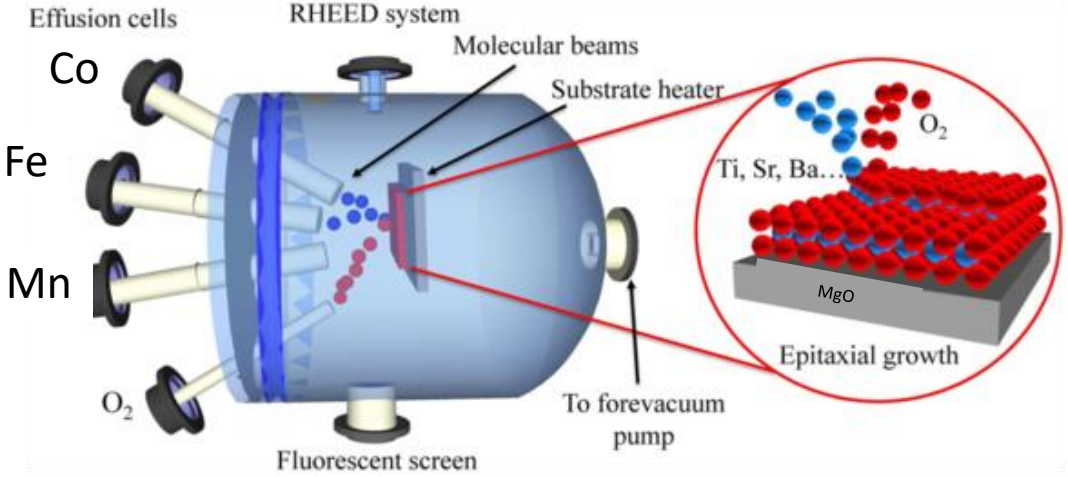
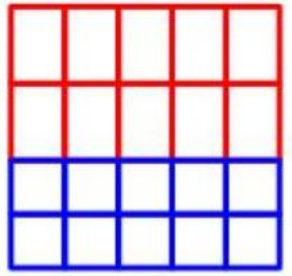
Spinel Thin Films
$Mn_xFe_{3-x}O_4$ system

Run 2: 6th to 7th April, 2019

350 ^{0}C, 1E-6, pure O_2, MgO (001)

Thin film fabrication using MBE





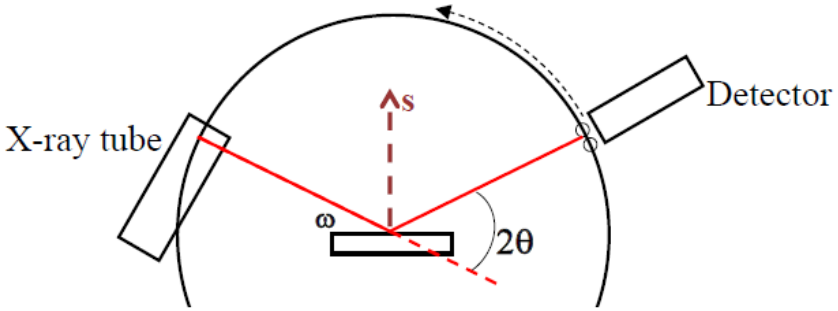
Epitaxial

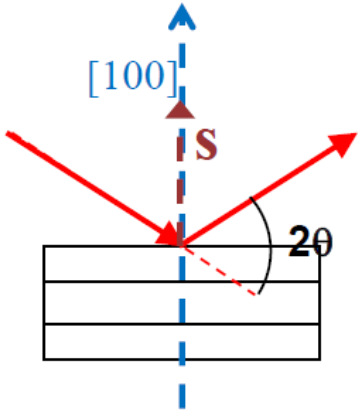
Synthesis:

- Thin films were grown on MgO (001) substrate at 350 °C in pure O_2 at a partial pressure of 1E-6. Thickness of the film varies from 57 to 70 nm.

Struct. formula	Mg O	Structure type	NaCl
Cell parameter	4.217(1) 4.217(1) 4.217(1) 90. 90. 90.	Space group	F m -3 m (225)
Struct. formula	Fe3 O4	Structure type	Spinel-Al2MgO4
Cell parameter	8.3941(7) 8.3941(7) 8.3941(7) 90. 90. 90.	Space group	F d -3 m Z (227)
Struct. formula	Mn3 O4	Structure type	CdMn2O4
Cell parameter	5.7574(4) 5.7574 9.4239(9) 90. 90. 90.	Space group	I 41/a m d S (141)

$Mn_xFe_{3-x}O_4$ – HR-XRD (Coupled 2theta-omega scan)





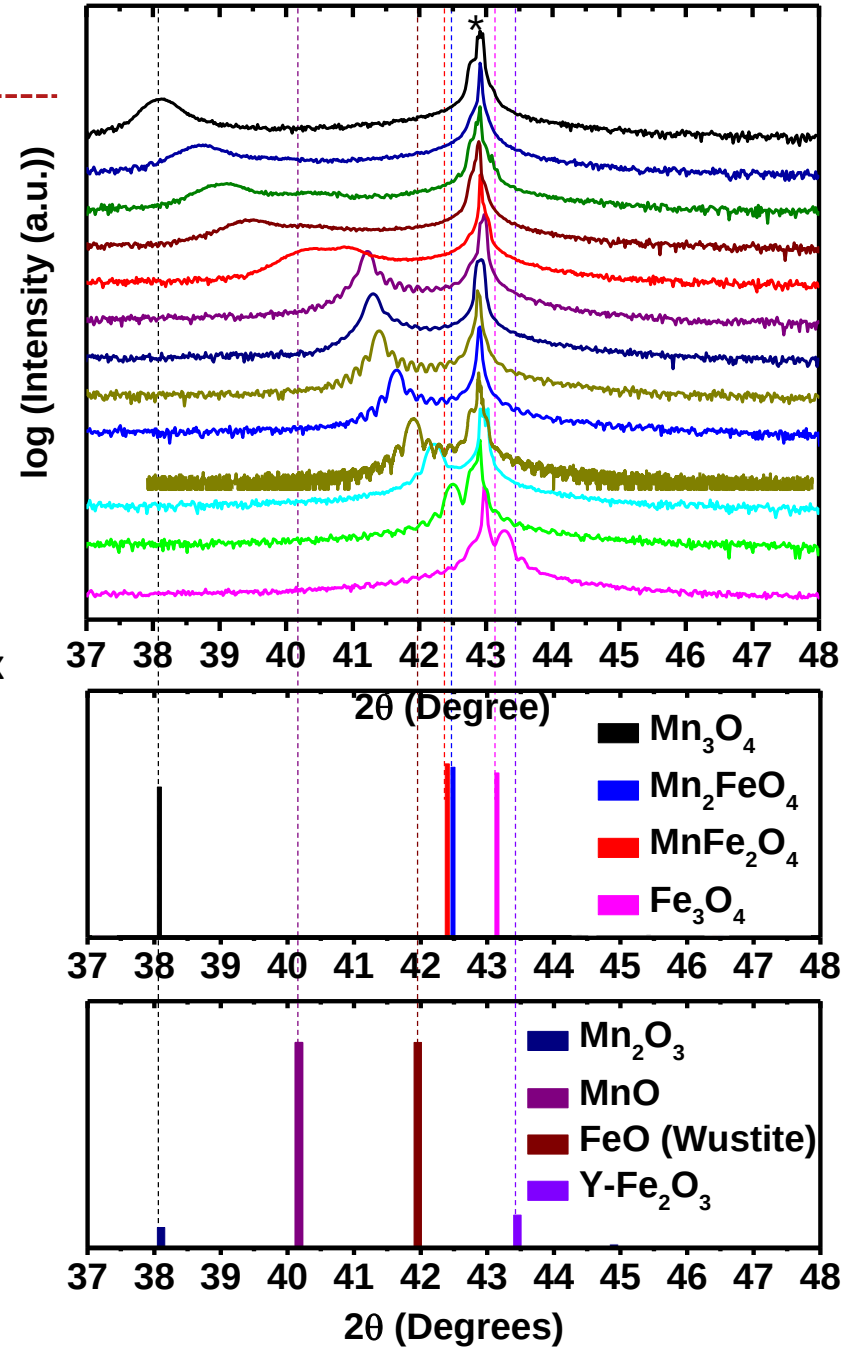
A coupled scan of a single crystal produces only one family of Bragg peaks in the diffraction pattern.

