Supplementary Information: Intrinsic ferroelectricity in charge-ordered magnetite

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Rocking curves

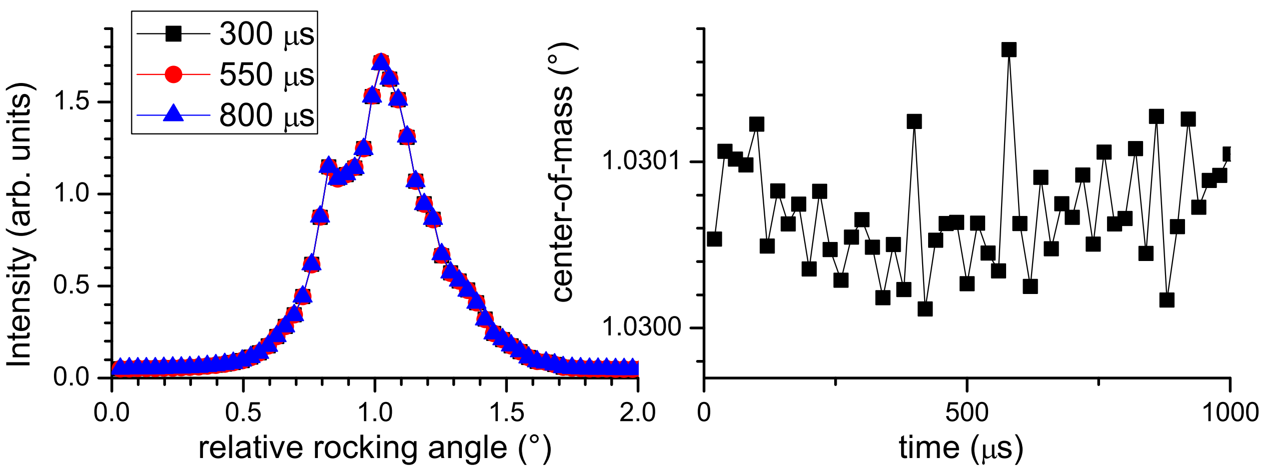

Figure S1: a) Examples of rocking curves of the $(2, \overline{2}, \overline{10})$ reflection at specific times within the cycle. The 0 of the rocking angle has been chosen to match the start of the rocking curves b) Time-dependence of the center-of-mass of the rocking curves, using a binning of $20\,\mu$s. The data displayed in this figure are from the same in-situ measurement with applied voltage pulses as the data shown in Fig. 5 of the main text.

Domains and calculation of intensity change

The structure factors displayed in table S1 have been calculated with JANA2006 (Ref. 44 of the main text), using as a model the refined Cc structure reported by Senn and coworkers (Ref. 3 of the main text). Concerning the polarization components in the Cc cell, different values a and c are obtained depending on whether the refined or a calculated (Ref. 4 of the main text) and point charge model or Berry phase methods are employed. However, c is either similar to a or significantly larger. For the sample investigated, the distribution of domain populations is unknown though it is a fair assumption that all domains are contributing with approximately equal weight. Furthermore, it is not known whether all domains switch polarization upon application of the (larger) voltage

Sym	**Reflection**	$\mathbf{F_c^2}$	$\mathbf{F^2_{c,Friedel}}$	$\mathbf{\Delta}$ (%)	**P**	$\mathbf{\Delta_P}$ (%)
1	$(\overline{4},0,20)_m = (\overline{2},2,10)_c$	120353	115281	4.306	$(-a,a,2c)$	4.306
2_{001}	$(4,0,20)_m = (2,\overline{2},10)_c$	117169	111670	4.807	$(a,-a,2c)$	4.807
2_{010}	$(0,4,\overline{20})_m = (2,2,\overline{10})_c$	113192	117101	-3.395	$(a,a,-2c)$	3.395
2_{100}	$(0,\overline{4},\overline{20})_m = (\overline{2},\overline{2},\overline{10})_c$	113192	117101	-3.395	$(-a,-a,-2c)$	3.395
3^+_{111}	$(12,8,4)_m = (10,\overline{2},2)_c$	113947	112782	1.028	$(2c,-a,a)$	1.028
$3^+_{1\overline{1}\overline{1}}$	$(\overline{12},\overline{8},4)_m = (\overline{10},2,2)_c$	112594	113226	-0.559	$(-2c,a,a)$	-0.559
$3^+_{\overline{1}11}$	$(\overline{8},\overline{12},\overline{4})_m = (\overline{10},\overline{2},\overline{2})_c$	101309	103452	-2.094	$(-2c,-a,-a)$	2.094
$3^+_{\overline{1}1\overline{1}}$	$(8,12,\overline{4})_m = (10,2,\overline{2})_c$	105554	105983	-0.406	$(2c,a,-a)$	0.406
3^-_{111}	$(\overline{8},12,\overline{4})_m = (2,10,\overline{2})_c$	101309	103452	-2.094	$(a,2c,-a)$	2.094
$3^-_{\overline{1}1\overline{1}}$	$(8,\overline{12},\overline{4})_m = (\overline{2},\overline{10},\overline{2})_c$	105554	105983	-0.406	$(-a,-2c,-a)$	0.406
$3^-_{1\overline{1}\overline{1}}$	$(\overline{12},8,4)_m = (\overline{2},10,2)_c$	112594	113226	-0.559	$(-a,2c,a)$	-0.559
$3^-_{\overline{1}11}$	$(12,\overline{8},4)_m = (2,\overline{10},2)_c$	113947	112782	1.028	$(a,-2c,a)$	1.028

Table S1: Calculated intensities for the 24 domains contributing to the intensity observed for the $(2,\overline{2},\overline{10})_c$ reflection. Listed are the symmetry operations of the 23 group of twin laws, the reflection in monoclinic and cubic indices, the calculated intensities (absolute squares of the structure factors) of these reflections, the calculated intensities of the corresponding Friedel mates (corresponding to additional symmetry operation $\overline{1}$), the relative intensity difference going from reflection to its Friedel mate, the polarization of the domain in original cubic indices (a and c correspond to the polarization components in the Cc cell), and the relative intensity difference going from positive to negative cubic c component of the polarization.

pulse or only those with a large (i.e. $2c$ or $-2c$) polarization component in the cubic (001) direction. Depending on this, different values of overall intensity changes can be obtained. The largest possible relative intensity change, for the unlikely case of a particular single-domain sample, is 4.8%. The lowest possible relative intensity change for arbitrary domain population is zero, as there are both positive and negative contributions by some domains. For the more likely case of all domains being approximately equally populated and all domains switching the polarization in $(001)_c$ direction with the applied field, the intensity change is 1.8%. For equally populated domains but only those domains with $2c$ polarizations along $(001)_c$ switching an intensity change of 1.3% is obtained. In short, without detailed knowledge of the actual domain population, a quantification of the intensity change is not possible, but for realistic scenarios a change of the order of 1 to 2% would be expected.