

Mapping strain modulated electronic structure perturbations in mixed phase bismuth ferrite thin films

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Supplementary 1

Peak Fitting of the Experimental Near Edge Oxygen K Spectral Character

In acquiring the O K edge near fine structure across the MPB we analyzed the structure using multiple linear least squares peak fitting (MLLS). Figure S1(a) plots the change in relative peak shift for each of the six peaks (from 0 to 5) as a function of distance whilst S1(b) plots the normalized peak area for each peak as a function of distance along the profile line.

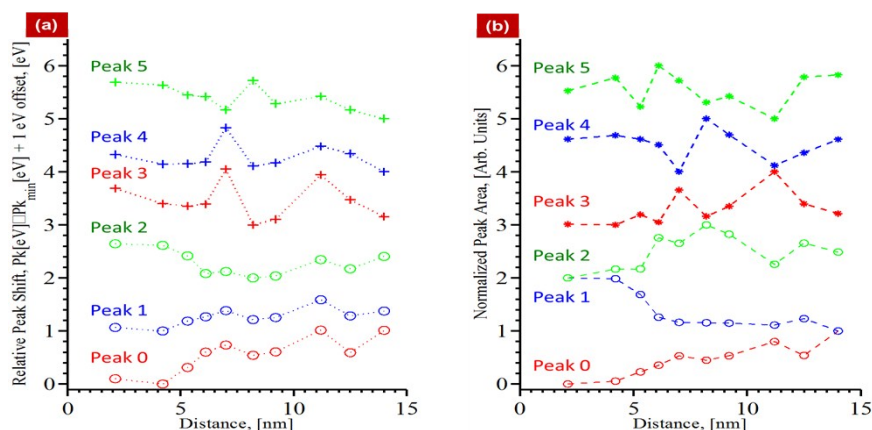


Fig. S1 Multiple least linear square fitting for O-k spectra across R-T phase (a) peak shift and (b) peak area.

Supplementary 2

The effect of shear on T-phase BFO was calculated for two different shear angles 2 and 5 degrees. The spectrum was calculated for symmetry with 3 and 4 nearest atoms and the average spectrum is reported. From the figure it can be observed that the peak 0 appears predominantly at 5 degree shear, while all the other peaks show no variation.