XRD shows (002) peak for MgO substrate and (004) peak for the $Mn_xFe_{3-x}O_4$ thin films

'x' values based on MBE flux

* MgO (001) substrate

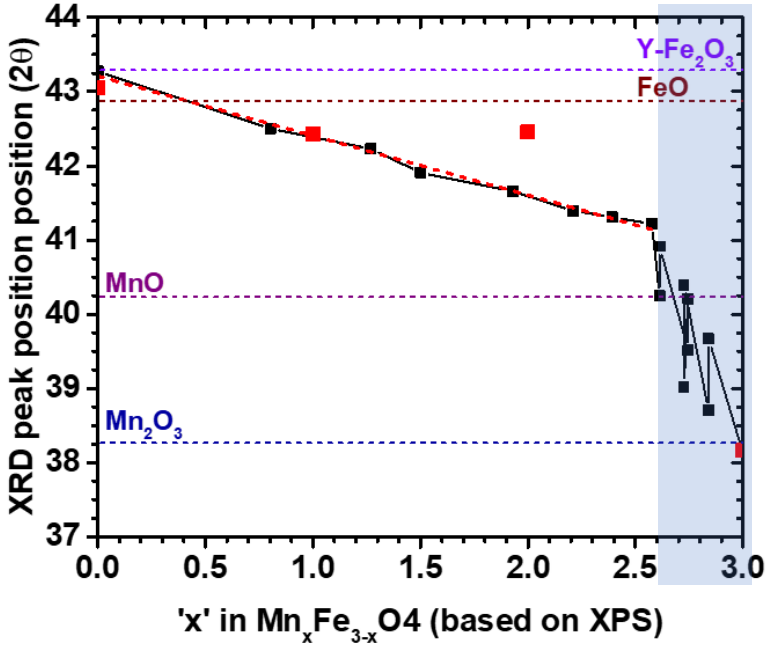
- AB037 $Mn_{3.00}Fe_{1.00}O_4$
- AB035 $Mn_{2.67}Fe_{0.33}O_4$
- AB034 $Mn_{2.50}Fe_{0.50}O_4$
- AB033 $Mn_{2.33}Fe_{0.67}O_4$
- AB032 $Mn_{2.00}Fe_{1.00}O_4$
- AB031 $Mn_{1.67}Fe_{1.33}O_4$
- AB030 $Mn_{1.50}Fe_{2.50}O_4$
- AB029 $Mn_{1.33}Fe_{1.67}O_4$
- AB028 $Mn_{1.00}Fe_{2.00}O_4$
- AB027 $Mn_{0.67}Fe_{2.33}O_4$
- AB026 $Mn_{0.50}Fe_{2.50}O_4$
- AB025 $Mn_{0.33}Fe_{2.67}O_4$
- AB004 Fe_3O_4



HR-XRD peak positions wrt correct ‘x’ values

- **$Mn_xFe_{3-x}O_4$ JCPDS standards**

Dashed lines show the peak positions of the possible impurity phases



- XRD peaks are fitted with Gaussian curves to extract the peak positions
- For x ≥ 2, two peaks are observed in XRD, indicating phase purity for x < 2, and phase segregation for x ≥ 2
- MBE flux ratio has ~ 10% error even after calibration
- Mn:Fe correct values determined using XPS
- For phase pure samples, XPS sufficient to calculate correct ‘x’ values
- XRD peak position is inversely proportional to out-of-plane lattice spacing

[1]Scafetta, Mark D., et al. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **37.3** (2019): 031511

HR-XRD further analysis

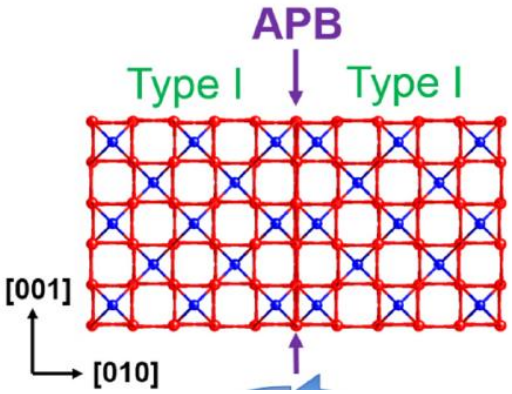
- MBE flux during growth **has ~ 10% error** even after calibration, hence ‘x’ values mentioned till now are not correct
- For phase pure samples, XPS is used to calculate Mn:Fe ratio and thus the correct ‘x’ values (assuming the samples are phase pure)

For phase pure samples

➢ a linear trend is observed between XRD peak position and the corrected ‘x’ values (see dashed red line).

For samples with 2 XRD peaks

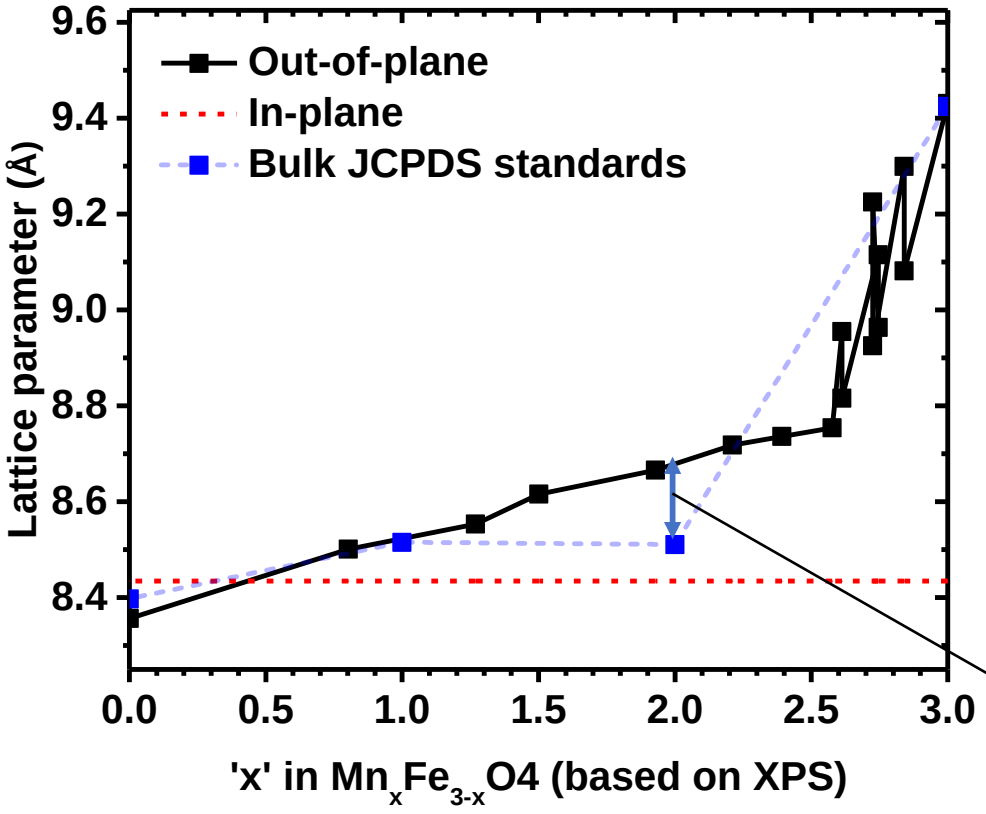
➢ a similar observation was made in another system[1] which attributed 2 XRD peaks to the presence of anti-phase boundaries (APB) which leads to formation Mn-rich and Fe-rich regions in the thin films (this needs to be confirmed with TEM)



The antiphase boundaries are formed as growth defects, due to the fact that the lattice constant of spinel is twice as large as the lattice constant of the underlying substrate, MgO. When different islands meet, they can be shifted or rotated with respect to each other, thus yielding an antiphase boundary.

[1]Scafetta, Mark D., et al. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **37.3** (2019): 031511

HR-XRD lattice parameters wrt correct ‘x’ values



- Out-of-plane (OOP) lattice parameter calculated from (004) peak position of coupled 2theta-omega scan
- In-plane lattice parameter calculated from $(\bar{2}\ \bar{2}\ 6)$ Reciprocal space maps (RSMs)

‘x’ in $Mn_xFe_{3-x}O_4$	OOP strain wrt bulk standard
0	-0.488 %
1	0.094 %
2	1.974 %

