Crystal and magnetic structures of the brownmillerite Ca$_2$Cr$_2$O$_5$

Angel M. Arevalo-Lopez and J. Paul Attfield*

Powder neutron diffraction and magnetic susceptibility measurements at 10–300 K have been used to determine the crystal and magnetic structures of brownmillerite type Ca$_2$Cr$_2$O$_5$, which was obtained by reduction of the high pressure phase CaCrO$_3$ through hard–soft chemistry. The ambient temperature crystal structure of Ca$_2$Cr$_2$O$_5$ is refined in space group $\text{i2}m\overline{b}$ and the unusual tetrahedral coordination of Cr$^{3+}$ results in local structural distortions. Cr$^{3+}$ spins order antiferromagnetically below 220 K and a substantial observed canting of moments shows that Heisenberg exchange is weak or frustrated and competes with antisymmetric Dzialoshinskii–Moriya interactions.

Introduction

Metastable, perovskite-related oxides of transition metals in unusual oxidation states or coordination geometries offer new materials that may have useful magnetic or electronic properties. We have recently used 'hard–soft' chemistry, in which the instability of a dense precursor prepared under 'hard' high pressure-temperature conditions is partially relieved through 'soft' post-synthesis modification, to synthesise new vacancy-ordered perovskite oxides.

Low-temperature hydrogen reductions of the cubic perovskite SrCrO$_3$, which requires synthesis pressures in excess of 4 GPa,$^{2,3}$ gave two new SrCrO$_3$ phases with oxygen deficiencies $\delta = 0.2$ and 0.25.4 These have complex superstructures due to oxide loss and reconstruction of widely-spaced cubic-(111) anion planes, which relaxes Cr$^{4+}$ coordination from the octahedral geometry imposed at high pressure to tetrahedral. The SrCrO$_{2.8}$ superstructure has subsequently been stabilised at ambient pressure by substitution of Fe for Cr.$^5$ The perovskite SrCrO$_2$ and the reduced SrCrO$_{2.8}$ structure were also stabilised epitaxially as thin films, with rapid oxygen uptake or loss on cycling between the two phases.$^6$

The hard–soft route was also used to discover three reduced CaCrO$_3$ phases.$^7$ The high pressure precursor CaCrO$_3$ has an orthorhombically-distorted perovskite structure.$^{8,9}$ Reductions using a 90% Ar/10% H$_2$ gas mixture at 400–450 °C revealed that three oxygen-deficient superstructure phases were formed, as shown in Fig. 1. The CaCrO$_{3-\delta}$ perovskite superstructures are based on stacking of tetrahedral (T) and octahedral (O) layers, with increasing $\text{T}/(\text{T}+\text{O})$ ratio $\delta = 0.33 \rightarrow 0.4 \rightarrow 0.5$ as reduction proceeds. This structural mechanism had not previously been reported for reduced ternary ABO$_{3-\delta}$ perovskites but is found in CaTi$_{1-x}$Fe$_x$O$_{3-x}$ where Fe-content determines the $\text{T}/(\text{T} + \text{O})$ layer ratio.$^{10}$ Magnetic ordering transitions were observed for the three reduced CaCrO$_{3-\delta}$ phases at 150–200 K.$^7$

The most reduced CaCrO$_{3-0.5}$ phase, Ca$_2$Cr$_2$O$_5$, has a brownmillerite (Ca$_3$Fe$_2$O$_5$)$^{11}$ type structure where tetrahedral layers are stacked out-of-phase with their neighbours resulting in the OTOT' stacking sequence shown in Fig. 1. There is one prior report of a Ca$_2$Cr$_2$O$_5$ brownmillerite prepared at ambient pressure,$^{12}$ but the structure was not characterized. Ca$_2$Cr$_2$O$_5$ is notable as the brownmillerite structure contains Cr$^{3+}$ in both octahedral and tetrahedral environments. The latter coordination is rare as crystal field effects provide strong stabilisation of Cr$^{3+}$ in octahedral environments. The structure of Ca$_2$Cr$_2$O$_5$ was refined in the aristotype $\text{Inmm}$ brownmillerite structure, in which the chains of tetrahedra in the T layers are disordered, as the X-ray data in the previous study were not
sensitive to possible ordered superstructures. Here we report a neutron diffraction study of Ca$_2$Cr$_2$O$_5$ which has provided structural characterisation of the chain order, and has also enabled us to solve the low temperature magnetic order of Cr$^{3+}$ spins.

