Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting information

Self-flux grown $Ba_4Fe_4ClO_{9.5-x}$ crystals exhibiting structures with tuneable modulation

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Reconstruction of the reciprocal space cross sections

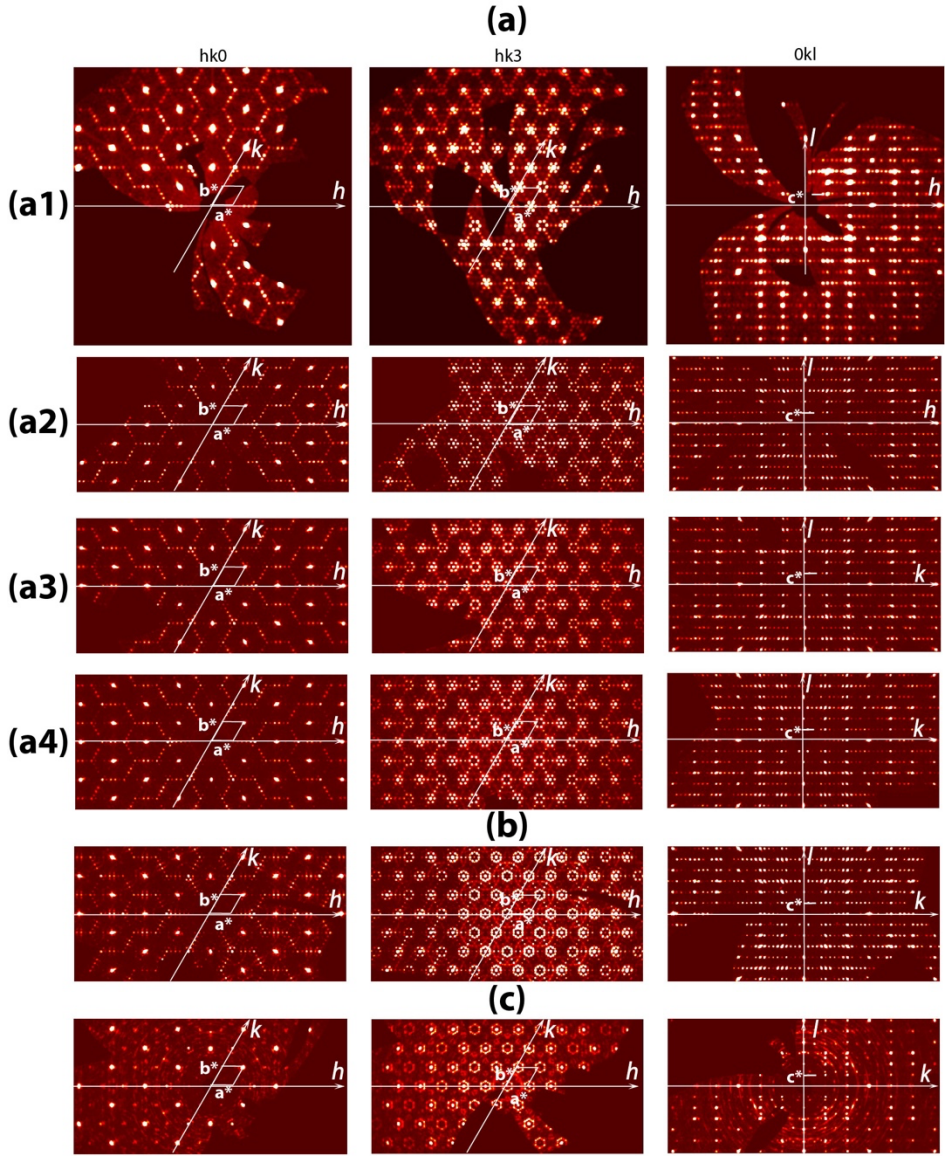

Figure S1. Representative cross sections of the reciprocal space reconstruction for $Ba_4Fe_4ClO_{9.5-x}$ crystals treated under different redox conditions: (a) oxidation conditions (group **I**), (b) high-temperature neutral (group **II**), and (c) reducing conditions (group **III**). Horizontal panel (a1) corresponds to as-grown crystal; the XRD experiment was taken at 100 K. Horizontal panel (a2) corresponds the crystal baked at 550 C in air; the XRD experiment was taken at 100 K is similar to one