Understanding *in-situ* RHEED

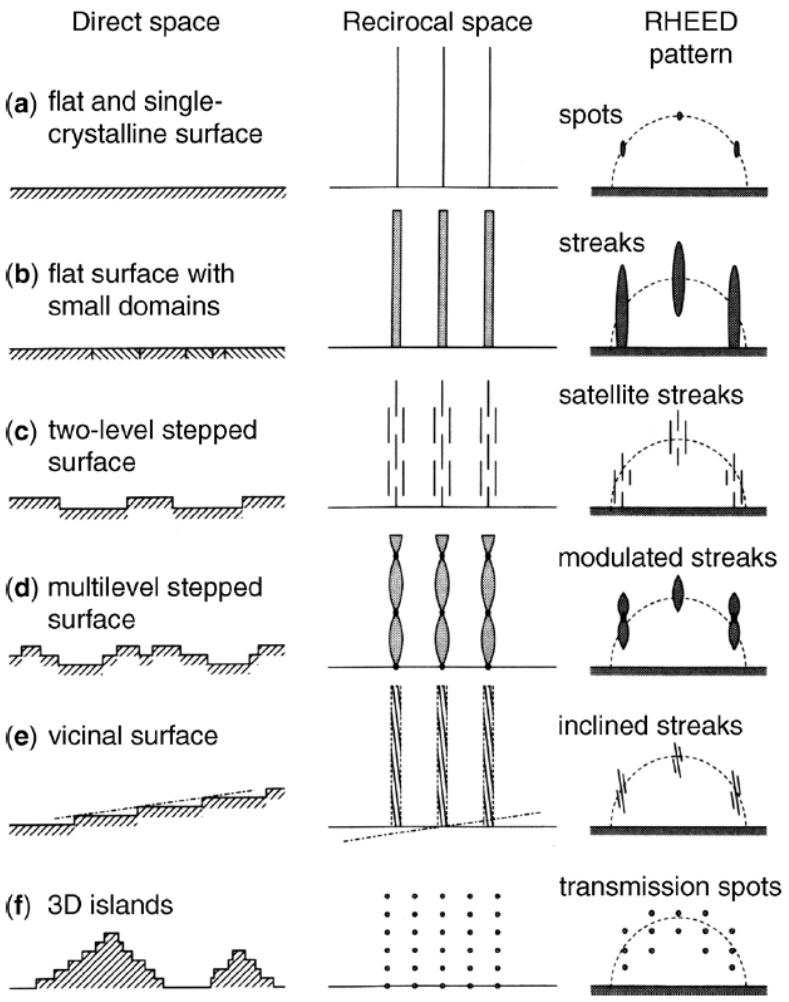
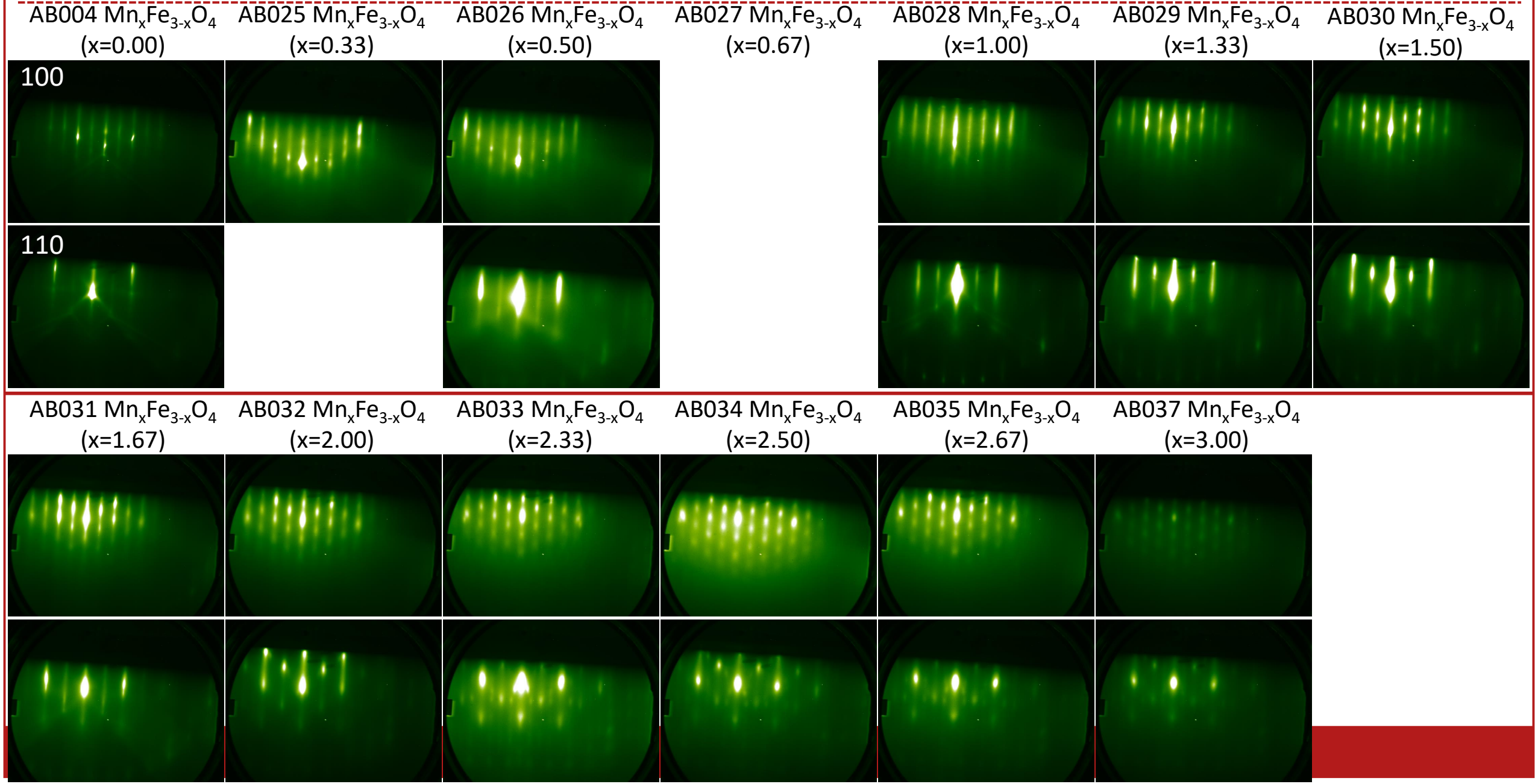


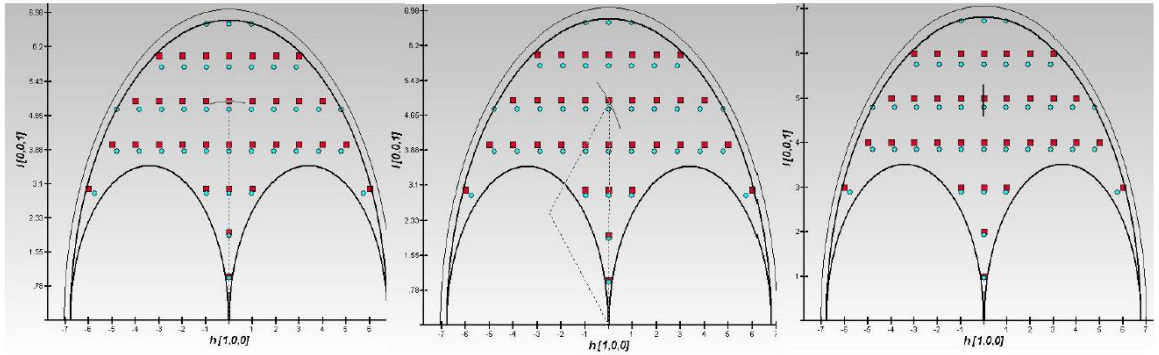
Figure 3. Schematics of various kinds of realistic surfaces, in real-space morphology, in reciprocal space, and their RHEED patterns (courtesy by Yoshimi Horio).

- RHEED pattern gives information on the smoothness of the surface and the domain size
- For the $Mn_xFe_{3-x}O_4$ films, RHEED shows smooth surfaces for $x < 2$ samples, and rough surfaces for $x \geq 2$ samples. Overall film quality is getting bad with increasing Mn content

$Mn_xFe_{3-x}O_4$ – *in-situ* RHEED to determine surface smoothness



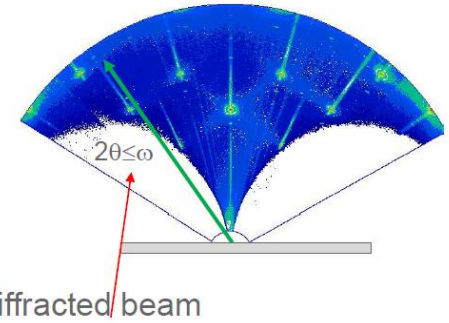
Understanding Reciprocal Space Maps (RSMs)

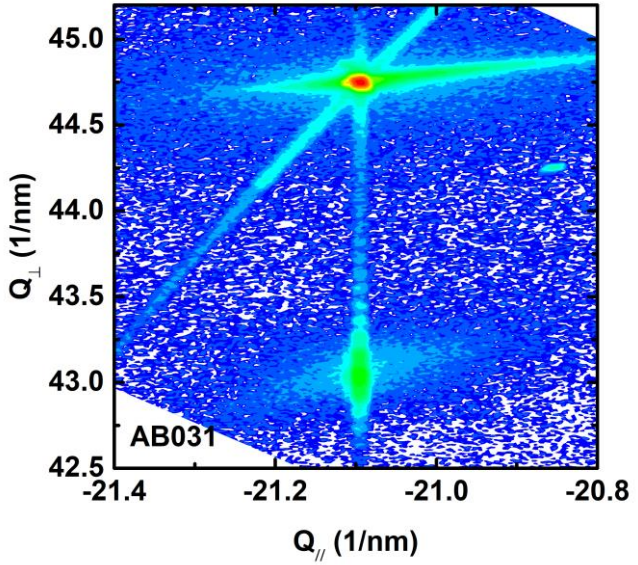


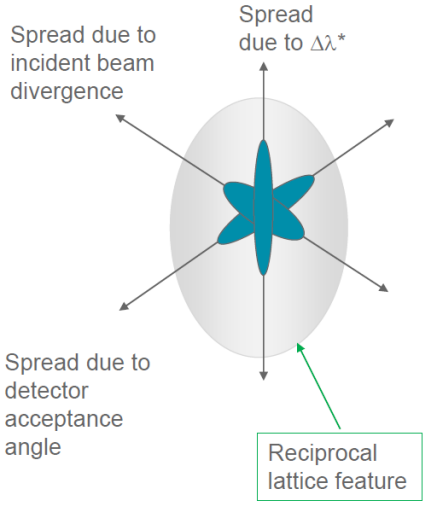
- The rocking curve (omega scan) is an arc centered on the origin
- The detector scan (2theta scan) is an arc along the Ewald sphere circumference
- The couple scan (2theta-omega scan) is a straight line pointing away from the origin

The typical way to collect recriprocal space maps is to vary relative omega and collect multiple 2theta-omega coupled scans

