Cluster spin glass formation in the double double perovskite CaMnFeTaO$_6$

Padraig Kearins,† Elena Solana-Madruga,† Kunlang Ji†, Clemens Ritter,‡ and J. Paul Attfield*†

†Centre for Science at Extreme Conditions (CSEC) and School of Chemistry, University of Edinburgh, Peter Guthrie Tait Road, Edinburgh EH9 3FD (UK)
‡Institut Laue-Langevin, 38042 Grenoble Cedex, France.
* Email: j.p.attfield@ed.ac.uk

Abstract: CaMnFeTaO$_6$ has been synthesised at 1200 °C under 10 GPa pressure. Powder neutron diffraction shows that CaMnFeTaO$_6$ adopts a double double perovskite structure (tetragonal space group $P4_2/n$), lattice parameters $a = 7.683(3)$ and $c = 7.685(7)$ Å with cation disorder at all transition metal sites. Magnetization measurements reveal an apparent ferrimagnetic ordering at $T_m = 51$ K and a susceptibility peak at $T_m = 20$ K, but no long-range magnetic order is observed by neutron diffraction down to 1.5 K. This is attributed to formation of superparamagnetic clusters of ferrimagnetically ordered spins below $T_m$ that freeze into a cluster spin glass at $T_g = T_m$. AC magnetisation measurements confirm the cluster spin glass ground state. Disorder from substitution of Fe$^{2+}$ for Mn$^{2+}$ and Fe$^{3+}$/Ta$^{5+}$ inversion disrupts the network of superexchange interactions leading to the cluster spin glass ground state, in contrast to other $P4_2/n$ double double perovskites where long range magnetic order is stabilised.

Introduction

The ABO$_3$ perovskite structure is known to accept a wide range of different cations onto the A- and B-sites, and also for the ability to order multiple cations, giving rise to double perovskites AA′B$_2$O$_6$ or A$_2$B′B″O$_6$. Cation ordering gives rise to ferrimagnetism and half metallicity in the A$_2$B′B″O$_6$ family with rocksalt-type B-cation order, notably in Sr$_2$FeMoO$_6$. In recent years, high pressure synthesis has been used to prepare analogous double perovskites in which magnetic Mn$^{2+}$ replaces non-magnetic A-site cations like Sr$^{2+}$, giving rise to further ferrimagnetic materials such as Mn$_2$FeReO$_6$, and Mn$_6$ReO$_6$ analogs (M = Mn, Co, Ni) which display complex low temperature antiferromagnetic orders. This high pressure synthetic research also led to discovery of a new AA′BB′O$_6$ double double perovskite structure with tetragonal space group $P4_2/n$, which is doubly cation ordered with columnar A-site order and rocksalt B-ordering. This was first reported for MnRMnSbO$_6$ (R = rare earth) and subsequently for CaMnMnReO$_6$ (B = Mn, Fe, Co, Ni) phases.

The $P4_2/n$ double double perovskite structure is notable for having five different cation sites as two inequivalent positions (with tetrahedral and square-planar coordination) are formed within the A-site Mn$^{2+}$ columns. Magnetic couplings between the multiple spin sublattices give rise to complex magnetic orders. MnRMnSbO$_6$ perovskites display two ferromagnetic sublattices at the two Mn sites in the structure which are antiferromagnetically coupled to each other with magnetic ordering temperatures ranging from 46 to 76 K. CaMnFeReO$_6$ shows antiparallel Fe$^{3+}$/Re$^{5+}$ ferrimagnetic ordering at 500 K and a second ferrimagnetic ordering of the opposed inequivalent tetrahedral and square-planar A-site Mn$^{2+}$ at 70 K. CaMnMnReO$_6$ displays antiferromagnetic B-site spin ordering at 120 K, but ferromagnetic ordering of the A-site spins at 100 K. CaMnCoReO$_6$ orders ferrimagnetically below Curie temperature $T_C = 188$ K and CaMnNiReO$_6$ is a rare example of an insulating ferromagnetic perovskite oxide where all four distinct spin sublattices are collinearly ordered below $T_C = 152$ K. All of these previously studied double double perovskites have displayed long range magnetic order at low temperatures. In this paper, we report a new double double perovskite CaMnFeTaO$_6$ that is notable for not forming a long-range spin order below apparent magnetic transitions, and a cluster spin glass ground state is proposed.