**Experimental**

CaCr$_2$O$_4$ precursors were synthesized from a stoichiometric mixture of Ca$_3$Cr$_2$O$_6$ and Cr$_2$O$_3$ in a multi-anvil Walker-type press at 9 GPa and 1100$^\circ$ C. A 90% Ar/10% H$_2$ gas mixture was used to reduce CaCr$_2$O$_4$ samples to Ca$_2$Cr$_2$O$_5$.

Magnetization data were measured on a Quantum Design MPMS SQUID magnetometer. Susceptibilities in zero field cooled (ZFC) and field cooled (FC) conditions were recorded in the 2–300 K temperature range with a 0.5 T applied field.

Time-of-flight neutron diffraction data were collected using the GEM diffractometer at the ISIS neutron facility. Several samples were combined in order to obtain a suitable amount for the experiment (~140 mg). Profiles were recorded at 10, 100, 200 and 300 K. Structural and magnetic models were fitted to data from banks 3, 4 and 5, centred respectively at 2$\theta = 35$, 64 and 91$^\circ$.

**Results and discussion**

**Crystal structure**

No structural phase changes were observed between 10 and 300 K, and the crystal structure of Ca$_2$Cr$_2$O$_5$ was refined using the GEM di

---

### Table 1

Refined parameters for Ca$_2$Cr$_2$O$_5$ in space group $I2\bar{1}m$ from the fit to 300 K neutron powder diffraction data

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>8c</td>
<td>0.497(3)</td>
<td>0.1074(4)</td>
<td>0.012(2)</td>
</tr>
<tr>
<td>Cr1</td>
<td>4a</td>
<td>0.501(4)</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Cr2</td>
<td>4b</td>
<td>-0.007(4)</td>
<td>0.25</td>
<td>0.936(2)</td>
</tr>
<tr>
<td>O1</td>
<td>8c</td>
<td>0.734(2)</td>
<td>0.4919(5)</td>
<td>0.746(2)</td>
</tr>
<tr>
<td>O2</td>
<td>8c</td>
<td>0.022(2)</td>
<td>0.1398(3)</td>
<td>0.036(1)</td>
</tr>
<tr>
<td>O3</td>
<td>4b</td>
<td>0.162(2)</td>
<td>0.75</td>
<td>0.366(2)</td>
</tr>
</tbody>
</table>

$^a$ Cell parameters $a = 5.420(4)$, $b = 14.770(10)$, and $c = 5.509(4)$ Å; isotropic thermal parameter $U_{	ext{iso}} = 0.038(2)$ Å$^2$; residuals $R_p = 0.066$ and $R_p^\prime = 0.052$.

---

### Table 2

Bond distances (Å), angles ($^\circ$), and bond valence sums (BVS) for the Cr sites in Ca$_2$Cr$_2$O$_5$ from refinement against 300 K diffraction data

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Angle ($^\circ$)</th>
<th>BVS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr1–O1 × 2</td>
<td>1.94(2)</td>
<td>131.2(10)</td>
<td>3.02</td>
</tr>
<tr>
<td>Cr1–O1 × 2</td>
<td>1.94(2)</td>
<td>154.3(6)</td>
<td>BVS(Cr1)</td>
</tr>
<tr>
<td>O1–Cr1–O1 × 2</td>
<td>88.9(1)</td>
<td>92.5(12)</td>
<td>106.9(7)</td>
</tr>
<tr>
<td>O1–Cr1–O1 × 2</td>
<td>88.9(12)</td>
<td>92.5(12)</td>
<td>106.9(7)</td>
</tr>
<tr>
<td>O1–Cr1–O1 × 2</td>
<td>92.5(12)</td>
<td>87.5(6)</td>
<td>106.9(7)</td>
</tr>
<tr>
<td>O1–Cr1–O1 × 2</td>
<td>88.2(6)</td>
<td>154.3(6)</td>
<td>106.9(7)</td>
</tr>
<tr>
<td>O1–Cr1–O1 × 2</td>
<td>88.2(6)</td>
<td>172.5(5)</td>
<td>106.9(7)</td>
</tr>
<tr>
<td>O1–Cr1–O1 × 2</td>
<td>88.2(6)</td>
<td>172.5(5)</td>
<td>106.9(7)</td>
</tr>
<tr>
<td>O1–Cr1–O1 × 2</td>
<td>88.2(6)</td>
<td>154.3(6)</td>
<td>106.9(7)</td>
</tr>
<tr>
<td>O1–Cr1–O1 × 2</td>
<td>92.6(6)</td>
<td>172.5(5)</td>
<td>106.9(7)</td>
</tr>
<tr>
<td>O2–Cr1–O2</td>
<td>173.9(15)</td>
<td>132.1(10)</td>
<td>106.9(7)</td>
</tr>
</tbody>
</table>