taken from the crystal baked at 400 C at the same T = 100 K. Horizontal panel (a3) corresponds to the crystal baked at 500 C in O_2 flow; the XRD experimental data are similar at both RT and 100 K. Horizontal panel (a4) corresponds to the crystal baked at 550 C in vacuum; the experiments are similar at both RT and 100 K. The sections *hk*0, *hk*3, 0*kl* demonstrate the brightest main reflections, and weaker satellite reflections, and specific features of diffuse scattering. The main reflections define the basic reciprocal unit cell (white rhombuses for **a***, **b*** in *hk*0 and *hk*3 and white dash in 0*kl* sections), which is identical for all the crystals.

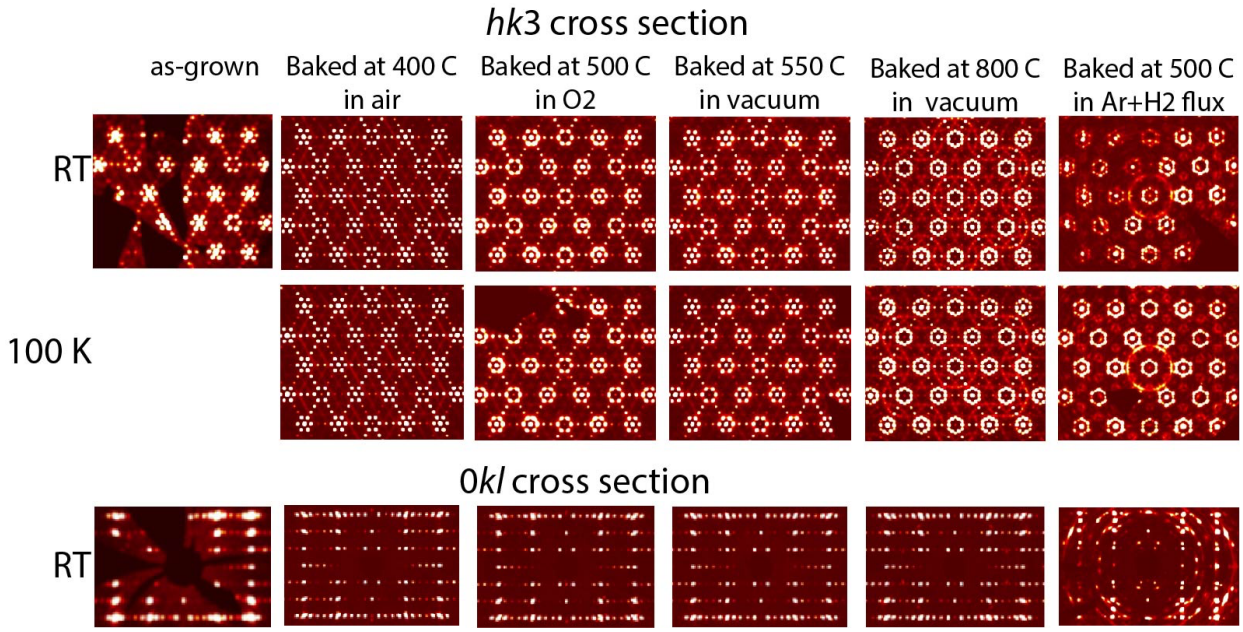

Figure S2. Diffuse scattering for $Ba_4Fe_4ClO_{9.5-x}$ crystals treated under different redox conditions.

