Supplementary material

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Incommensurately modulated ordering of tetrahedral chains in $Ca_2Fe_2O_5$ at elevated temperatures

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Abstract

The basic building units of brownmillerite-type $A_2B_2O_5$ structures are perovskite like layers of corner sharing BO_6 octahedra and *zweier* single chains of BO_4 tetrahedra. A three-dimensional framework is formed by alternate stacking of octahedral layers and sheets of tetrahedral chains. The compound $Ca_2Fe_2O_5$ is known to have $Pnma$ symmetry at ambient conditions. Space group $Imma$ was reported to be evident above 963K. New HT single crystal X-ray diffraction experiments at 1100K revealed, that $Ca_2Fe_2O_5$ forms an incommensurately modulated structure adopting superspace group $Imma(00\gamma)s00$, with γ=0.588(2). The modulation affects the sequence of the enantiomorph (right- and left-handed) oriented tetrahedral chains within the layer, breaking the lattice periodicity along c. This ordering can be modelled with crenel occupation modulation functions for the tetrahedrally coordinated Fe, as well as for the oxygen atom interconnecting the tetrahedra.

Table 1: Atomic Coordinates and Equivalent Isotropic Displacement Factors (Å^2). $U(eq)$ is defined as one third of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
Fe1	0	0	0.5	0.0218(2)
Fe2	0.94636(15)	0.25	0.56860(18)	0.0204(2)
Ca1	0	0.10808(7)	0.02377(19)	0.0304(3)
O1	0.75	0.0131(2)	0.75	0.0259(9)
O2	0	0.1413(2)	0.4317(8)	0.0370(11)
O3	0.4021(7)	0.25	0.6255(9)	0.0265(14)

Table 2: Anisotropic displacement parameters (Å^2). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe1	0.0133(3)	0.0378(5)	0.0142(4)	-0.0010(4)	0	0
Fe2	0.0234(4)	0.0163(4)	0.0213(5)	0	-0.0001(3)	0
Ca1	0.0395(5)	0.0233(4)	0.0284(5)	0.0008(4)	0	0
O1	0.0178(12)	0.0364(17)	0.0236(16)	0	0.0094(12)	0
O2	0.052(2)	0.0231(16)	0.036(2)	-0.0070(16)	0	0
O3	0.0187(19)	0.031(3)	0.030(3)	0	-0.0051(17)	0

Table 3: Fourier coefficients of the modulation functions: $u_i(x_4) = A_{1,i}\sin(2\pi x_4) + B_{1,i}\cos(2\pi x_4), i = 1, 2, 3$, and x_4^0 centres of crenel occupation functions of width $\Delta = 0.5$

Atom	x_4^0	$A_{1,1}$	$A_{1,2}$	$A_{1,3}$	$B_{1,1}$	$B_{1,2}$	$B_{1,3}$
Fe1		0.00333(17)	0	0	0	0	0
Fe2	0.6452(7)						
Ca1		0.0088(2)	0	0	-0.0115(2)	0	0
O1		0.0039(6)	0	0.0023(9)	0	-0.0015(3)	0
O2		-0.0039(9)	0	0	-0.0191(9)	0	0
O3	0.178(3)						

Table 4: Bonding angles of tetrahedrally and octahedrally coordinated iron, including averages (ave) and extrema caused by the modulation. Part 1