---

**O–Cr1–O angles are close to 90 or 180$^\circ$. However, the Cr2O$_4$ tetrahedron is highly distorted with Cr2–O distances of 1.73–1.90 Å and opening of the O2–Cr2–O2 angle to 141$^\circ$ while other bond angles lie in the range 99–107$^\circ$. The corresponding
GaO₄ tetrahedron in isostructural Ca₂Ga₂O₅ is far less distorted, with Ga–O distances of 1.82–1.89 Å and O–Ga–O angles of 106–122°. As Cr³⁺ and Ga³⁺ have almost identical ionic radii (0.615 and 0.62 Å for octahedral coordination) this comparison suggests that the excess distortion of Ca₂Cr₂O₅ reflects the instability of tetrahedrally-coordinated Cr³⁺, as this cation generally has a strong preference for octahedral coordination which maximises crystal field stabilisation energy of the 3d⁴ electronic configuration. The Ca²⁺ site coordination is comparable to that in other brownmillerites,¹⁴–¹⁶ with seven short Ca–O bonds in the range 2.43–2.62 Å while other Ca–O distances are >2.85 Å.

A previously reported study of multiple La₁₋ₓAₓMnO₂₋ₓ (A = Ca, Sr, Ba) brownmillerite compositions showed that the different structural phases fall into distinct regions on a plot of the tetrahedral layer separation (b/2), which has value 7.385 Å for Ca₂Cr₂O₅, against the deviation of the tetrahedral layer separation (Ca, Sr, Ba) brownmillerite compositions showed that the instability of tetrahedrally-coordinated Cr³⁺, as this cation generally has a strong preference for octahedral coordination which maximises crystal field stabilisation energy of the 3d⁴ electronic configuration. The Ca²⁺ site coordination is comparable to that in other brownmillerites,¹⁴–¹⁶ with seven short Ca–O bonds in the range 2.43–2.62 Å while other Ca–O distances are >2.85 Å.

A previously reported study of multiple La₁₋ₓAₓMnO₂₋ₓ (A = Ca, Sr, Ba) brownmillerite compositions showed that the different structural phases fall into distinct regions on a plot of the tetrahedral layer separation (b/2), which has value 7.385 Å for Ca₂Cr₂O₅, against the deviation of the tetrahedral layer chains from 180°.¹⁹ The latter angle is defined as 180°–(O3–O3–O3 angle) and takes value 50.3(7)° in the 300 K structure of Ca₂Cr₂O₅. The point for Ca₂Cr₂O₅ lies within the domain of the II₄mb superstructure on the reported structure map, corroborating the space group assignment from the comparison of neutron fits above.

**Magnetic structure**

Magnetization measurements for the Ca₂Cr₂O₅ sample revealed a Curie tail at low temperatures and a trace of ferromagnetic material, as found in our previous study of CaCrO₃₋ₓ phases.² These impurity contributions were subtracted to yield the susceptibility shown in Fig. 3. A transition is apparent near 200 K with no divergence between ZFC and FC data, suggesting that the spin order is antiferromagnetic. The inverse susceptibility shows linear variation with temperature suggesting that the spin order is antiferromagnetic. The Ca²⁺ site coordination is comparable to that in other brownmillerites,¹⁴–¹⁶ with seven short Ca–O bonds in the range 2.43–2.62 Å while other Ca–O distances are >2.85 Å.

A transition is apparent near 200 K with no divergence between ZFC and FC data, suggesting that the spin order is antiferromagnetic. The inverse susceptibility shows linear variation with temperature suggesting that the spin order is antiferromagnetic. The Ca²⁺ site coordination is comparable to that in other brownmillerites,¹⁴–¹⁶ with seven short Ca–O bonds in the range 2.43–2.62 Å while other Ca–O distances are >2.85 Å.