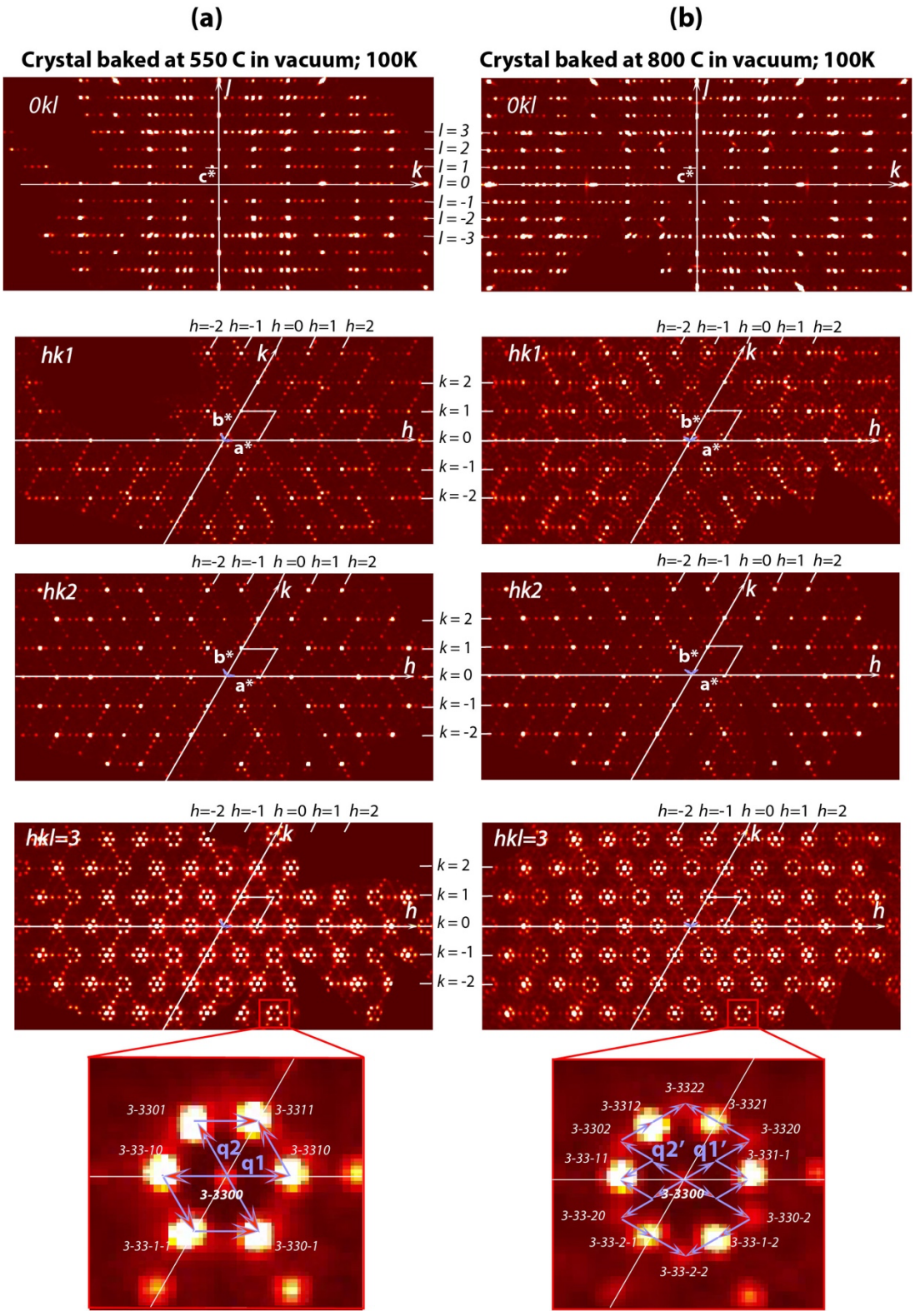

Figure S3. Reciprocal space sections and indexing of reflections for crystal Group **I** (vertical panel (a)) and Group **II** (vertical panel (b)) of $Ba_4Fe_4ClO_{9.5-x}$. Panel (a): typical patterns and indexing of reflections (bottom) for crystal of Group **I** using **q1** = 1/5**a*** and **q2** = 1/5**b***. Panel (b): typical patterns and indexing of reflections (bottom) for crystal of Group **II** using **q1'** = 1/15**a*** **+** 1/15**b*** and **q2'** = -2/15**a*** + 1/15**b***, which are related to the vectors in (a) as **q1'** + **q2'** = **q1** and **2q2'** + **q1'** = **q2**. The *hklmn* index of each reflection is defined by the vector sum *h***a*** + *k***b*** + *l***c*** + *m***q1** + *n***q2** and *h***a*** + *k***b*** + *l***c*** + *m***q1'** + *n***q2'** for Group **I** and **II**, respectively.