Experimental

CaMnFeTaO$_6$ was synthesised under high pressure and high temperature conditions by mixing stoichiometric amounts of Ca$_2$Fe$_2$O$_5$, MnO and Ta$_2$O$_5$. Ca$_2$Fe$_2$O$_5$ was prepared by mixing stoichiometric proportions of CaCO$_3$ and Fe$_2$O$_3$ and heating at 1200 °C under a N$_2$ flow. The CaMnFeTaO$_6$ precursor mixture was packed into a Pt capsule and compressed to 10 GPa using a Walker-type multi-anvil press. The sample was heated over 10 minutes to 1200 °C, held at this temperature for 20 minutes before quenching to room temperature, after which the pressure was slowly released. Powder X-ray diffraction was used to confirm that a single phase perovskite sample was formed.

Neutron powder diffraction data from a ~50 mg sample were collected on the D20 beamline at the Institut Laue-Langevin, Grenoble. Data were analysed using the
Fullprof suite.\textsuperscript{15} Magnetisation measurements were made using a PPMS Quantum Design magnetometer.

Results and Discussion

The crystal structure of CaMnFeTaO$_6$ was analysed by fitting 300 K neutron powder diffraction data with wavelength $\lambda = 1.54$ Å. The Rietveld fit (Figure 1) confirms that CaMnFeTaO$_6$ adopts the above $P4_2/n$ double double perovskite structure in tetragonal space group. The lattice parameters were refined to be $a = 7.683(3)$ and $c = 7.685(7)$ Å. The high contrast between neutron scattering lengths of the three transition metals present; Mn (-3.73 fm), Fe (9.45 fm) and Ta (6.91 fm);\textsuperscript{16} allowed their proportions at each site to be refined. The use of a single dataset without other contrast information, e.g. from resonant X-ray data, only enables two elements to be refined at each site. However, an extensive combined neutron and resonant X-ray study of cation disorder in an oxide of comparable complexity - the Tl$_0.5$Pb$_0.5$Sr$_2$Ca$_3$Cu$_4$O$_{10}$ superconductor - showed that only one type of doping at each site was favored, e.g. Ca was specifically substituted by Tl rather than by Pb or Sr.\textsuperscript{17} This likely indicates that while all dopants would lead to similar increases in lattice entropy, cross-substitution of one dopant is enthalpically favored in complex oxides.

A substantial amount of disorder was discovered in CaMnFeTaO$_6$ as shown by the results in Table 1. The Ca-site within the A-cation columns is fully occupied, but the tetrahedral A1 and square-planar A2 sites that alternate along the columns of Mn were found to contain 12(4)% and 24(1)% Fe respectively. The preference of Fe$^{3+}$ for the square-planar environment likely reflects crystal field effects - Fe$^{3+}$ is found in this environment in the reduced oxide SrFeO$_2$.\textsuperscript{18} (3)Fe/Ta antisite disorder between the B/B$'$-cation positions was also observed. The refined composition of CaMn$_{0.82}$Fe$_{1.18}$TaO$_6$ is thus Fe-rich and Mn-poor relative to the ideal stoichiometry. The refined crystal structure is shown in Figure 2.

![Figure 1](image1.png)

**Figure 1:** Rietveld fit to 300 K powder neutron diffraction data for CaMnFeTaO$_6$ ($\lambda = 1.54$ Å). Scattering from an empty sample can has been subtracted from these data. The magenta ticks represent the Bragg positions of the $P4_2/n$ double double perovskite phase.

![Figure 2](image2.png)

**Figure 2:** Structure of CaMnFeTaO$_6$ in space group $P4_2/n$ along with the arrangement of tetrahedral and square planar Mn$^{2+}$ coordination sites within the A-site columns.