Omega > 2Theta/2



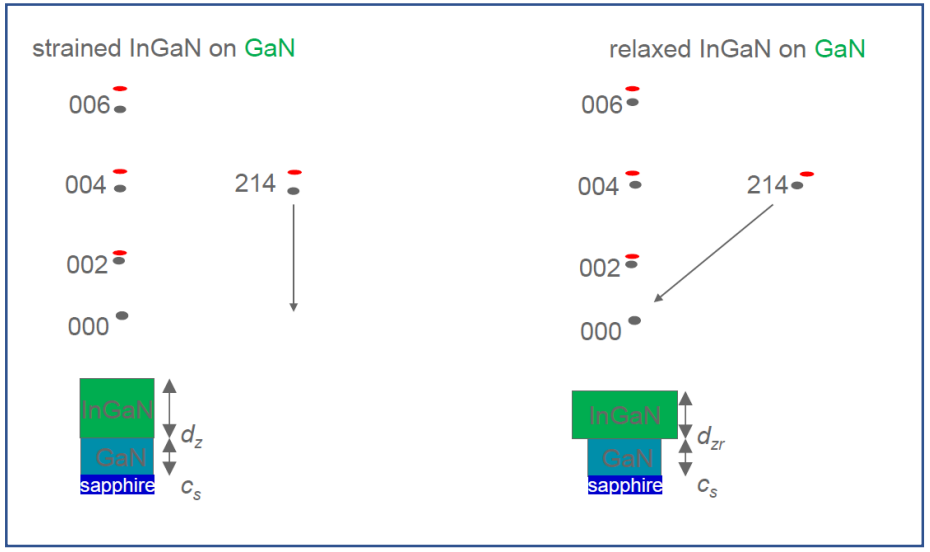


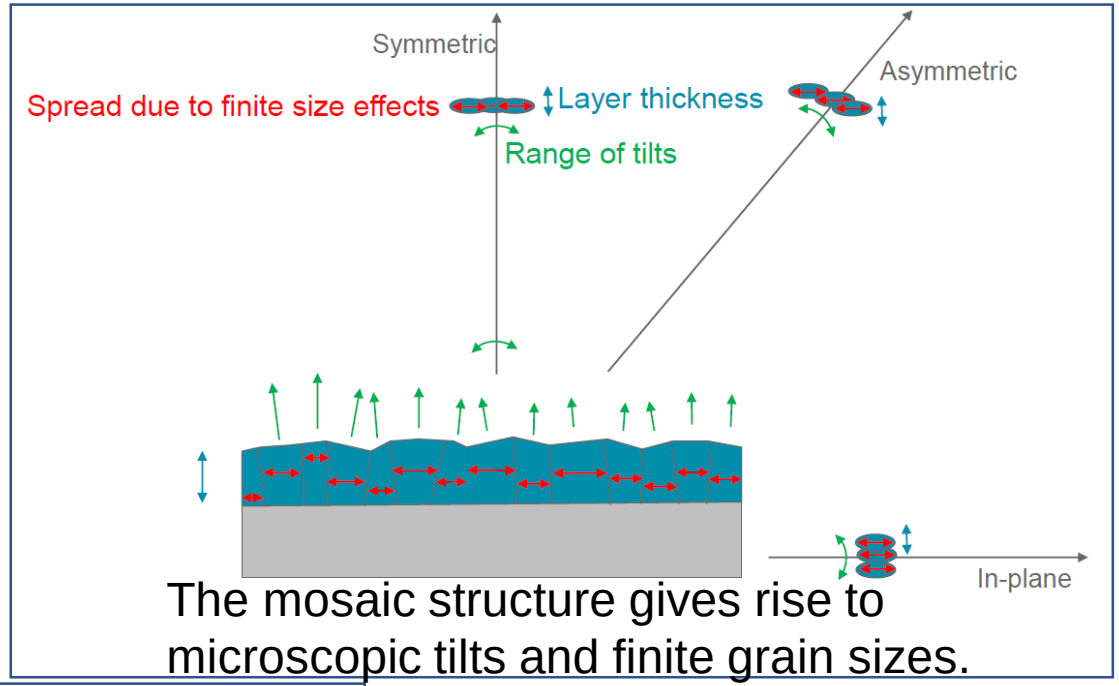


MgO ($\bar{1}\ \bar{1}\ 3$)

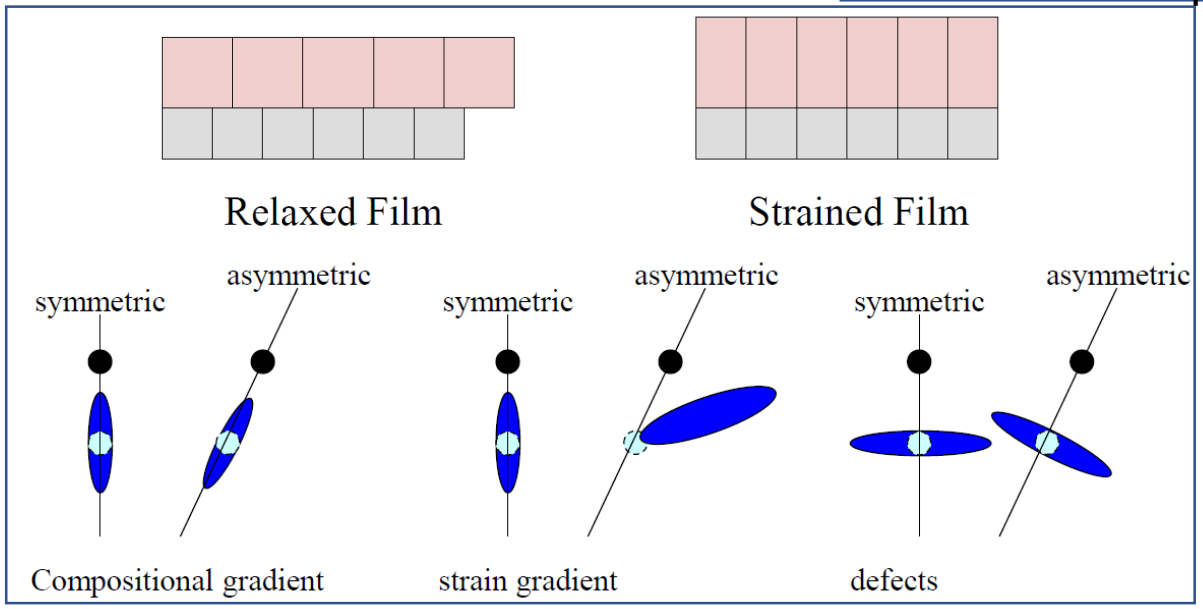
$Mn_xFe_{3-x}O_4$ ($\bar{2}\ \bar{2}\ 6$)

Understanding Reciprocal Space Maps (RSMs)





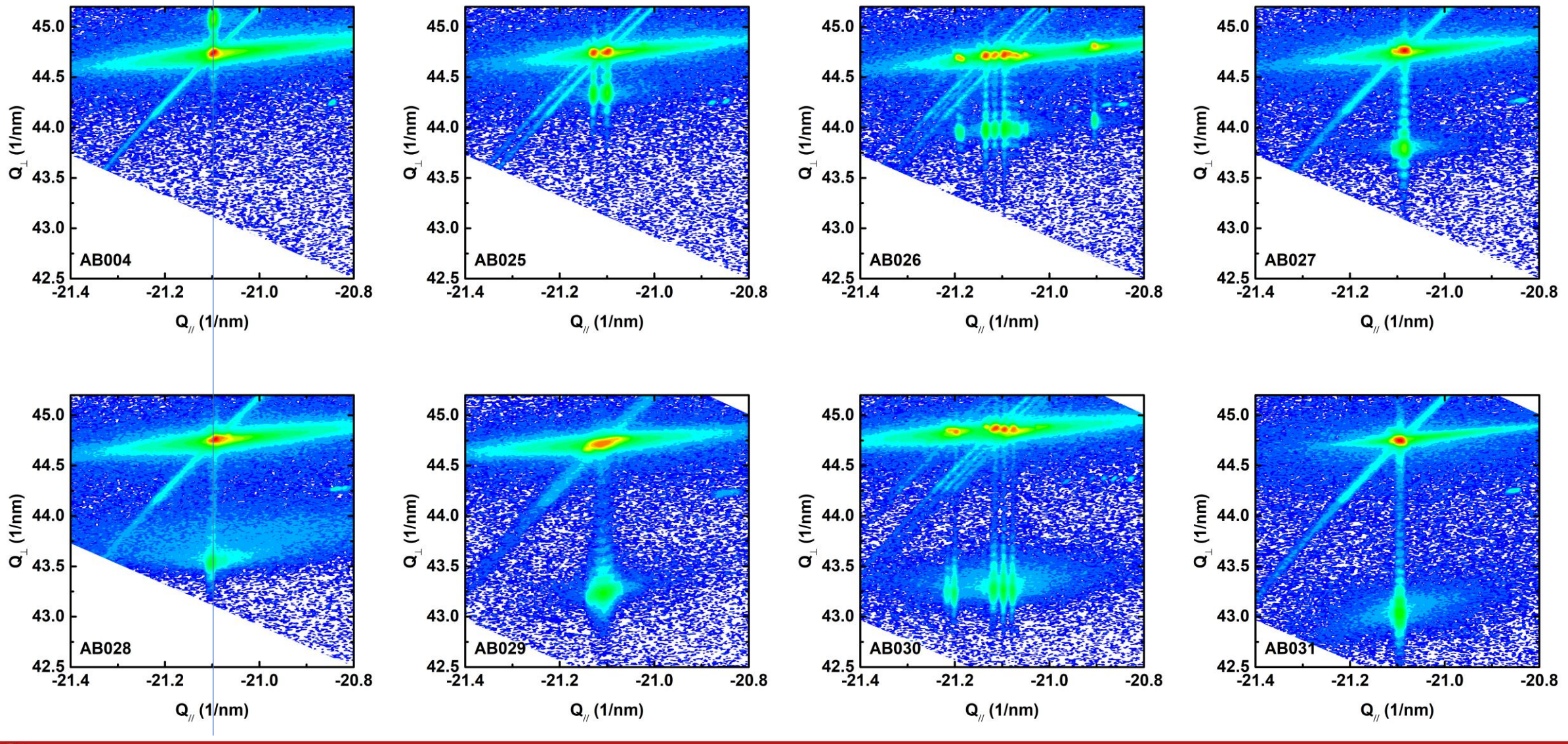
The mosaic structure gives rise to microscopic tilts and finite grain sizes.