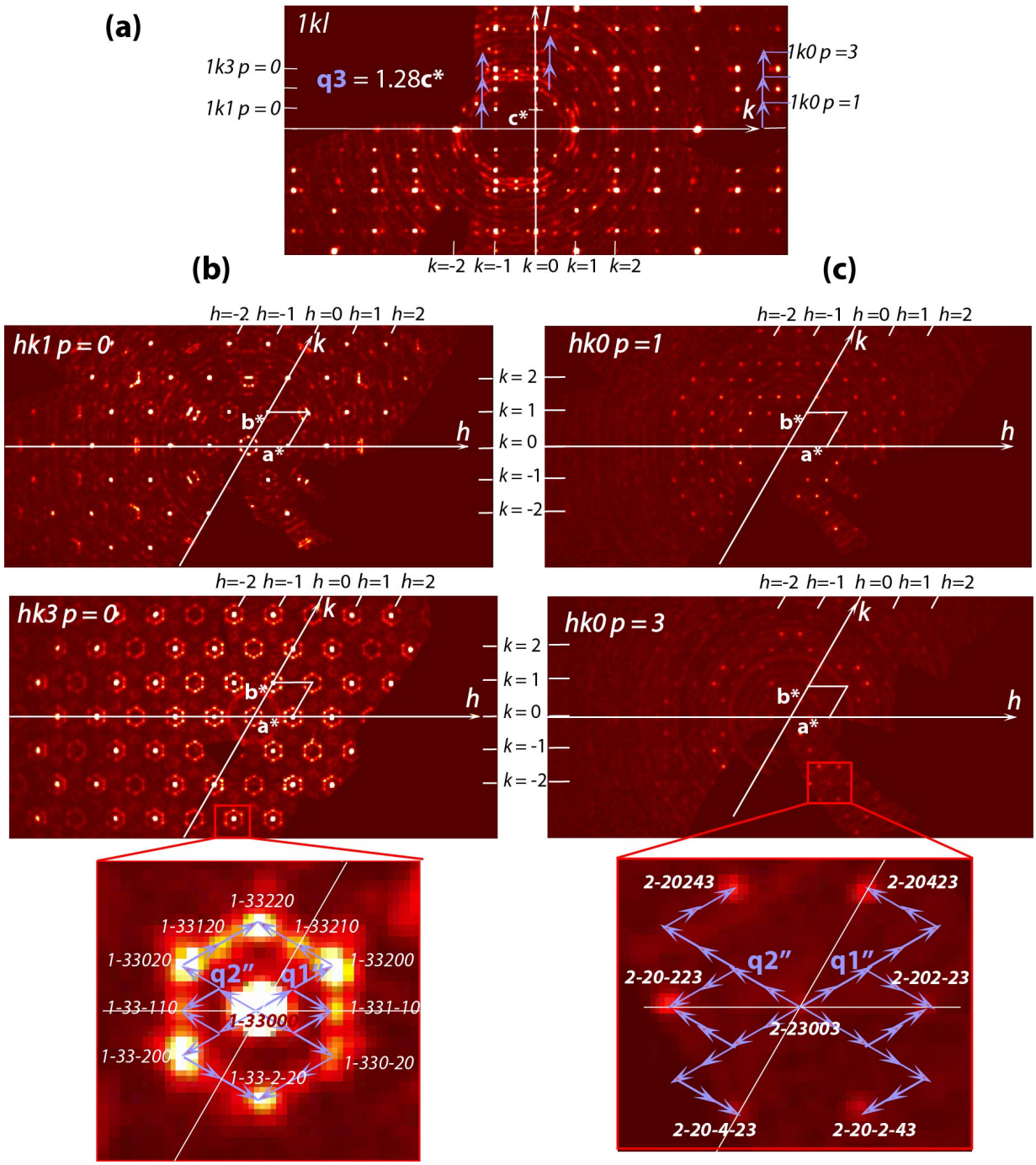

Figure S4. Reciprocal space sections and indexing of reflections for crystal Group **III** of $Ba_4Fe_4ClO_9$. Panel (a): 1*kl* cross section shows incommensurate vectors (blue arrows) **q3** = 1.277**c*** applied to *hk*0 and *hk*2 reflection lines. Panel (b) shows reflections, which can be indexed in *hk*1 and *hk*3 planes using **q1''** = 1/16**a*** + 1/16**b*** and **q2''** = -2/16**a*** + 1/16**b*** as shown at the bottom. Panel (c) shows satellite reflections, which can be only indexed using the additional **q3** vector as shown at the bottom. The *hklmnp* indexation uses the vector sum: *h***a*** + *k*b* + *l***c*** + *m***q1''** + *n***q2''** + *p***q3''**.