Refined oxygen coordinates enable precise bond distances and angles to be calculated. Bond Valence Sum (BVS) calculations\textsuperscript{19} using the distances shown in Table 1 give values of 1.80, 1.46, 1.31, 2.34 and 4.16 for Ca, A1, A2, B1 and B2 sites respectively. These are consistent with the ideal formula Ca$^{2+}$Mn$^{2+}$Fe$^{3+}$Ta$^{5+}$O$_6$ but values for the transition metals are low reflecting the substantial disorder at their sites. Ca sits in a large 10-fold site and the bond lengths shown are in good agreement with values from other double double perovskites.\textsuperscript{12,13,14} Bond angles of Fe-O1-Ta, along the $z$-axis, and Fe-O2-Ta and Fe-O3-Ta in the $xy$ plane are 144.3(5), 144.4(3) and 149.7(3)$^\circ$, which correspond to B/B$'$-O octahedra tilt angles of 17.9(3), 17.8(2), and 15.2(2)$^\circ$ respectively. The $P4_2/n$ double double perovskite structure is stabilised by these substantial tilts which create the distinct 10-coordinate Ca and 4-coordinate Mn A-site columns, as seen in Figure 2. The values for CaMnFeTaO$_6$ lie within the range of 15 to 20° octahedral

<table>
<thead>
<tr>
<th>Atom*</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$B_{iso}$ (Å$^2$)</th>
<th>occ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>0.250</td>
<td>0.750</td>
<td>0.776(1)</td>
<td>1.33(15)</td>
<td>1</td>
</tr>
<tr>
<td>A1</td>
<td>0.750</td>
<td>0.750</td>
<td>0.7500</td>
<td>0.65(3)</td>
<td>0.88/</td>
</tr>
<tr>
<td>(Mn/Fe)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(12)</td>
</tr>
<tr>
<td>A2</td>
<td>0.250</td>
<td>0.250</td>
<td>0.7500</td>
<td>0.65</td>
<td>0.76/</td>
</tr>
<tr>
<td>(Mn/Fe)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.24(1)</td>
</tr>
<tr>
<td>B1</td>
<td>0.000</td>
<td>0.000</td>
<td>0.5000</td>
<td>0.65</td>
<td>0.82/</td>
</tr>
<tr>
<td>(Fe/Ta)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.18(3)</td>
</tr>
<tr>
<td>B2</td>
<td>0.000</td>
<td>0.000</td>
<td>0.5000</td>
<td>0.65</td>
<td>0.82/</td>
</tr>
<tr>
<td>Ta</td>
<td>0.1214</td>
<td>0.057(1)</td>
<td>0.036(1)</td>
<td>0.58</td>
<td>0.58</td>
</tr>
<tr>
<td>O1</td>
<td>0.752(3)</td>
<td>0.567(1)</td>
<td>0.249(2)</td>
<td>0.58(4)</td>
<td>1</td>
</tr>
<tr>
<td>O2</td>
<td>0.242(2)</td>
<td>-0.047(1)</td>
<td>0.565(1)</td>
<td>0.58</td>
<td>1</td>
</tr>
<tr>
<td>O3</td>
<td>-0.252(3)</td>
<td>0.057(1)</td>
<td>-0.036(1)</td>
<td>0.58</td>
<td>1</td>
</tr>
</tbody>
</table>

*Wyckoff sites are Ca 4e; A1 2a; A2 3b; B1 6i; B2 6j; O1 18e; O2 18e; O3 18e.
The magnetic susceptibility against temperature plot for CaMnFeTaO₆ in Fig. 3a reveals paramagnetic behavior at high temperatures. A fit of the Curie-Weiss equation to inverse susceptibility above 150 K gave an effective paramagnetic moment of $\mu_{\text{eff}} = 6.71 \mu_B$ per formula unit (f.u.) and a Weiss temperature of $\theta = -72$ K. The moment is smaller than the theoretical spin-only value for CaMnFeTaO₆ of $\mu_{\text{spin}} = 8.37 \mu_B$ f.u. This may reflect the off-stoichiometry observed from the cation site refinement, and also suggests that higher temperature data would be needed to obtain a more accurate estimate of $\mu_{\text{eff}}$. The negative Weiss temperature indicates that dominant spin-spin couplings are antiferromagnetic, consistent with the antiparallel, ferrimagnetic couplings of A and B site spins observed in other double double perovskites. Two apparent magnetic transitions are observed at low temperatures. A discontinuity as susceptibility deviates away from Curie-Weiss behavior is observed at $T_{m1} = 51$ K, and a susceptibility maximum below which zero field cooled (ZFC) and field cooled (FC) data diverge is seen at $T_{m2} = 20$ K.