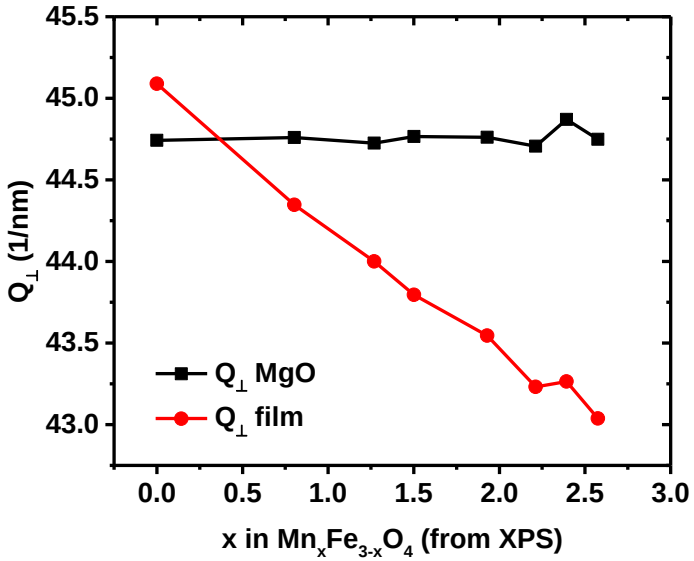
$Mn_xFe_{3-x}O_4$ – Reciprocal Space Maps (RSMs)

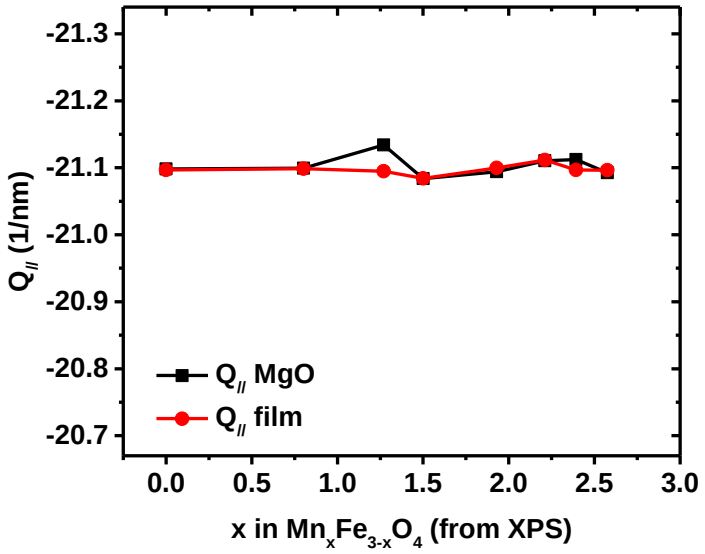
MgO ($\bar{1}\,\bar{1}\,3$)

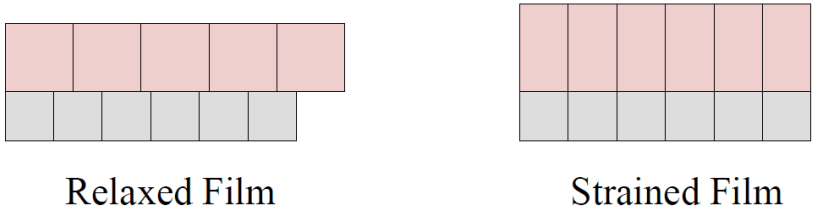
$Mn_xFe_{3-x}O_4$ ($\bar{2}\,\bar{2}\,6$)



$Mn_xFe_{3-x}O_4$ – Reciprocal Space Maps (RSMs)

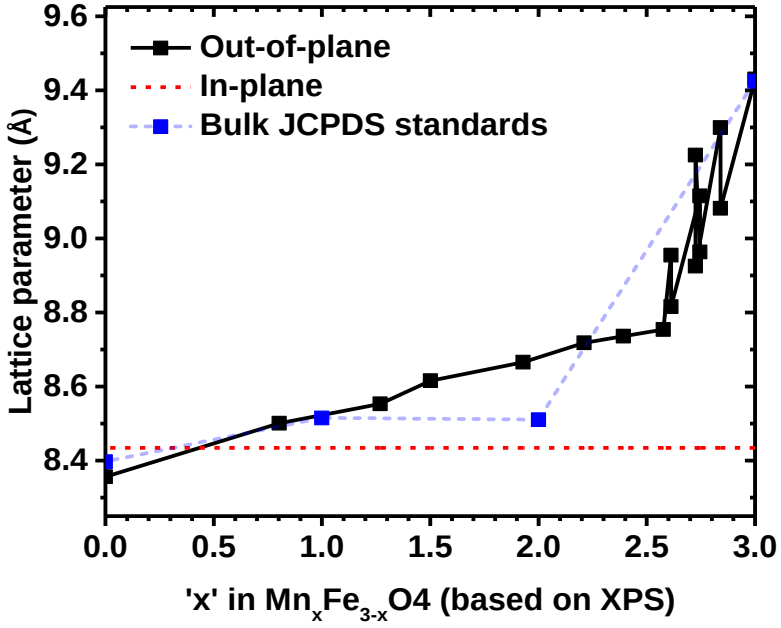




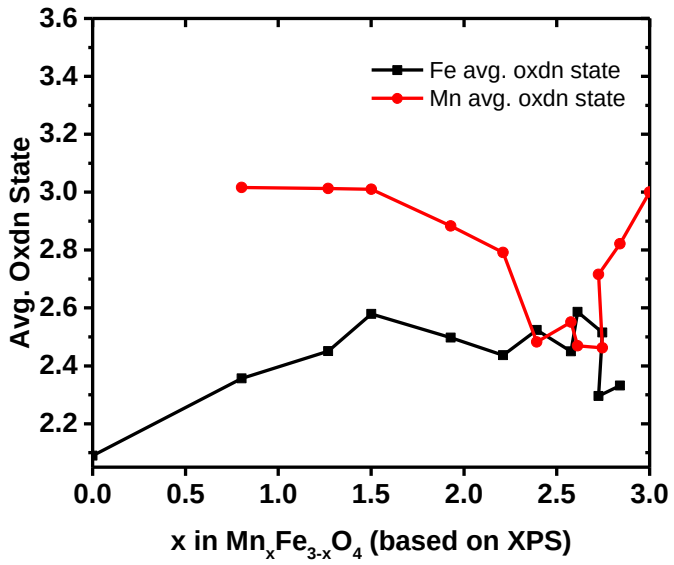


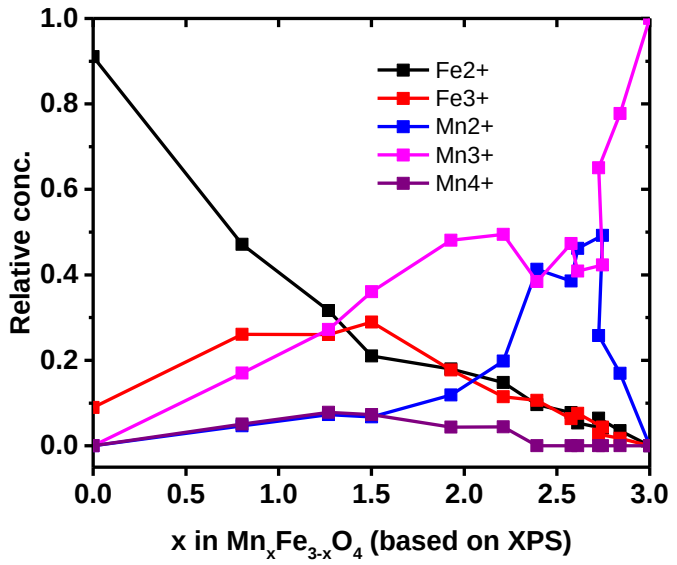
A formerly cubic unit cell is now tetragonal

- In-plane lattice constant same as the MgO substrate
  - This implies that the films are strained
- Out-of-plane lattice constant increases with increasing Mn content



$Mn_xFe_{3-x}O_4$ – XPS analysis





- XPS was used to extract the relative conc. of cation species, but as of now it is not sufficient to determine the active species or the number of hopping pairs

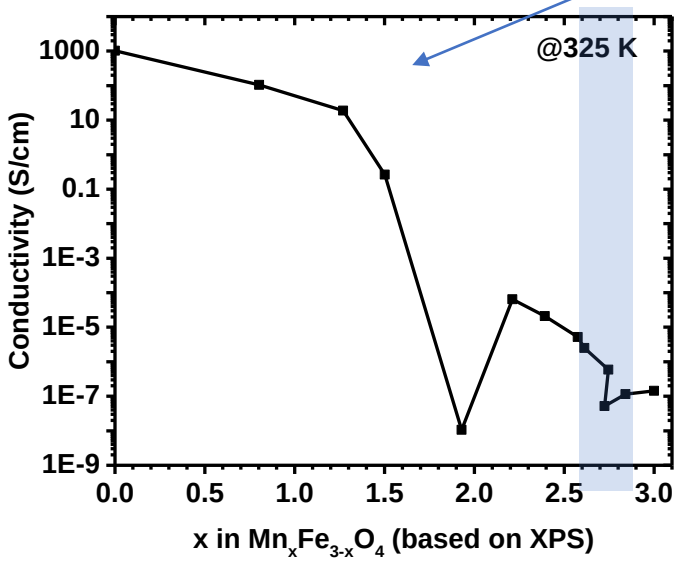
- Need XES or EXAFS to determine the conc of cations at tetrahedral and octahedral sites

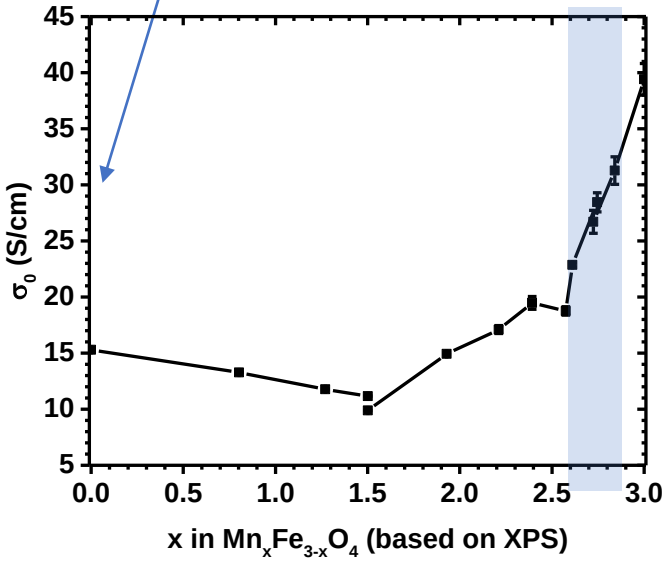
$$(Mn_{1-i}^{2+}Fe_i^{3+})[Mn_yFe_{2-y}]O_4$$