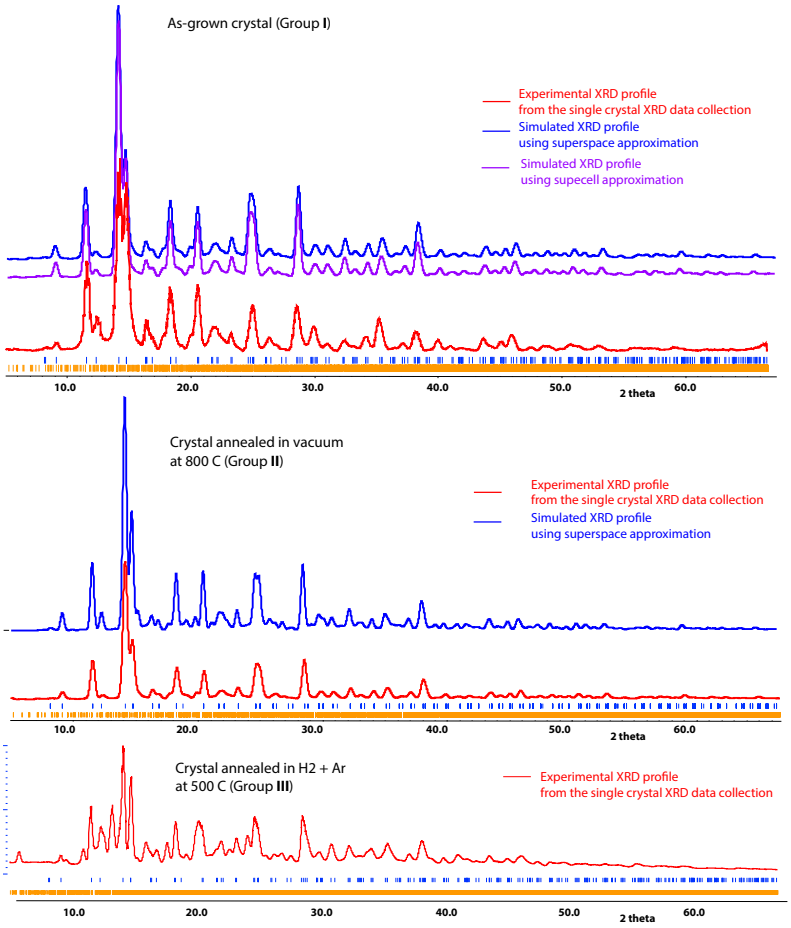

Figure S5. Comparison of the simulated XRD profiles and those calculated on the basis of the experimental diffraction data (Mo Kα-radiation) measured for single crystals $Ba_4Fe_4ClO_{9.5-x}$ of Groups **I** and **II**. At the figure bottom, the experimental diffraction data (Mo Kα-radiation) measured for a single crystal $Ba_4Fe_4ClO_9$ of crystal Groups **III** is also shown. Blue and orange strips indicate positions of the main and satellite reflections, respectively.