![Figure 3](image-url) **Figure 3:** (a) Magnetic susceptibility (ZFC and FC data) and inverse magnetic susceptibility (FC, inset) for CaMnFeTaO₆ measured at a field of 0.1 T. Red line shows the Curie-Weiss fit. (b) Hysteresis loop of CaMnFeTaO₆ at 2 K with low field data expanded in the inset.

The magnetization-field ($M-H$) loop at 2 K in Fig. 3b has a sharp hysteretic magnetisation feature at fields below 0.1 T (shown in the inset). This is most likely due to traces of a magnetic impurity such as (Fe,Mn)₃O₄ spinel, below the limit of detection in our diffraction experiments. The $M-H$ variation otherwise evidences superparamagnetic or glassy rather than ferromagnetic behavior, as $M(H)$ shows continuous curvature with very little hysteresis and does not saturate even at the highest field of 9 T.

Further D20 neutron diffraction scans using wavelength $\lambda = 2.41$ Å were taken at 30 K and 1.5 K to detect any changes in neutron scattering below $T_{m1} = 51$ K and $T_{m2} = 20$ K respectively. The low angle scattering region where magnetic peaks are expected is shown in Fig. 4a. Previously investigated double double perovskites have all had low temperature spin orders with propagation vector $k = [0 0 0]$ giving magnetic diffraction contributions at nuclear peak positions. However, no magnetic peaks are observed for CaMnFeTaO₆ from $k = [0 0 0]$ or other vectors at either 30 or 1.5 K. An additional magnetic diffraction peak is observed at 20 = 28.5°, but this is the intense (1/2 1/2) diffraction peak from a trace of MnO impurity (consistent with the Mn-poor composition of the double double perovskite phase) which orders antiferromagnetically below 120 K. Other additional features (sharp peak at 34°, broad signals at 41-44° and 53-56°) are spurious scattering from the instrument or sample environment. (These were also seen for other samples studied during the same neutron experiment, and so are not from the CaMnFeTaO₆ sample.)

Rietveld fits to the neutron diffractions scans at 1.5 and 30 K were carried out using the nuclear structure model from the 300 K refinement (Table 1). The magnetic MnO peak was Le Bail fitted as the nuclear peaks from this phase are not visible, and the spurious scattering regions were excluded. A magnetic structure fit was attempted using a $k = [0 0 0]$ ferrimagnetic model, with A1 and A2 site Mn spins antiparallel to those from Fe at B1 sites. However, this made no visible difference or statistical improvement to the profile fitting, and magnetic moments were within their estimated standard deviations. We therefore conclude that any long-range ordered magnetic moments in CaMnFeTaO₆ are below the effective limit of ~0.5 $\mu_B$ for their detection in these neutron diffraction experiments. Formation of such small, long range ordered moments is unlikely given that ideal ordered moments of 5 $\mu_B$ are expected for high spin $S = 5/2$ Fe$^{3+}$ and Mn$^{3+}$ cations. The 1.5 K fit is shown in Fig. 4b. Refined lattice parameters were $a = 7.662(1)$ and $c = 7.661(1)$, and $a = 7.664(1)$ and $c = 7.663(2)$ Å, at 1.5 K and 30 K respectively.

The absence of magnetic peaks in the neutron diffraction profiles demonstrates that the transitions observed in the magnetisation data correspond to short range spin orders. The magnetisation peak at $T_{m2} = 20$ K is typical of a spin glass, however, spin glasses do not usually also show a Curie-like transition as seen for CaMnFeTaO₆ at $T_{m1} = 51$ K. A likely
explanation is that superparamagnetic clusters of ferrimagnetically-aligned spins are formed below the Curie-like transition at \( T_{m1} \), and that these freeze into a cluster spin glass at \( T_{m2} \). The correlation length for the spin ordering within clusters is too short for any magnetic diffraction peaks to be seen in the neutron scattering data, and there is no long-range correlation between frozen cluster spin directions. Any diffuse magnetic scatter is not distinguished from other background contributions in our low temperature data (Fig. 4a).