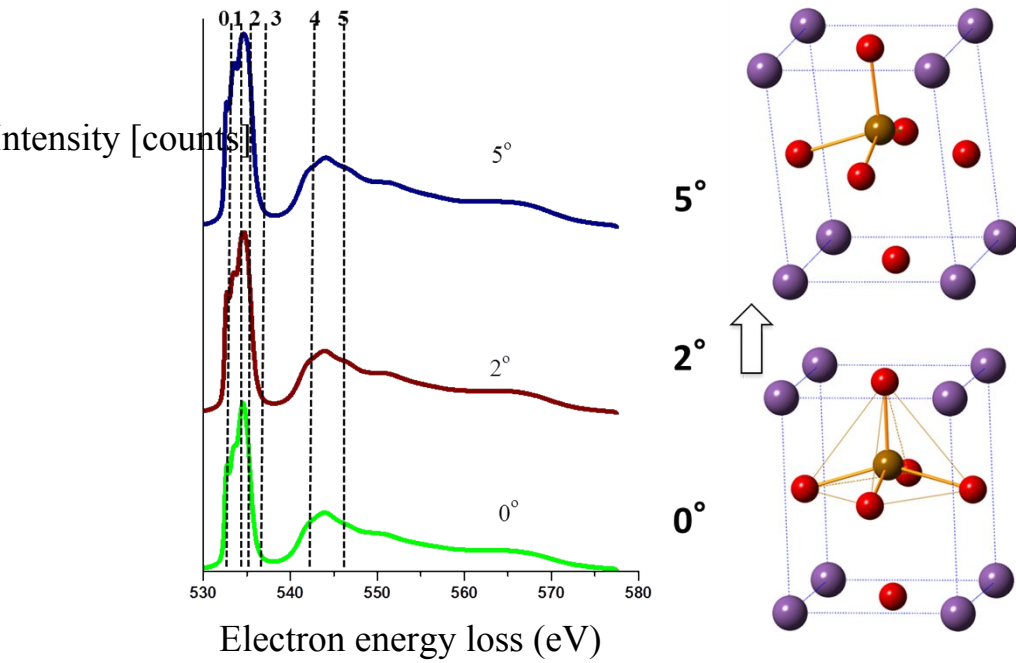


Fig.S2 Simulated O-k EEL spectra for T-phase BFO with varied shear angles.

S3. Fitting Theoretical and Experimental Spectra

For each spectrum, following peak normalization where the maximum intensity was set to one, the same initial six peaks were input into a multiple linear least squares peak fitting algorithm and used to fit all spectra. The peaks were fit within a 19.5 eV window beyond the edge onset.

The following initial peak parameters were applied:

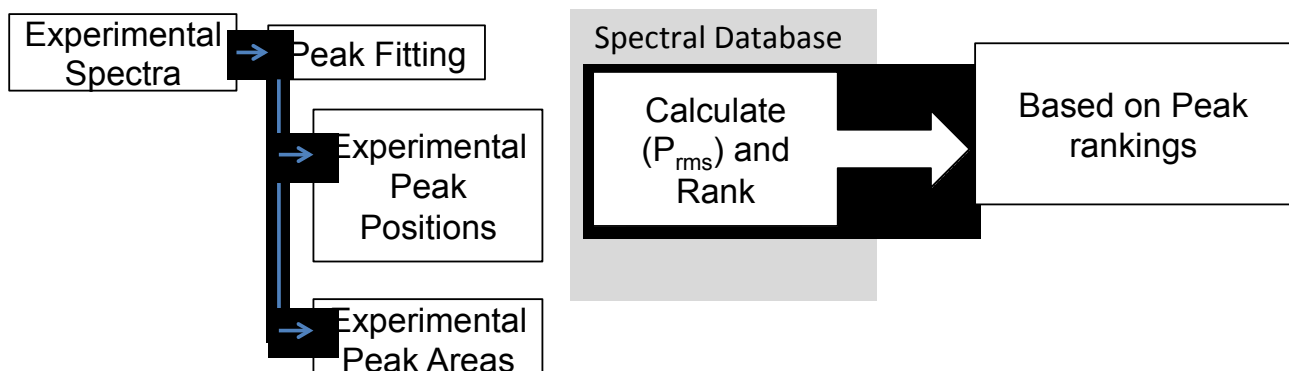
Intensity (Counts)	Relative Energy Position Beyond the Edge Onset	Peak Width (eV)
0.3	2.75	2
0.8	4.5	2
0.8	6.75	3.5
0.2	11.5	1.5
0.65	13	2.5
0.40	16	4.5

Following these initial parameters, a table of fits was established for each calculated and experimental spectra ensuring a better than 80% confidence based on deviation of the peak positions based on the following equation

Peak Position (eV) Deviation :

$$P_{rms} = \sqrt{\frac{(P_1^1 - P_1^2)^2 + (P_2^1 - P_2^2)^2 + \dots + (P_n^1 - P_n^2)^2}{n}}$$

where P_1^1 and P_1^2 are the energy positions for the same peak for two separate spectra and n is the number of peaks used to fit the spectra. Based on this metric, the results were tabulated and compared using a genetic search algorithm. Based on the outcome of the genetic search algorithm, illustrated below, we compared and ranked the calculated spectra against experimental spectra.



As an example we show below partial data, which shows the various fitting results as a function of c/a on the peak positions only. For simplicity only P_{rms} is primarily considered. However, when two candidate fits exhibited close P_{rms} values, the spectra that matched intensities as well as positions was manually chosen. We find for example, based on P_{rms} alone the T phase shows a lower deviation compared to the T' phase at position 6, that is the interface. (8. 2nm). However when taking the over all shape the T' produced a much better confidence of fit.