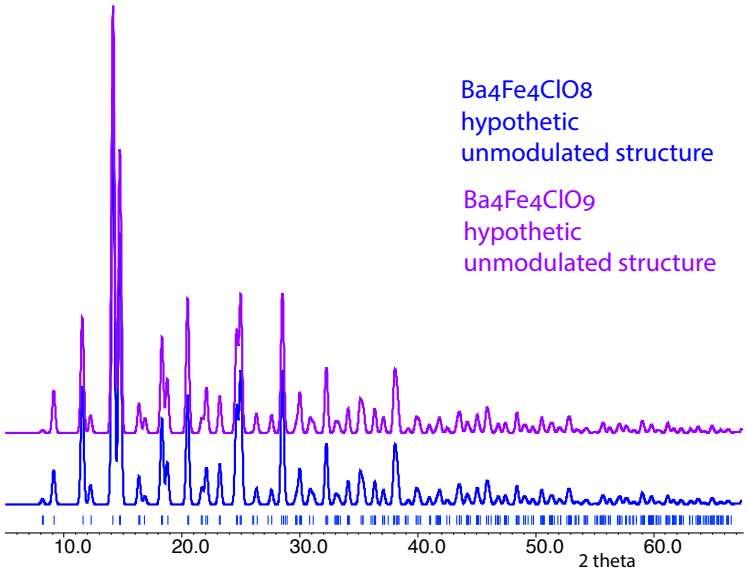

Figure S6. Powder XRD patterns calculated for the hypothetic unmodulated structures (Mo Kα-radiation).

Experimental details for $Ba_4Fe_4ClO_{9.5-x}$ average structure determination and refinement

Table S1. Experimental details for $Ba_4Fe_4ClO_{9.5-x}$ average structure determination and refinement using crystals processed under different conditions. For all crystals: hexagonal space group, $P\bar{6}m2$, Z = 1; experiments were carried out with Mo Kα radiation.

	Group **I**			Group **II**	Group **III**
Crystal processing condition	As-grown	Baking at 400 C in air	Baking at 500 C in O_2 flow	Baking at 800 C in vacuum	Baking at 500 C in ($Ar+H_2$) flow
Crystal data					
Chemical formula	$Ba_4Fe_4ClO_{9.4(1)}$	$Ba_4Fe_4ClO_{9.5(1)}$	$Ba_4Fe_4ClO_{9.5(1)}$	$Ba_4Fe_4ClO_{9.4(1)}$	$Ba_4Fe_4ClO_{9.0(1)}$
a, *c* (Å)	5.7612(6), 9.9792(12)	5.7625(5), 9.9880(11)	5.7625(5), 9.9859(12)	5.7655(5), 10.0022(12)	5.7585(5), 9.9796(12)
V (Å^3)	286.85	287.23	287.17	287.94	286.59
Data collection					
Temperature (K)	100	100	100	293	100
No. of measured, independent and observed reflections	1969, 432, 424 [$I > 3\sigma(I)$]	4402, 449, 442 [$I > 3\sigma(I)$]	4986, 409, 360 [$I > 5\sigma(I)$]	5182, 421, 419 [$I > 3\sigma(I)$]	2759, 393, 393 [$I > 3\sigma(I)$]
R_{int}	0.029	0.067	0.079	0.086	0.063
Refinement					
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.032, 0.088, 2.38	0.040, 0.100, 4.12	0.030, 0.081, 3.66	0.030, 0.080, 3.42	0.040, 0.100, 3.61
No. of reflections	424	442	360	419	393
No. of parameters	38	34	29	32	29
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.28, -3.42	5.03, -3.14	5.37, -3.20	3.23, -1.43	5.48, -2.50

Table S2. Experimental details for $Ba_4Fe_4ClO_{9.5-x}$ modulated structure determination and refinement using crystals processed at different conditions. For all crystals: hexagonal crystallographic system is fitted space group $P\bar{6}m2$ for the average structure; experiments were carried out with Mo Kα radiation at 100 K.