![Figure 4](image)

**Figure 4:** (a) Comparison of low angle \( \lambda = 2.41 \) Å neutron diffraction patterns of CaMnFeTaO\(_6\) at 1.5 and 30 K. (b) Rietveld fit to the 1.5 K profile. CaMnFeTaO\(_6\) peak positions are shown by the green ticks, and those from the magnetic MnO impurity phase, with Le Bail fitted intensities are magenta.

AC magnetisation data at varying frequencies \( \omega \) were recorded to explore the proposed cluster spin glass ground state (Fig. 5). The susceptibility peak for CaMnFeTaO\(_6\) shows an increase with frequency confirming that it corresponds to a spin freezing transition at \( T_f = T_{m2} \). The \( \Delta T_f = 0.23 \) K increase over the observed frequency range corresponds to a shift per frequency decade \( \phi = \Delta T_f / (T_f \Delta \log \omega) = 0.006 \). This is below the typical range of 0.01 to 0.1 for standard spin glasses, but is in good agreement with values for reported cluster spin glass materials; \( \phi = 0.005 \) for \( \text{U}_2\text{IrSi}_3 \) and \( \phi = 0.002 \) for the oxygen deficient perovskite \( \text{BaBi}_{0.28}\text{Co}_{0.72}\text{O}_{2.2} \). The variation of \( T_f \) can be fitted by the Vogel-Fulcher function \( \omega = \omega_0 \exp[-E_f/k_B(T_f - T_0)] \) as shown in the inset to Fig. 5. However, attempts to fit the ideal glass temperature \( T_g \), characteristic frequency \( \omega_0 \) and activation energy \( E_f \) simultaneously gave highly correlated values. \( E_f/k_B \) is typically in the range 0.2-2\( T_f \) for cluster spin glasses but 2-10\( T_f \) for conventional spin glasses. Fixing \( E_f/k_B = 0.5T_f = 13 \) K gave \( \omega_0 = 1.5(11) \) GHz and \( T_0 = 25.3(1) \) K for CaMnFeTaO\(_6\), comparable to \( E_f/k_B = 0.24T_f = 6(1) \) K fitted at fixed \( \omega_0 = 1 \) GHz for the cluster spin glass \( \text{BaBi}_{0.28}\text{Co}_{0.72}\text{O}_{2.2} \) which has a similar \( T_0 = 25.0(1) \) K.

Other features of cluster spin glasses apparent in our susceptibility measurements for CaMnFeTaO\(_6\) are strong suppression of \( T_f \) by applied magnetic field and slow relaxation dynamics. \( T_f \) changes by 23% from 26 K at zero field in the AC data to 20 K at 0.1 T in the DC measurement (Fig. 3a). A 50% reduction of \( T_f \) over the same field change was observed in \( \text{BaBi}_{0.28}\text{Co}_{0.72}\text{O}_{2.2} \) and a 36% suppression was reported for the cation disordered perovskite cluster spin glass \( \text{SrMn}_{0.5}\text{Ti}_{0.5}\text{O}_3 \) (\( \text{Sr}_x\text{MnTiO}_3 \)) as field increased from 0.01 to 1 T. Slow relaxation dynamics in CaMnFeTaO\(_6\) are evidenced by the changes of slope seen in the AC susceptibility data of Fig. 5 at 20 and 30 K, where the cooling rate was changed by a factor of two, but were not explored more systematically.

![Figure 5](image)

**Figure 5:** Real part of the AC magnetic susceptibility data for CaMnFeTaO\(_6\), collected at the frequencies \( \omega \) shown while cooling from 70 to 2 K in steps of 0.5 K between 30 and 20 K and of 1 K outside this range. Each step was recorded for 1 min in zero applied field with an AC drive field of 16 Oe. Inset shows Vogel-Fulcher fit to the \( T_f \) values.