**Table 3** Irreducible representations and basis vectors of magnetic moments m for propagation vector (111) applied to the Cr cation positions in space group I2mb

<table>
<thead>
<tr>
<th>Irreps</th>
<th>Basis vectors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Γ₁</td>
<td>(0, 0, 0)</td>
</tr>
<tr>
<td>Γ₂</td>
<td>(0, 1/2, 0)</td>
</tr>
<tr>
<td>Γ₃</td>
<td>(x, 1/4, z)</td>
</tr>
<tr>
<td>Γ₄</td>
<td>(x, 3/4, −z)</td>
</tr>
</tbody>
</table>

Magnetic structure of Ca₂Cr₂O₅ consists of antiferromagnetic order of spins, following standard convention for magnetic order in perovskites.²⁰ Although the Cr1 and Cr2 site moments are not symmetry-related, refining their spin components independently did not give a significantly improved fit over a model where their components were constrained to be the same, so the latter description was used as the final model. The m₁ and m₂ moment components at 10 K have values of 1.08(5) and 1.33(7) μB, and the resultant moment is m = 1.7(1) μB. Neutron diffraction shows that the Néel temperature for Ca₂Cr₂O₅ is >200 K (see inset to Fig. 2), and hence somewhat higher than the susceptibility features observed in Fig. 3. An estimate of Tₙₑ ≈ 220 K is obtained by fitting the temperature variation of the moment in Fig. 4a with a critical law m(T) = m(0)[1 − (T/Tₙₑ)]β for an exponent β ≈ 0.3, in keeping with theoretical models such as the three-dimensional XY magnet for which β = 0.34.

The magnetic structure of Ca₂Cr₂O₅ consists of antiferromagnetic planes of Cr1 and Cr2 moments as shown in Fig. 4b. Spins lie in the bc-plane and are tilted by 51(4)° from the b-axis. Neighbouring Cr1 and Cr2 spins connected through Cr1–O–Cr2 bridges are canted by ~100° suggesting that anti-symmetric Dzialoshinskii–Moriya exchange is significant, given the absence of a centre of symmetry or other symmetry relations between Cr1 and Cr2, and that Cr1–O–Cr2 Heisenberg exchange interactions are weak or frustrated. This reduction in the low temperature ordered moment of 1.7 μB from the ideal value of 3 μB for 3d³ Cr³⁺ is also consistent with some frustration in the spin order. Such spin canting is unusual in brownmillerites, as most have simple collinear antiferromagnetic structures with moments parallel to a or b.
actions determine spin directions.
the high pressure perovskite phase CaCrO₃ is a brownmillerite
and adopts the ordered superstructure at ambient temperature. The unusual tetrahedral coordination of Cr³⁺ results in local structural distortions. The observation of Cr³⁺ in this unconventional environment illustrates the use of hard–soft chemistry to stabilise unusual coordination geometries. This brownmillerite material containing a high concentration of oxygen vacancies in cubic-perovskite (100) planes may offer high mobility for oxide ion transport, as was found in the hard–soft product SrCrO₂.⁸,⁶ These stoichiometric reduced phases may also be useful model compounds to help understand oxide ion migration in chromium perovskite mixed conductors used in fuel cell anodes such as (La₁−ₓSrₓ)(Cr₁−yMₓ)O₃−δ (M = Mn, Fe, Co, Ni).²¹

Conclusions

This study confirms that Ca₂Cr₂O₅ synthesised by reduction of the high pressure perovskite phase CaCrO₃ is a brownmillerite and adopts the ordered I2mb superstructure at ambient temperature. The unusual tetrahedral coordination of Cr³⁺ results in local structural distortions. The observation of Cr³⁺ in this unconventional environment illustrates the use of hard–soft chemistry to stabilise unusual coordination geometries. This brownmillerite material containing a high concentration of oxygen vacancies in cubic-perovskite (100) planes may offer high mobility for oxide ion transport, as was found in the hard–soft product SrCrO₂.⁸,⁶ These stoichiometric reduced phases may also be useful model compounds to help understand oxide ion migration in chromium perovskite mixed conductors used in fuel cell anodes such as (La₁−ₓSrₓ)(Cr₁−yMₓ)O₃−δ (M = Mn, Fe, Co, Ni).²¹

Ca₂Cr₂O₅ displays an antiferromagnetic spin ordering transition near 220 K, which is comparable to the 280 K Néel temperature for the perovskite LaCrO₃. Substantial canting of moments in successive layers is observed, suggesting that symmetric Heisenberg exchange interactions are weak or frustrated so that competing antisymmetric Dzialoshinskii–Moriya interactions determine spin directions.

Acknowledgements

We thank Dr I. da Silva (ISIS) and Dr Elise Pachoud (Edinburgh) for assistance with diffraction measurements. We also thank EPSRC, STFC and the Royal Society for support.

Notes and references