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Synthesis, crystal structure and magnetic properties of MnFe₃O₅

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$MnFe_3O_5$ has been synthesised under a pressure of 10 GPa at 1400 °C. $MnFe_3O_5$ has an orthorhombic structure (space group *Cmcm*, a = 2.9137(1), b = 9.8565(7) and c = 12.6143(6) Å at 300 K) and is isostructural with Fe_4O_5. Magnetic measurements reveal an antiferromagnetic transition at 350 K and a broad Curie transition at 150 K, similar to the spin ordering temperatures of Fe_4O_5. Variable temperature synchrotron X-ray diffraction shows that the structure undergoes anisotropic thermal expansion below 350 K, but no long range charge ordering is observed in the crystal structure.

Introduction

Magnetite (Fe_3O_4) has been one of the most intensively studied transition metal oxide systems since the discovery of the low temperature Verwey transition in 1939.[1] However, due to the difficulties in obtaining experimental evidence to test Verwey's charge ordering hypothesis, the ground state structure was only recently solved.[2] This revealed a complex charge and orbital ordered arrangement with weak Fe-Fe bonding interactions giving rise to trimerons, linear orbital molecule clusters of three Fe ions.

Fe_3O_4 may be described as the n = 3 member of the $MFe_{n-1}O_{n+1}$ family (with M^{2+} = Fe), and other members have recently been explored.[3] Fe_4O_5 was synthesised using high pressure and high temperature methods,[4] and a structural study revealed anisotropic thermal expansion in the lattice parameters when cooled below room temperature. An incommensurate charge order is observed at T_{CO} = 150 K, below which dimeron and trimeron like groups of Fe ions are formed.[5] Two magnetic transitions were also found, an antiferromagnetic ordering at 320 K and a further spin canting transition at 85 K. Subsequent work has shown that a related series of Fe_nO_{n+1} homologues can be made for larger n, also at pressure.[6] n = 4, 5, and 6 phases were also reported in an early study of the M = Ca system,[7] and a coupled structural and magnetic transition is observed at 360 K in $CaFe_5O_7$, associated with Fe^{2+} and Fe^{3+} charge order and accompanying orbital and spin orders.[8]
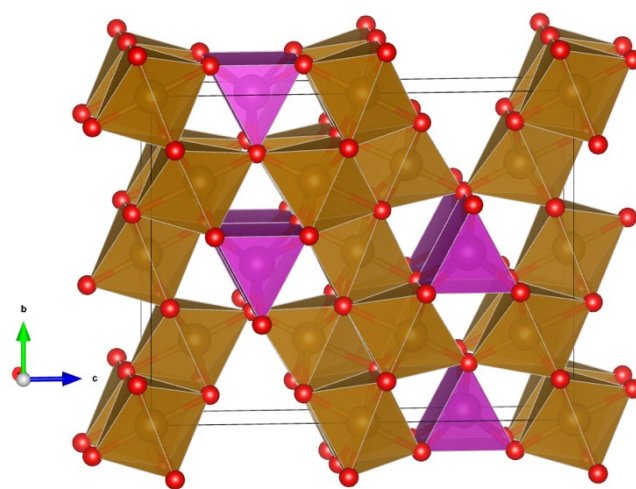

Figure 1. The *Cmcm* structure of $MnFe_3O_5$ with FeO_6 edge sharing octahedra shown in brown, MnO_6 triangular prisms in purple and the oxygens represented by red spheres.[9]

The n = 4 $MFe_{n-1}O_{n+1}$ phases adopt the orthorhombic $Sr_2Tl_2O_5$ type structure in which M^{2+} cations occupy triangular prismatic sites within a network of corner and edge-sharing FeO_6 octahedra, as shown in Figure 1. As M = Fe and Ca phases are already known, it seems likely that an M = Mn analogue should also be accessible at pressure. High pressure is known to stabilise high spin Mn^{2+} ion in unusual coordination environments, for example, at the A cation sites of the ABO_3 perovskite structure in $MnVO_3$;[10] double perovskites Mn_2FeSbO_6[11], Mn_2ScSbO_6[12], Mn_2FeReO_6[13,14], and Mn_2MnReO_6 (Mn_3ReO_6);[15] 134 types ζ-Mn_2O_3[16] and $MnCu_3V_4O_{12}$;[17] and the new 'double double' cation ordered phases $MnRMnSbO_6$ (R = La, Pr, Nd, Sm).[18] We report here the synthesis and initial characterisation of the structure and magnetic properties of $MnFe_3O_5$.