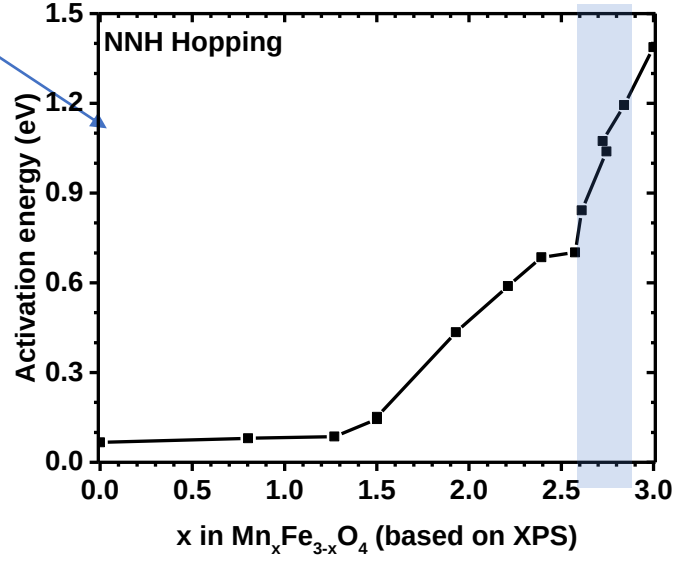
$Mn_xFe_{3-x}O_4$ – Charge transport study

- Measurements limited to smaller temp range because of extremely high resistivity at low temp
- Hopping mechanism is NNH for phase pure samples and is **NOT** NNH for phase impure samples (see SI for fits of Arrhenius plots)
- Below are the extracted values from the fits (for now, the plots below show the complete ‘x’ range assuming the mechanism to be NNH)

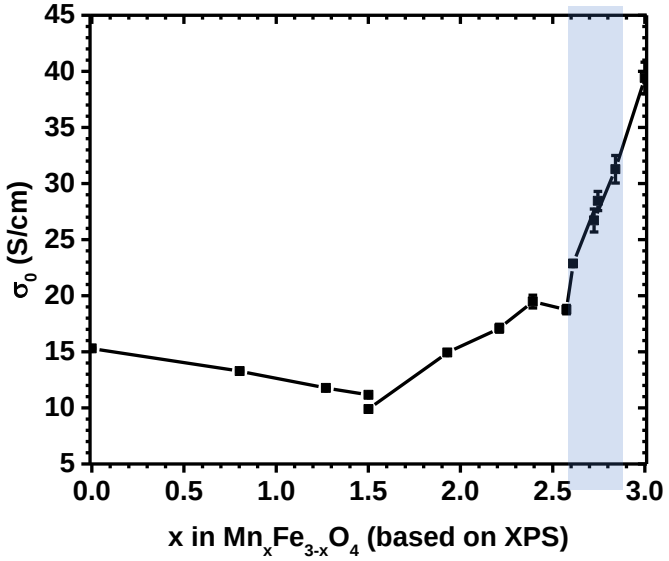
$$\sigma(T) = \sigma_0 \cdot \exp\left(-\frac{E_A}{k_B T}\right)$$







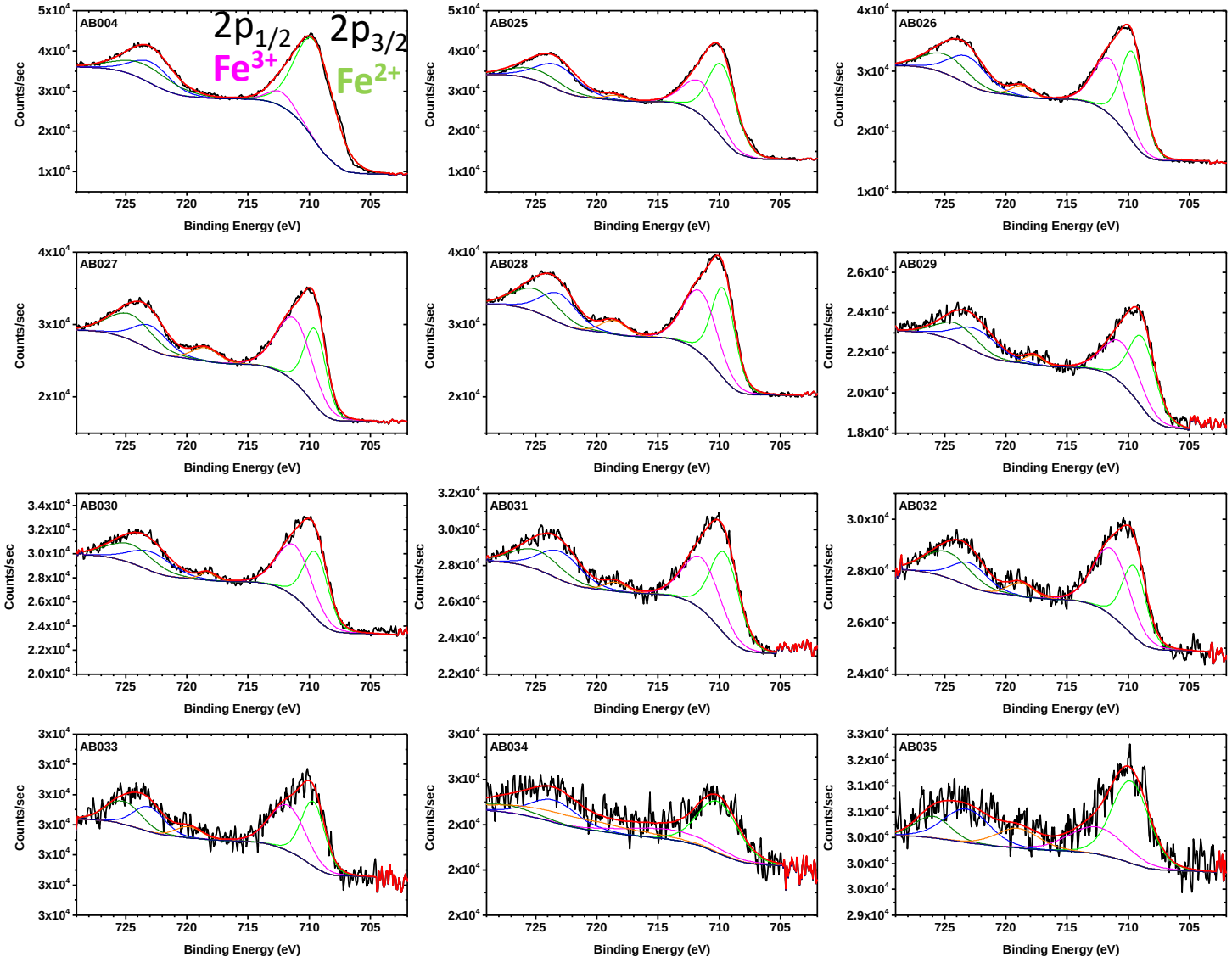
$Mn_xFe_{3-x}O_4$ – Charge transport study



- Volcano trend with a minima is observed at x=1.5. This is exactly the opposite of what was observed in the $Co_xMn_{3-x}O_4$ system (volcano trend with a maxima at x=1.5)
- It would be interesting to see what cations species and hopping pairs lead to such behavior