Probe	Distance (nm)	Peak Position 1	Peak Position 2	Peak Position 3	Peak Position 4	Peak Position 5	Peak Position 6	Deviation, (P_{rms})
Position 1	2.10	2.54	4.09	6.60	11.58	12.96	15.95	
<i>Fitted R: c/a 0.98</i>			3.68	6.43	11.72		15.94	0.23
<i>Bulk R Phase Displacement</i>			4.19	6.92			15.06	0.55
<i>Bulk R Phase</i>		2.28	4.75	5.89		13.55		1.04
Position 2	4.20	2.29	3.94	6.71	11.77	13.38	16.85	
<i>Fitted R: c/a 0.98</i>			3.68	6.43	11.72		15.94	0.50
<i>Bulk R Phase Displacement</i>			4.19	6.92			15.06	1.05
<i>Bulk R Phase</i>		2.28	4.75	5.89		13.55		1.15
Position 3	5.30	2.36	4.06	6.74	11.42	12.82	15.45	
<i>Fitted R: c/a 0.98</i>			3.68	6.43	11.72		15.94	0.38
<i>Bulk R Phase Displacement</i>			4.19	6.92			15.06	0.26
<i>Bulk R Phase</i>		2.28	4.75	5.89		13.55		1.15
Position 4	6.10	2.35	3.84	6.45	11.62	13.15	15.81	
<i>Fitted R: c/a 0.98</i>			3.68	6.43	11.72		15.94	0.11
<i>Bulk R Phase Displacement</i>			4.19	6.92			15.06	0.55
<i>Bulk R Phase</i>		2.28	4.75	5.89		13.55		0.57
Position 5	7.00	2.41	4.01	6.54	11.41	12.63	15.26	
<i>Fitted R: c/a 0.98</i>			3.68	6.43	11.72		15.94	0.41
<i>Bulk T Phase c/a 1.23 Displacement</i>		3.25	4.85	5.30			14.28	0.99
<i>Bulk T Phase c/a 1.28 Displacement</i>			3.21	6.45			14.71	0.56
<i>Bulk T Phase</i>			3.55	5.38		13.91	13.91	1.12
Position 6	8.20	1.44	3.57	6.59	10.95	12.80	16.34	
<i>Fitted T'</i>			3.97	6.19	11.11		15.30	0.60
<i>Fitted T: c/a 1.18</i>			3.46	6.10		12.10	16.24	0.43
<i>Bulk T Phase c/a 1.23 Displacement</i>		3.25	4.85	5.30			14.28	1.65
<i>Bulk T Phase c/a 1.28 Displacement</i>			3.21	6.45			14.71	0.96
<i>Bulk T Phase</i>			3.55	5.38		13.91	13.91	1.47
Position 7	9.20	2.09	3.66	6.71	10.89	12.75	16.35	
<i>Fitted T: c/a 1.18</i>			3.46	6.10		12.10	16.24	0.46
<i>Bulk T Phase c/a 1.23 Displacement</i>		3.25	4.85	5.30			14.28	1.51
<i>Bulk T Phase c/a 1.28 Displacement</i>			3.21	6.45			14.71	0.99
<i>Bulk T Phase</i>			3.55	5.38		13.91	13.91	1.51
Position 8	11.20	2.45	4.23	6.91	11.39	12.46	14.91	
<i>Fitted T: c/a 1.18</i>			3.46	6.10		12.10	16.24	0.89
<i>Bulk T Phase c/a 1.23 Displacement</i>		3.25	4.85	5.30			14.28	1.00
<i>Bulk T Phase c/a 1.28 Displacement</i>			3.21	6.45			14.71	0.65
<i>Bulk T Phase</i>			3.55	5.38		13.91	13.91	1.21
Position 9	12.50	2.13	3.87	6.75	11.23	12.72	15.30	
<i>Fitted T: c/a 1.18</i>			3.46	6.10		12.10	16.24	0.68
<i>Bulk T Phase c/a 1.23 Displacement</i>		3.25	4.85	5.30			14.28	1.16
<i>Bulk T Phase c/a 1.28 Displacement</i>			3.21	6.45			14.71	0.54
<i>Bulk T Phase</i>			3.55	5.38		13.91	13.91	1.15
Position 10	14.00	1.87	3.85	7.11	11.40	12.72	15.77	
<i>Fitted T: c/a 1.18</i>			3.46	6.10		12.10	16.24	0.66
<i>Bulk T Phase c/a 1.23 Displacement</i>		3.25	4.85	5.30			14.28	1.45
<i>Bulk T Phase c/a 1.28 Displacement</i>			3.21	6.45			14.71	0.81
<i>Bulk T Phase</i>			3.82	5.26		14.49	19.34	2.20