Results and Discussion

A polycrystalline sample of $MnFe_3O_5$ was synthesised using a high pressure solid-state synthetic method as described in the experimental section. Laboratory powder X-ray diffraction confirmed that $MnFe_3O_5$ is isostructural with previous MFe_3O_5 phases (M = Ca, Fe) and has an

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orthorhombic structure with space group *Cmcm*. The room temperature lattice parameters of $MnFe_3O_5$ (a = 2.9137(1), b = 9.8565(7) and c = 12.6143(6) Å) are larger than those for Fe_4O_5 (a = 2.8906(1), b = 9.8024(3) and c = 12.5804(4) Å),[5] consistent with the relative ionic sizes of Mn^{2+} and Fe^{2+}. There are two iron sites in $MnFe_3O_5$ which form edge-sharing FeO_6 octahedra in layers perpendicular to the c axis. Layers are interleaved by channels of Mn^{2+} ions in triangular prisms that share faces along the a axis (Fig. 1).
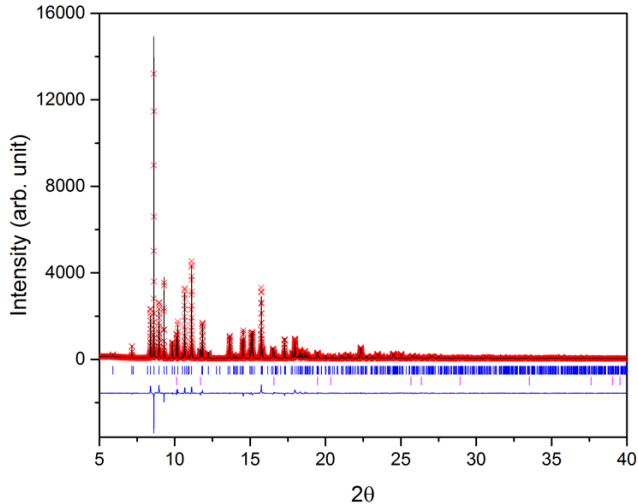

Figure 2. Rietveld fit to synchrotron powder diffraction profiles for $MnFe_3O_5$ at 300 K, with upper tick marks indicating the $MnFe_3O_5$ phase and lower for platinum.[19]

Synchrotron powder x-ray diffraction data were recorded between 90 and 400 K. No structural phase transition was observed in this range. Rietveld fitting of the room temperature synchrotron diffraction data is shown in Figure 2. A small amount of platinum from the capsule used in the high pressure synthesis was also observed. The changes in lattice parameters and cell volume with temperature are shown in Figure 3a and b, respectively. Similar to Fe_4O_5, anisotropic thermal expansion is observed in $MnFe_3O_5$,[5] with a and c contracting with decreasing temperature, whilst b expands. The onset of the anisotropic behaviour is close to the 350 K magnetic ordering transition described later, and thus the lattice distortion appears to be magnetostrictive. However, no long range structural change accompanying possible charge order is seen down to 90 K in $MnFe_3O_5$, which may reflect the presence of some Mn/Fe cation disorder although this cannot be quantified in our X-ray structure refinements.