Spin glass ground states are found in many doped or disordered perovskite oxides such as and sometimes result from freezing of magnetic polarons, ferromagnetic clusters of up to \( \sim100 \) spins, e.g. in \( \text{La}_2\text{Sr}_x\text{CoO}_3 \). The observation of a Curie-like magnetisation discontinuity in CaMnFeTaO\(_6\)
suggests that the magnetic clusters are much larger, comprising up to $10^6$ spins in the superparamagnetic regime. Cluster spin glass behaviour has been reported in BaB$_{12}$CO$_3$Ta$_2$O$_{22}$ as above$^{20}$ and several disordered double perovskites such as Sr$_5$Mn$_{12}$Fe$_{14}$MoO$_{38}$, where Mn and Fe are randomised at one of the B-sites$^{23}$, and Sr$_6$FeCoO$_{24}$ $^{24}$ and Sr$_2$MnTiO$_{20}$, where B-cations are fully disordered. Observation of thermoremanent magnetization with slow relaxation dynamics and other memory effects were used to evidence the cluster spin glass state in the latter material, and similar experiments could be used to further characterise CaMnFeTaO$_6$.

The formation of a glassy magnetic ground state in the double double perovskite CaMnFeTaO$_6$ reflects both the dilution effect of introducing non-magnetic Ta$^{5+}$ into the B-cation network, and the effect of cation disorder at transition metal sites. Neither factor appears sufficient by itself; MnLaMnSbO$_6$ has the same concentration of $S=5/2$ cations as CaMnFeTaO$_6$ but has long range ferrimagnetic order below $T_c = 48$ K; and levels of cation disorder and non-stoichiometry observed in CaMnCoReO$_6$ (CaMn$_{0.72}$Co$_{0.28}$ReO$_6$) and CaMnNiReO$_6$ (CaMn$_{0.3}$Ni$_{0.7}$ReO$_6$) are similar to those in CaMnFeTaO$_6$ (CaMn$_{0.8}$Fe$_{1.2}$TaO$_6$) but the former materials based on $S=1/2$ Re$^{5+}$ have long range spin orders below $T_c = 188$ and 152 K respectively. Hence both the presence of non-magnetic Ta$^{5+}$ and the observed 18% inversion disorder in CaMnFeTaO$_6$ are important to disruption of the B-site spin order. The substitution of 12-24% Fe$^{3+}$ for Mn$^{2+}$ at the A1 and A2 sites is also likely to be disruptive as M-O-M superexchange interactions between the M = Mn$^{3+}$ and Fe$^{3+}$ d$^4$ cations are expected to be antiferromagnetic whereas M-O-Fe$^{2+}$ superexchange interactions can be ferromagnetic.$^{25}$ The effects of both Fe$^{3+}$/Ta$^{3+}$ and Fe$^{2+}$/Mn$^{2+}$ cation disorders on the complex network of exchange interactions between A1, A2, B1, (and B2) sites evidently creates enough randomness to disrupt long-range spin order in CaMnFeTaO$_6$ so that only short-range magnetic cluster glass behavior is observed down to 1.5 K.

CONCLUSIONS

CaMnFeTaO$_6$ extends the range of magnetic ground states observed in the $P4_2/n$ family of double double perovskites. Long range ferro-, ferri-, and antiferro- magnetic orders have all previously been reported, but CaMnFeTaO$_6$ has a cluster spin glass ground state without long range magnetic order. This opens possibilities for further glassy or even quantum spin liquid ground states to be discovered through chemical substitution and disorder tuning within this flexible structure type.

ACKNOWLEDGMENT

We acknowledge EPSRC for financial support and STFC for provision of beamline at the Institut Laue-Langevin.

REFERENCES


17 Aranda, M. A. G.; Sinclair, D. C.; Attfield, J. P. Cation distribution in the superconducting Tl,Pb-1223 phase ("Tl$_{0.5}$Pb$_{0.5}$Sr$_2$Ca$_2$Cu$_3$O$_{9+y}$") from resonant synchrotron powder X-ray diffraction. *Physica C*, **1994**, *221*, 304-310.


20 Klimeczuk, T.; Zandbergen, H. W.; Huang, Q.; McQueen, T. M.; Ronning, F.; Kusz, B.; Thompson, J. D.; Cava, R. J. Cluster-glass behavior of a highly oxygen deficient perovskite, BaBi$_{0.28}$Co$_{0.72}$O$_{2.2}$. *J. Phys.: Condens. Matter*, **2009**, *21*, 105801.


25 Goodenough, J. B. Magnetism and the Chemical Bond, New York: Wiley, **1963**.