Note : Peak energy values are defined beyond the edge onset

S4. Quantifying the Valence State of Iron

To quantify the valence state of iron in bismuth ferrite we performed multiple linear least squares fitting. Utilizing the reference spectra and protocols given in van Aken et al. [Physics and Chemistry of Minerals, **29**, 188-200 (2002)] Fits were made for various iron valence states ranging from Fe^{3+} to Fe^{2+} . After processing the experimental spectra, in Figure S4(a) we report the normalized weights for each of the major spectral components utilized to fit the experimental Fe L_3 peak in Figure S4(b).

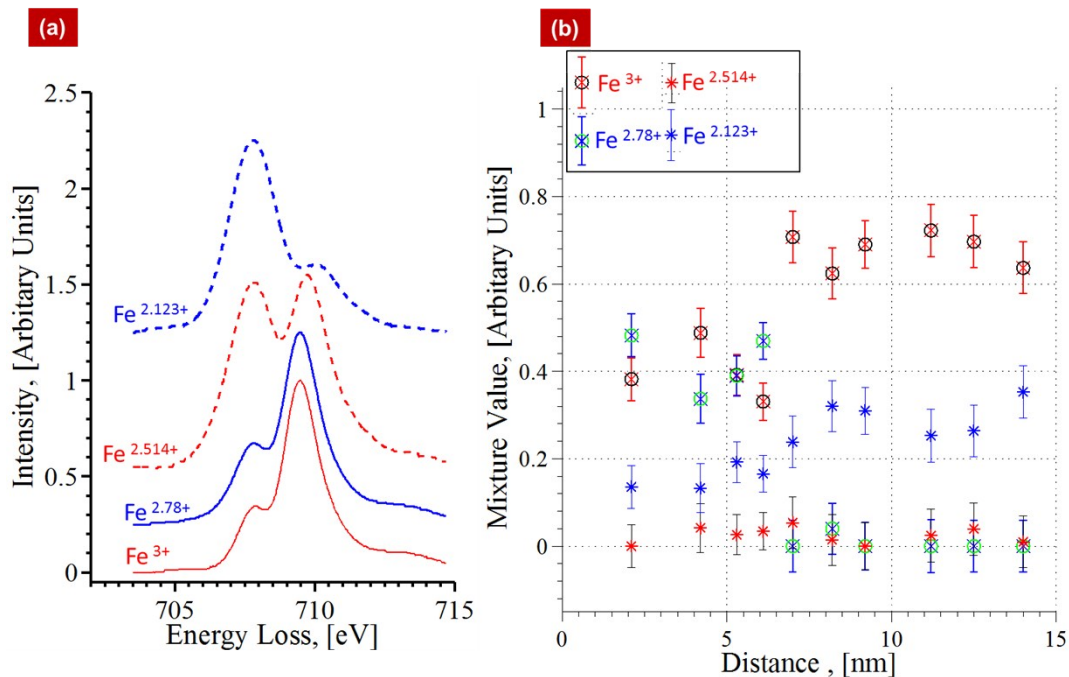


Fig.S4 The simulated Fe-L2,3 EEL spectra with their respective valence state and (b) the change in Fe valence state across T-R phase BFO.