	Group **I**			Group **II**
Crystal processing condition	As-grown		Baking at 400 C in O_2 flow	Baking at 800 C in vacuum
Structure refinement approximation	Superspace approach	Supercell approach	Supercell approach	Superspace approach
Chemical formula	$Ba_4Fe_4ClO_{9.4(1)}$	$Ba_4Fe_4ClO_{9.4(1)}$	$Ba_4Fe_4ClO_{9.5(1)}$	$Ba_4Fe_4ClO_{9.4(1)}$
Space / superspace group	$P\bar{6}m2$ (α,0,0)000(-α,α0)00 (No. 187.2.82.3) †	$P\bar{6}m2$ (No. 187)	$P\bar{6}m2$ (No. 187)	$P\bar{6}m2$ (α,α,0)000(-2α,α0)00 (No. 187.2.83.4) ‡
Wave **q**-vectors	$\mathbf{q}_1 = 0.2\mathbf{a}^*$; $\mathbf{q}_2 = -0.2\mathbf{a}^* + 0.2\mathbf{b}^*$	-	-	$\mathbf{q}_1 = 1/15\mathbf{a}^* + 1/15\mathbf{b}^*$; $\mathbf{q}_2 = -2/15\mathbf{a}^* + 1/15\mathbf{b}^*$
a, c (Å)	5.7612 (6), 9.9792 (12)	5.7612 × 5 = 28.806 (1), 9.9792 (12)	5.7625 × 5 = 28.813 (1), 9.9859 (12)	5.7655 (5), 10.0022 (12)
V (Å^3)	286.85 (5)	286.85 × 25 = 7171.25 (3)	287.17× 25 = 7180.77 (3)	287.94 (5)
No. of measured, independent and observed reflections	37819, 11036, 3368 [$I > 5\sigma(I)$]	37819, 8870, 3407 [$I > 5\sigma(I)$]	37905, 8879, 4231 [$I > 5\sigma(I)$]	58747, 9678, 4707 [$I > 5\sigma(I)$]
R_{int}	0.060	0.064	0.053	0.082
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.050, 0.117, 2.16	0.031, 0.072, 1.34	0.052, 0.127, 3.99	0.095, 0.231, 6.31
No. of reflections	3368	3407	4231	4707

No. of parameters	248	317	318	207
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	5.32, -6.20	1.97, -1.48	6.06, -2.14	19.41, -12.62

† Symmetry operations: (1) x_1, x_2, x_3, x_4, x_5; (2) $-x_2, x_1-x_2, x_3, -x_4-x_5, x_4$; (3) $-x_1+x_2, -x_1, x_3, x_5, -x_4-x_5$; (4) $x_1, x_2, -x_3, x_4, x_5$; (5) $-x_2, x_1-x_2, -x_3, -x_4-x_5, x_4$; (6) $-x_1+x_2, -x_1, -x_3, x_5, -x_4-x_5$; (7) $-x_2, -x_1, x_3, -x_4-x_5, x_5$; (8) $-x_1+x_2, x_2, x_3, x_5, x_4$; (9) $x_1, x_1-x_2, x_3, x_4, -x_4-x_5$; (10) $-x_2, -x_1, -x_3, -x_4-x_5, x_5$; (11) $-x_1+x_2, x_2, -x_3, x_5, x_4$; (12) $x_1, x_1-x_2, -x_3, x_4, -x_4-x_5$.

‡ Symmetry operations: (1) x_1, x_2, x_3, x_4, x_5; (2) $-x_2, x_1-x_2, x_3, -x_4-x_5, x_4$; (3) $-x_1+x_2, -x_1, x_3, x_5, -x_4-x_5$; (4) $x_1, x_2, -x_3, x_4, x_5$; (5) $-x_2, x_1-x_2, -x_3, -x_4-x_5, x_4$; (6) $-x_1+x_2, -x_1, -x_3, x_5, -x_4-x_5$; (7) $-x_2, -x_1, x_3, -x_4, x_4+x_5$; (8) $-x_1+x_2, x_2, x_3, x_4+x_5, -x_5$; (9) $x_1, x_1-x_2, x_3, -x_5, -x_4$; (10) $-x_2, -x_1, -x_3, -x_4, x_4+x_5$; (11) $-x_1+x_2, x_2, -x_3, x_4+x_5, -x_5$; (12) $x_1, x_1-x_2, -x_3, -x_5, -x_4$.

Table S3. Atomic position parameters (site symmetry, *xyz*, U_{eq} and occupancy) in $Ba_4Fe_4ClO_{9.5-x}$ average structure (sp.gr. $P\bar{6}m2$; $a \approx 5.76$, $c \approx 10.00$ Å) for crystals processed under different conditions.