Supporting Information

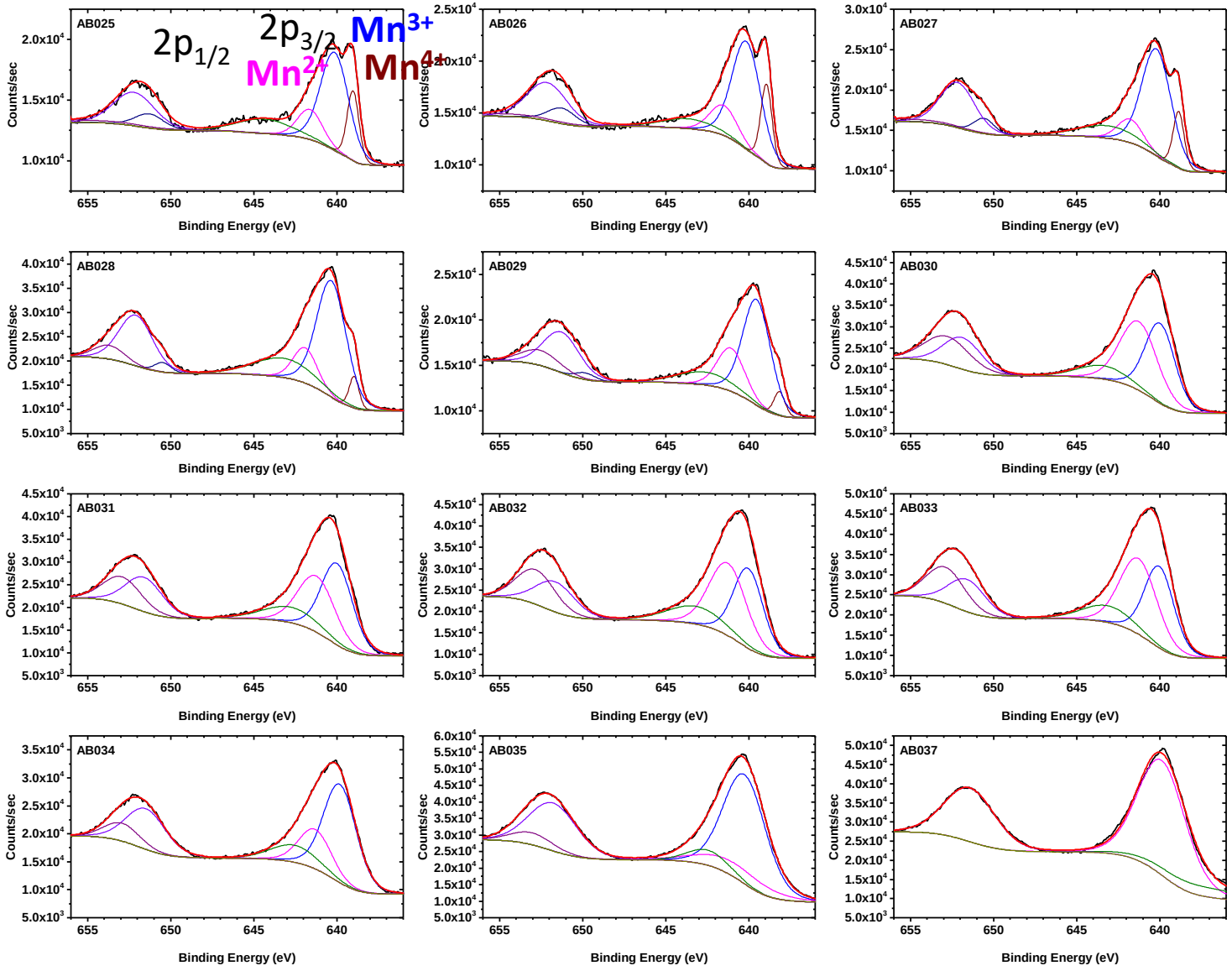
$Mn_xFe_{3-x}O_4$ – XPS Fe 2p



$2p_{1/2} = 0.5 \times 2p_{3/2}$

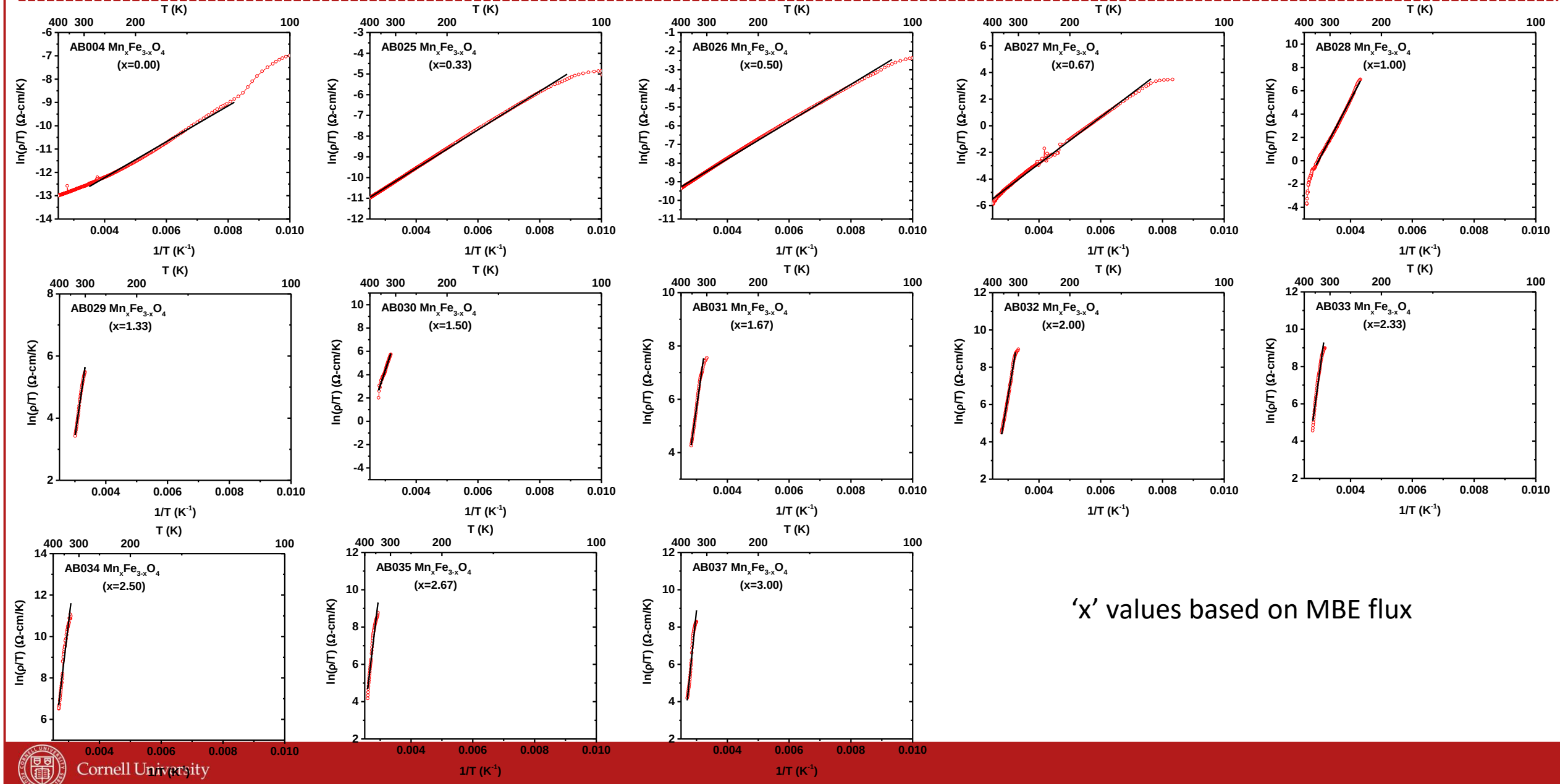
$2p_{1/2} = 13.4 + 2p_{3/2}$

$Mn_xFe_{3-x}O_4$ – XPS Mn 2p



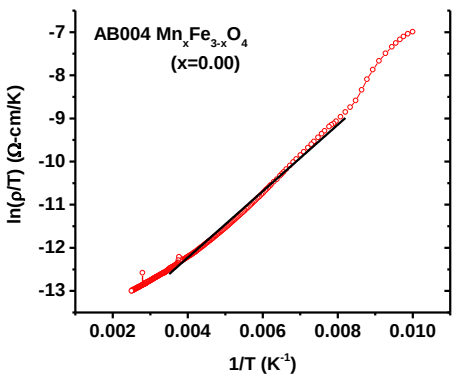
$2p_{1/2} = 0.5 \times 2p_{3/2}$

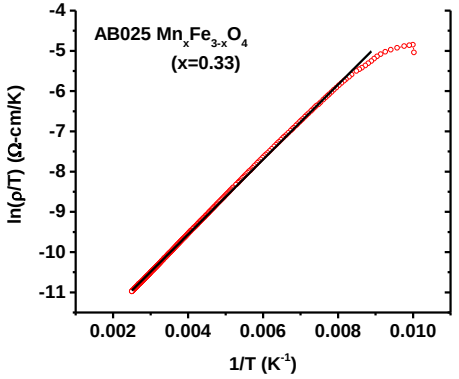
$Mn_xFe_{3-x}O_4$ – Fitting of electronic conductivity plots using NNH model

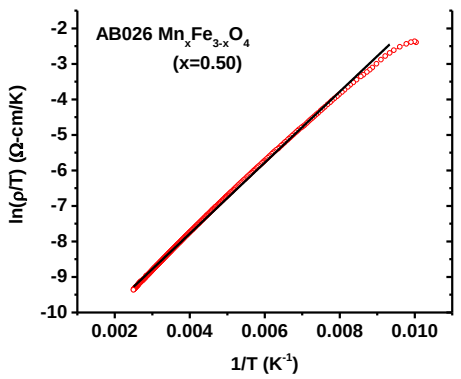


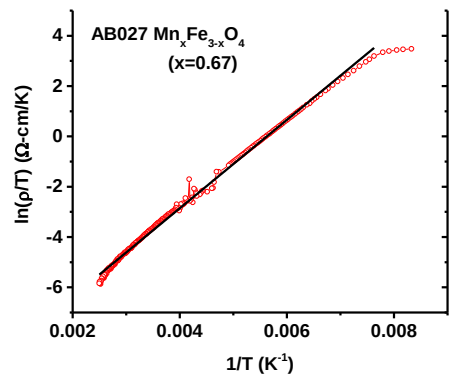
'x' values based on MBE flux

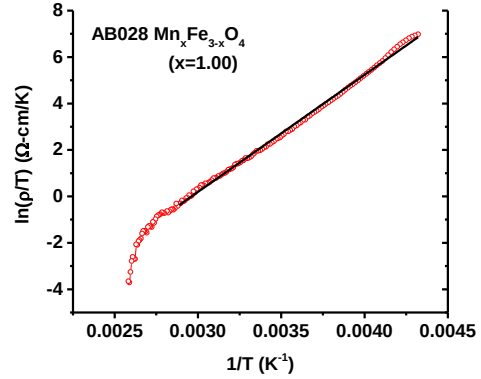
$Mn_xFe_{3-x}O_4$ – Fitting of electronic conductivity plots using NNH model