Details of the refined structure models for $MnFe_3O_5$ at 90 and 400 K are summarised in Tables 1 and 2. The average Mn-O bond distance is greater than that for the two Fe sites, confirming that the former site is occupied principally by Mn. Fe-O bond distances for the two Fe sites are very similar. The Bond Valence Sum (BVS) for each cation site was calculated using the standard Mn^{2+} parameter for the M = Mn1 site, and an interpolation method for the mixed Fe^{2+}/Fe^{3+} sites Fe1 and Fe2.[20,21] The BVS's of Mn1, Fe1 and Fe2 were estimated to be +1.65, +2.55 and +2.44 respectively at 400 K, confirming Mn^{2+} at the trigonal prismatic M = Mn1 site. However, it was not possible to refine the Fe/Mn populations of the cation sites directly given the very similar electron densities of the two elements, and neutron diffraction will be needed to confirm the overall composition and cation distribution. The similarity of the two Fe site BVS's shows that there is no long

range charge ordering between Fe1 and Fe2. Both Fe sites are occupied by Fe^{2+} and Fe^{3+} according to the average formal charge state of $Fe^{2.67+}$.

It is notable that the Fe-Fe distances within edge-sharing octahedral chains parallel to the a-axis shrink significantly on cooling from 400 to 90 K (this is equivalent to the a-axis contraction shown in Figure 3(a)), whereas the other short Fe1-Fe2 distance expands. This suggests that some weak Fe-Fe bonding may occur within the chains of the magnetically ordered phase, as observed in the dimeron and trimeron units found in Fe_4O_5 and the trimerons of Fe_3O_4.[2,5]

Magnetic susceptibility measurements shown in Figure 4a reveal two magnetic transitions for $MnFe_3O_5$ at similar temperatures to those in Fe_4O_5. The susceptibility maximum at 350 K evidences an antiferromagnetic transition, as observed at 320 K in Fe_4O_5. A broad susceptibility upturn below 150 K evidences spin canting or some other ferro- or ferri- magnetic transition. This is close to the 150 K charge ordering and 85 K spin rearrangement transition temperatures of Fe_4O_5.
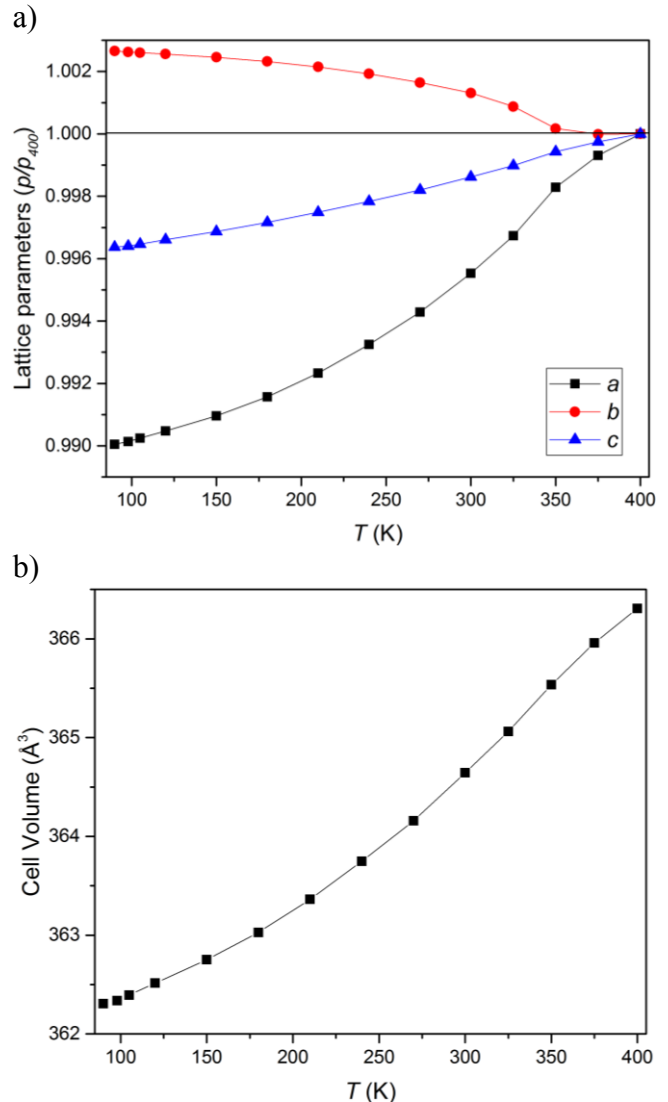

Figure 3. Changes in the a) lattice parameters relative to 400 K values (which are shown in Table 1) and b) cell volume of $MnFe_3O_5$ between 90 and 400 K.