	Group **I**			Group **II**	Group **III**
Crystal processing condition	As-grown	Baking at 400 C in air	Baking at 500 C in O_2 flow	Baking at 800 C in vacuum	Baking at 500 C in ($Ar+H_2$) flow
Ba11 1f: (2/3 1/3 ½)	U_{eq} = 0.007; occ. = 1	U_{eq} = 0.008; occ. = 1	U_{eq} = 0.003; occ. = 1	U_{eq} = 0.016; occ. = 1	U_{eq} = 0.017; occ. = 1
Ba12 1e: (1/3 2/3 0)	U_{eq} = 0.012; occ. = 1	U_{eq} = 0.018; occ. = 1	U_{eq} = 0.014; occ. = 1	U_{eq} = 0.022; occ. = 1	U_{eq} = 0.008; occ. = 1
Ba21 2g: (0 0 z)	z = 0.3046, U_{eq} = 0.003; occ. = 0.47	z = 0.3054, U_{eq} = 0.003; occ. = 0.41	z = 0.3074, U_{eq} = 0.001; occ. = 0.51	z = 0.3052, U_{eq} = 0.008; occ. = 0.45	z = 0.3040, U_{eq} = 0.004; occ. = 0.50
Ba22 2g: (0 0 z)	z = 0.1958, U_{eq} = 0.005; occ. = 0.53	z = 0.1952, U_{eq} = 0.009; occ. = 0.59	z = 0.1977, U_{eq} = 0.003; occ. = 0.49	z = 0.1977, U_{eq} = 0.011; occ. = 0.55	z = 0.1955, U_{eq} = 0.008; occ. = 0.50
Fe1 2h: (1/3 2/3 z)	z = 0.3434, U_{eq} = 0.012; occ. = 1	z = 0.3468, U_{eq} = 0.013; occ. = 1	z = 0.3522, U_{eq} = 0.008; occ. = 1	z = 0.3489, U_{eq} = 0.022; occ. = 1	z = 0.3394, U_{eq} = 0.022; occ. = 1
Fe2 2h: (2/3 1/3 z)	z = 0.1574, U_{eq} = 0.015; occ. = 1	z = 0.1630, U_{eq} = 0.021; occ. = 1	z = 0.1669, U_{eq} = 0.012; occ. = 1	z = 0.1663, U_{eq} = 0.012; occ. = 1	z = 0.1568, U_{eq} = 0.013; occ. = 1
Cl1 1a: (0 0 0)	U_{eq} = 0.046; occ. = 0.47	U_{eq} = 0.008; occ. = 0.41	U_{eq} = 0.008; occ. = 0.51	U_{eq} = 0.026; occ. = 0.45	U_{eq} = 0.001; occ. = 0.50
Cl2 1b: (0 0 ½)	U_{eq} = 0.003; occ. = 0.53	U_{eq} = 0.037; occ. = 0.59	U_{eq} = 0.031; occ. = 0.49	U_{eq} = 0.030; occ. = 0.55	U_{eq} = 0.055; occ. = 0.50
O1 6n: (x -x z)	x = 0.502 z = 0.243 U_{eq} = 0.007; occ. = 1	x = 0.495 z = 0.246 U_{eq} = 0.007; occ. = 1	x = 0.493 z = 0.250 U_{eq} = 0.004; occ. = 1	x = 0.498 z = 0.252 U_{eq} = 0.015; occ. = 1	x = 0.501 z = 0.246 U_{eq} = 0.046; occ. = 1
O21b 6m: (xy ½)	x = 0.154 y = 0.424 U_{eq} = 0.043; occ. = 0.20	-----	x = 0.154 y = 0.428 U_{eq} = 0.008; occ. = 0.20	---	---

O21b 3k: (x 2x ½)	----	x = 0.215 y = 0.430 U_{eq} = 0.046; occ. = 0.333	----	----	----
O21a 3k: (x 2x ½)	---	---	---	x = 0.3693 U_{eq} = 0.281; occ. = 0.400	x = 0.186 U_{eq} = 0.018; occ. = 0.667
O22a 3j: (x 2x 0)	x = 0.642 U_{eq} = 0.023; occ. = 0.064	x = 0.637 U_{eq} = 0.012; occ. = 0.333	---	x = 0.634 U_{eq} = 0.018; occ. = 0.064	x = 0.7045 U_{eq} = 0.012; occ. = 0.333
O22a 1e: (2/3 1/3 0)	---	---	U_{eq} = 0.004; occ. = 0.30	---	---
O22b 3j: (x 2x 0)	x = 0.815 U_{eq} = 0.017; occ. = 0.667	x = 0.824 U_{eq} = 0.046; occ. = 0.493	x = 0.822 U_{eq} = 0.013; occ. = 0.667	x = 0.817 U_{eq} = 0.018; occ. = 0.667	---