Atoms	$ave[^\circ]$	$min[^\circ]$	$max[^\circ]$	symmetry codes
Fe1-O1				$-1+x, y, z$
O1-Fe1-O1	179.36(15)	178.99(17)	180	$1-x, -y, 1-z$
O1-Fe1-O1	87.83(14)	87.83(16)	87.83(12)	$1-x, y, z$
O1-Fe1-O1	92.18(14)	91.98(14)	92.37(14)	$-1+x, -y, 1-z$
O1-Fe1-O2	91.71(18)	89.57(16)	93.85(16)	x, y, z
O1-Fe1-O2	88.29(18)	86.79(19)	89.8(2)	$-x, -y, 1-z$
Fe1-O1				$1-x, -y, 1-z$
O1-Fe1-O1	179.36(15)	178.99(17)	180	$-1+x, y, z$
O1-Fe1-O1	92.18(14)	91.98(14)	92.37(14)	$1-x, y, z$
O1-Fe1-O1	87.83(14)	87.83(16)	87.83(13)	$-1+x, -y, 1-z$
O1-Fe1-O2	88.29(18)	86.79(19)	89.8(2)	x, y, z
O1-Fe1-O2	91.71(18)	89.57(16)	93.85(16)	$-x, -y, 1-z$
Fe1-O1				$1-x, y, z$
O1-Fe1-O1	87.83(14)	87.83(16)	87.83(13)	$-1+x, y, z$
O1-Fe1-O1	92.18(14)	91.98(14)	92.37(14)	$1-x, -y, 1-z$
O1-Fe1-O1	179.36(15)	178.99(17)	180	$-1+x, -y, 1-z$
O1-Fe1-O2	91.71(18)	89.57(16)	93.85(16)	x, y, z
O1-Fe1-O2	88.29(18)	86.79(19)	89.8(2)	$-x, -y, 1-z$
Fe1-O1				$-1+x, -y, 1-z$
O1-Fe1-O1	92.18(14)	91.98(14)	92.37(14)	$-1+x, y, z$
O1-Fe1-O1	87.83(14)	87.83(16)	87.83(12)	$1-x, -y, 1-z$
O1-Fe1-O1	179.36(15)	178.99(17)	180	$1-x, y, z$
O1-Fe1-O2	88.29(18)	86.79(19)	89.8(2)	x, y, z
O1-Fe1-O2	91.71(18)	89.57(16)	93.85(16)	$-x, -y, 1-z$
Fe1-O2				x, y, z
O2-Fe1-O2	177.80(19)	176.54(19)	180	$-x, -y, 1-z$
Fe1-O2				$-x, -y, 1-z$
O2-Fe1-O2	177.80(19)	176.54(19)	180	x, y, z

Table 5: Bonding angles of tetrahedrally and octahedrally coordinated iron, including averages (ave) and extrema caused by the modulation. Part 2

Atoms	$ave[^\circ]$	$min[^\circ]$	$max[^\circ]$	symmetry codes
Fe2-O2				$1+x, y, z$
O2-Fe2-O2	124.80(19)	123.86(19)	126.69(19)	$1+x, 1/2-y, z$
O2-Fe2-O3	107.02(15)	106.39(15)	108.40(15)	$3/2-x, 1/2-y, 3/2-z$
O2-Fe2-O3	105.23(17)	102.57(17)	106.45(17)	$1-x, y, z$
O2-Fe2-O3	116.09(13)	116.08(13)	116.09(13)	$1/2+x, 1/2-y, 3/2-z$
Fe2-O2				$1+x, 1/2-y, z$
O2-Fe2-O2	124.80(19)	123.86(19)	126.69(19)	$1+x, y, z$
O2-Fe2-O3	107.02(15)	106.39(15)	108.40(15)	$3/2-x, 1/2-y, 3/2-z$
O2-Fe2-O3	105.23(17)	102.57(17)	106.45(17)	$1-x, y, z$
O2-Fe2-O3	116.09(13)	116.08(13)	116.09(13)	$1/2+x, 1/2-y, 3/2-z$
Fe2-O3				$3/2-x, 1/2-y, 3/2-z$
O3-Fe2-O3	106.2(2)	106.2(2)	106.2(2)	$1-x, y, z$
Fe2-O3				$1-x, y, z$
O3-Fe2-O3	106.2(2)	106.2(2)	106.2(2)	$3/2-x, 1/2-y, 3/2-z$
O3-Fe2-O3	72.5(2)	72.5(2)	72.5(2)	$1/2+x, 1/2-y, 3/2-z$
Fe2-O3				$1/2+x, 1/2-y, 3/2-z$
O3-Fe2-O3	72.5(2)	72.5(2)	72.5(2)	$1-x, y, z$