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Table 1. Lattice parameters, atomic coordinates, and isotropic thermal displacements from synchrotron refinements in *Cmcm* space group of $MnFe_3O_5$ at 400 K (upper values) and 90 K (lower values). Estimated standard deviations in independent variables are shown in parentheses. R-factors are R_{wp} = 15.9 and 13.9 %, and R_p = 14.5 and 12.8 % at 400 and 90 K respectively.

a (Å)		b (Å)		c (Å)		Volume (Å^3)
2.93332(2)		9.86510(7)		12.65855(9)		366.307(5)
2.90413(2)		9.89136(5)		12.61259(8)		362.307(4)

Atom	Site	x	y	z	B_{iso} (Å^2)
Fe1	8f	½	0.23790(9)	0.11496(6)	0.38(1)
			0.23668(7)	0.11522(6)	0.03(1)
Fe2	4a	0	0	0	0.38
					0.03
Mn1	4c	0	0.48660(13)	¼	0.38
			0.48655(11)		0.03
O1	4c	½	0.32230(50)	¼	0.38
			0.32141(42)		0.03
O2	8f	0	0.35507(36)	0.04488(28)	0.38
			0.35691(31)	0.04536(24)	0.03
O3	8f	0	0.09194(38)	0.13836(24)	0.38
			0.09230(32)	0.14017(21)	0.03

Table 2. Metal-oxygen bond distances (Å), with mean values <> shown for $MnFe_3O_5$ at 400 K (upper values) and 90 K (lower values).

Bond	Distance	Bond	Distance
Mn1-O1 (x2)	2.187(4)	<Fe1-O>	2.068(3)
	2.186(3)		2.065(2)
Mn1-O3 (x4)	2.286(2)	Fe2-O2 (x4)	2.126(3)
	2.263(2)		2.107(2)
<Mn1-O>	2.253(3)	Fe2-O3 (x2)	1.973(3)
	2.237(2)		1.990(3)
Fe1-O1	1.901(2)	<Fe2-O>	2.075(3)
	1.895(2)		2.068(2)
Fe1-O2 (x2)	2.067(3)	Fe1-Fe2	2.967(1)
	2.073(2)		2.983(1)
Fe1-O2	2.220(4)	Fe1-Fe1, Fe2-Fe2	2.933(1)
	2.227(3)		2.904(1)
Fe1-O3 (x2)	2.077(3)		
	2.061(2)		

Magnetic hysteresis loops shown in Figure 4b reveal a small moment of 0.025 μ_B/formula unit at 300 K, which is probably due to traces of a magnetic impurity such as Fe_3O_4, below the limit of x-ray detection. Cooling through the 150 K transition confirms that $MnFe_3O_5$ adopts a ferrimagnetic spin order with a magnetisation of 1.0 μ_B fu^{-1} at 2 K. This value is consistent with a collinear order of two up-spin S = 5/2 d^5 ions (Mn^{2+} or Fe^{3+}) and down-spin S = 5/2 and S = 2 d^6 Fe^{2+} ions, leading to a resultant magnetisation of 1 μ_B fu^{-1}. Neutron diffraction will be needed to confirm the spin orders below the 350 and 150 K transitions, and also to provide contrast between Mn and Fe to determine whether any disorder occurs across the three cation sites.

Conclusions

The above results demonstrate that $MnFe_3O_5$ can be synthesised under high pressure and temperature conditions, suggesting that other $MFe_{n-1}O_{n+1}$ homologues may also be accessible. $MnFe_3O_5$ adopts the orthorhombic $Sr_2Tl_2O_5$ type