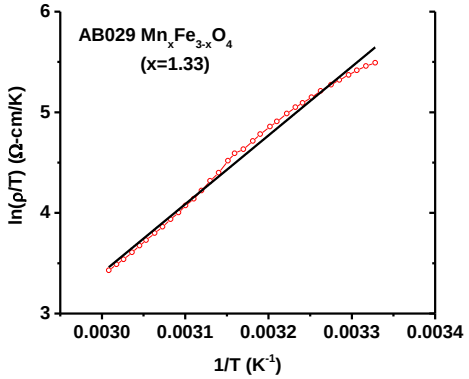


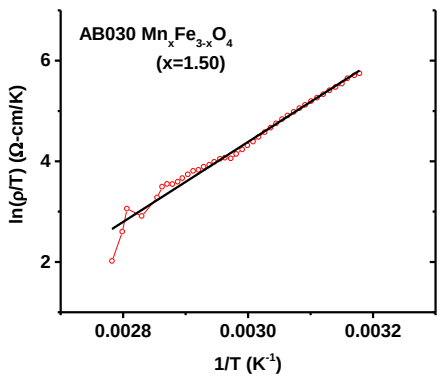


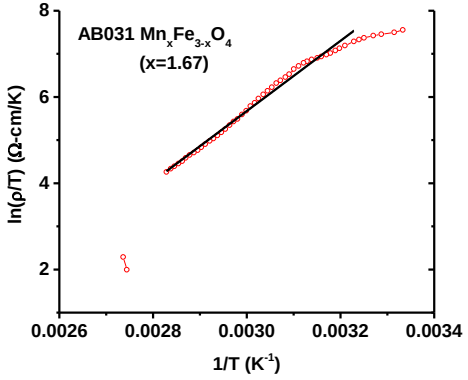


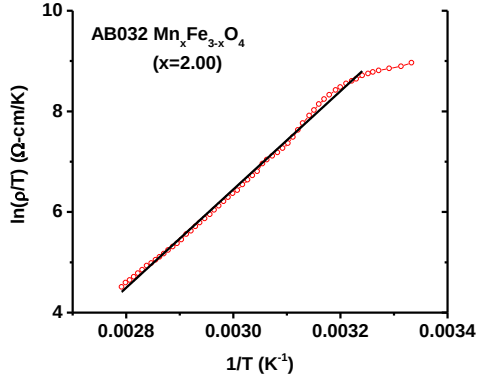


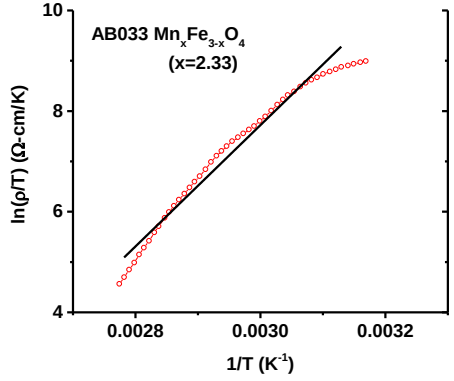


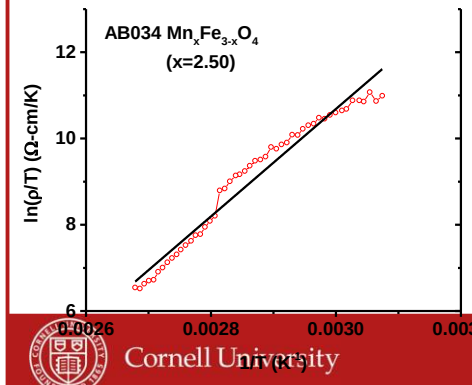


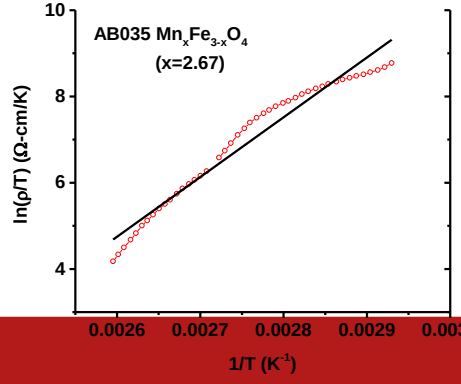


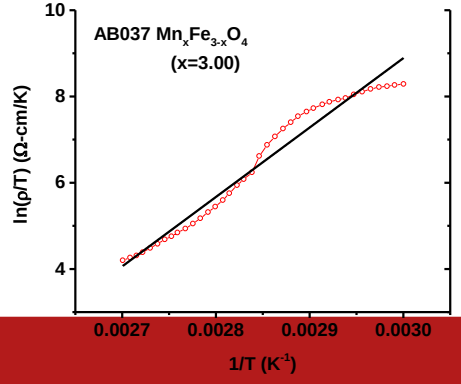






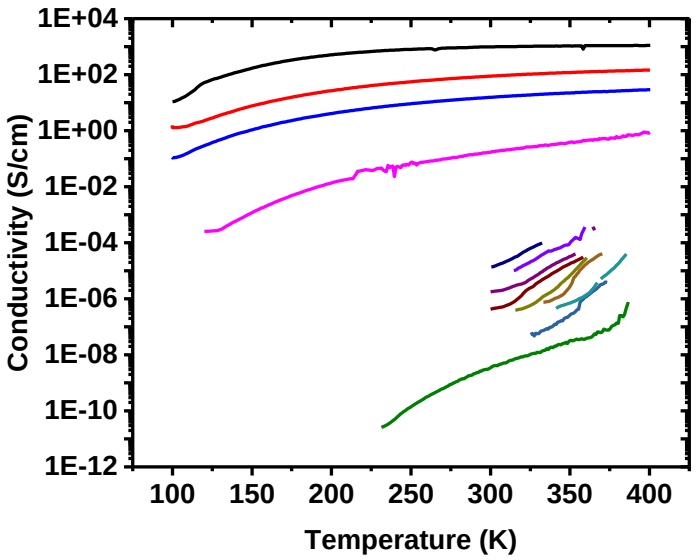


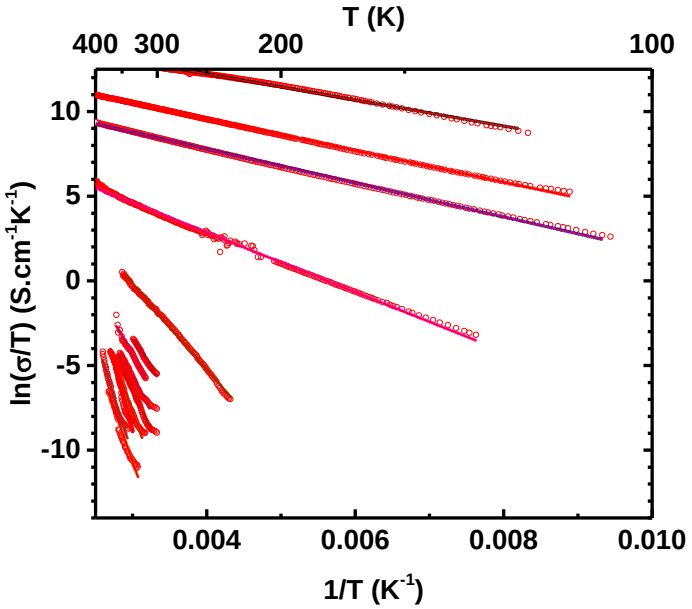




'x' values based on MBE flux

$Mn_xFe_{3-x}O_4$ – Conductivity vs Temp



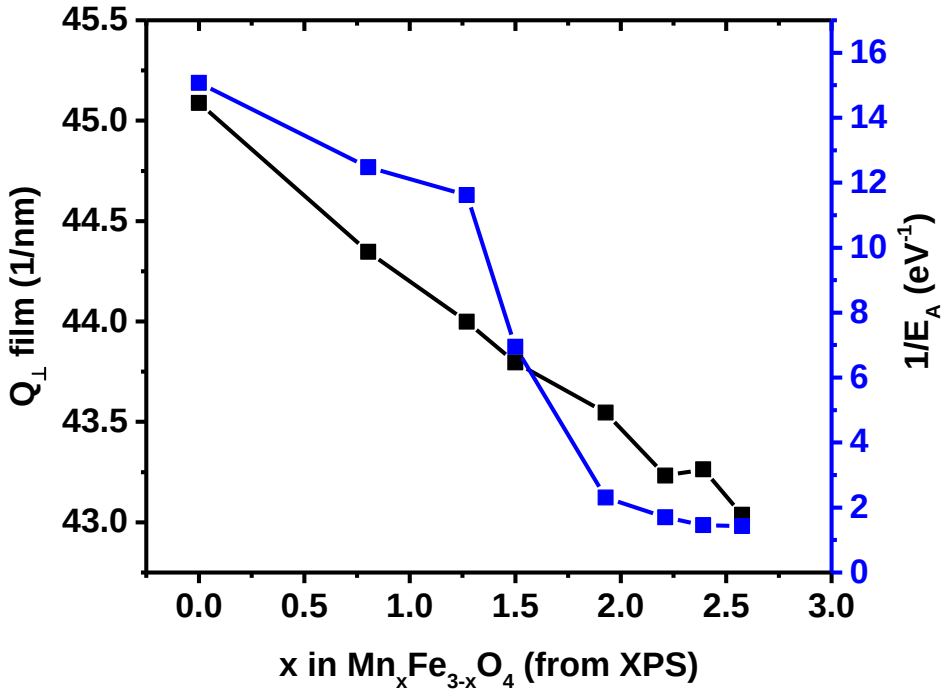


‘x’ values based on MBE flux

* MgO (001) substrate

- AB037 $Mn_{3.00}Fe_{1.00}O_4$
- AB035 $Mn_{2.67}Fe_{0.33}O_4$
- AB034 $Mn_{2.50}Fe_{0.50}O_4$
- AB033 $Mn_{2.33}Fe_{0.67}O_4$
- AB032 $Mn_{2.00}Fe_{1.00}O_4$
- AB031 $Mn_{1.67}Fe_{1.33}O_4$
- AB030 $Mn_{1.50}Fe_{2.50}O_4$
- AB029 $Mn_{1.33}Fe_{1.67}O_4$
- AB028 $Mn_{1.00}Fe_{2.00}O_4$
- AB027 $Mn_{0.67}Fe_{2.33}O_4$
- AB026 $Mn_{0.50}Fe_{2.50}O_4$
- AB025 $Mn_{0.33}Fe_{2.67}O_4$
- AB004 Fe_3O_4

Correlating hopping distance to activation energy



- A direct correlation is observed between the out-of-plane lattice parameter and the activation energy for the polaron hopping.
- Mn plays a role in manipulating both the number of hopping pairs as well as the activation energy!

$$\sigma(\mathrm{T}) = \sigma_0 \cdot \exp\left(-\frac{\mathrm{E_A}}{\mathrm{k_B T}}\right)$$