structure of Fe_4O_5, and undergoes similar anisotropic thermal expansion below an antiferromagnetic ordering transition at 350 K. An additional spin canting transition consistent with formation of a collinear ferrimagnetic state is observed at 150 K. However, no long range structural transition associated with charge ordering is observed down to 90 K. Neutron diffraction will be needed to confirm the spin orders and to determine the Mn/Fe order across the three cation sites.
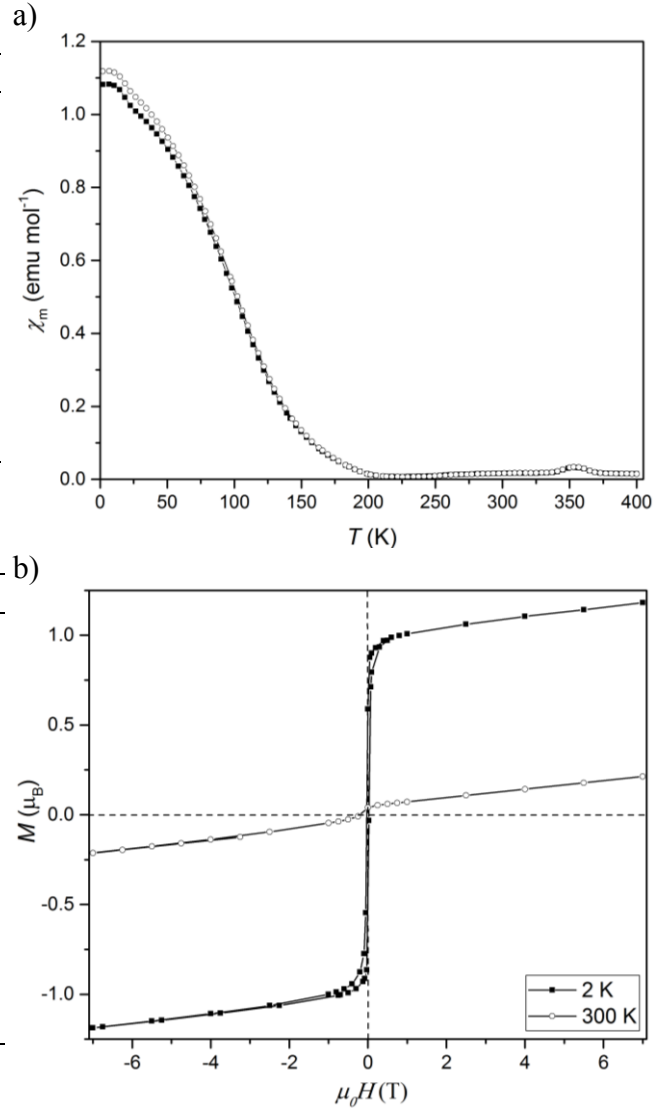
a)

b)

Figure 4. a) ZFC (closed symbols) and FC (open symbols) magnetic susceptibilities for $MnFe_3O_5$. b) Magnetisation-field measurements at 2 and 300 K.

Experimental Section

MnO and Fe_3O_4 were ground together in a 1:1 ratio and pressed into a pellet. The pellet was sealed inside an evacuated quartz tube and heated at 1100 °C for 12 hours. The resulting product was heated at 1400 °C in a Pt capsule for 20 mins under 10 GPa pressure, using a two-stage Walker-type module. Laboratory X-ray diffraction data were collected on a Bruker D2 diffractometer using Cu-Kα radiation.

High resolution powder X-ray diffraction data were collected at the ID22 beamline of the ESRF with incident wavelength 0.39996 Å. The powder was packed into a glass capillary with an outer diameter of 0.3 mm and spun during

acquisition. Data were collected at temperatures from 90 to 400 K using an Oxford Cryostream system.

Magnetic measurements were carried out using a Quantum Design MPMS XL SQUID magnetometer. Magnetic susceptibility was recorded in zero field cooled (ZFC) and field cooled (FC) conditions between 2 and 400 K with an applied magnetic field of 5000 Oe. Hysteresis loops were also measured at 2 and 300 K.

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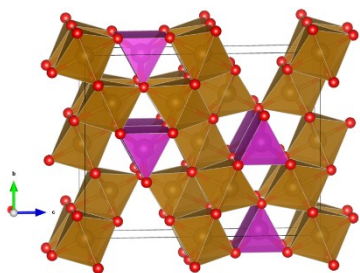
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