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

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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 $P2mb$ 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.1 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$_{3-\delta}$ 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$_{3-\delta}$ superstructure has subsequently been stabilised at ambient pressure by substitution of Fe for Cr.5 The perovskite SrCrO$_3$ 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$_{3-\delta}$ 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 T/(T + 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$_3$ where Fe-content determines the T/(T + 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 Imma 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

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Cite this: Dalton Trans., 2015, 44, 10661

Received 10th December 2014, Accepted 19th January 2015

DOI: 10.1039/c4dt03780d

www.rsc.org/dalton
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**

CaCrO$_3$ 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°C. A 90% Ar/10% H$_2$ gas mixture was used to reduce CaCrO$_3$ 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 2θ = 35, 64 and 91°.

**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 300 K neutron data. This structure was previously refined against X-ray data in the aristotype Imma brownmillerite structure, in which the tetrahedra are disordered. Ordered tilts of the tetrahedra can give rise to low symmetry superstructures, as found in other reported Ca$_2$M$_2$O$_5$ brownmillerites at room temperature. Ca$_2$Fe$_2$O$_5$ has a Pnma superstructure while the high pressure phases Ca$_2$Al$_2$O$_5$ and Ca$_2$Ga$_2$O$_5$ have polar I2am (a non-standard setting of Ima2) space group symmetry. A more complex Pcmn supercell with doubling of the c-axis parameter was recently reported in Ca$_3$Co$_2$O$_5$. Fits of the two simple ordering models to the 300 K profile of Ca$_2$Cr$_2$O$_5$ gave a slightly better goodness-of-fit $\chi^2$ = 1.63 for I2am than for Pnma where $\chi^2$ = 1.69, and no breaking of the body-centring reflection condition was observed. Hence the I2am model is reported here as the ordered brownmillerite superstructure for Ca$_2$Cr$_2$O$_5$ between 10 and 300 K, and this symmetry is corroborated by the analysis of structural parameters described below.

Fits to the profiles are shown in Fig. 2, and refinement results are summarised in Tables 1 and 2.

Bond distances and angles for Ca$_2$Cr$_2$O$_5$ in Table 2 allow a detailed analysis of the structural distortions. Bond valence sum (BVS) values for the two Cr sites are consistent with the presence of Cr$^{3+}$, although the value for the Cr2 site is high, as often occurs for strained coordinations. The Cr1O$_6$ octahedron is tetragonally distorted due to the structural connectivity, but it is tetragonally distorted due to the structural connectivity, but

The tetrahedra can give rise to low symmetry superstructures,13 as found in other reported Ca$_2$M$_2$O$_5$ brownmillerites at room temperature. The Cr$_1$O$_6$ octahedron is highly distorted with Cr$_2$–O1 angles of 176° and opening of the O2–Cr2–O2 angle to 141° while other bond angles lie in the range 99–107°. The corresponding

| Table 1 | Refined parameters for Ca$_2$Cr$_2$O$_5$ in space group I2am from the fit to 300 K neutron powder diffraction data
|---|---|---|---|---|
| Atom | Site | x | y | z |
| Ca | 8c | 0.497(3) | 0.1074(4) | 0.012(2) |
| Cr1 | 4a | 0.501(4) | 0.25 | 0.936(2) |
| Cr2 | 4b | -0.007(4) | 0.022(2) | 0.1398(3) |
| O1 | 8c | 0.734(2) | 0.4919(5) | 0.017(2) |
| O2 | 8c | 0.022(2) | 0.1398(3) | 0.036(1) |
| O3 | 4b | 0.162(2) | 0.75 | 0.366(2) |

| Table 2 | Bond distances (Å), angles (°), and bond valence sums (BVS) for the Cr sites in Ca$_2$Cr$_2$O$_5$ from refinement against 300 K diffraction data
|---|---|---|---|
| O1–Cr1–O1 × 2 | 1.93(2) | Cr2–O2 × 2 | 1.73(1) |
| Cr1–O1 × 2 | 1.94(2) | Cr2–O3 | 1.83(2) |
| Cr1–O2 × 2 | 2.08(1) | Cr2–O3 | 1.90(2) |
| BVS(Cr1) | 3.02 | BVS(Cr2) | 3.36 |
| O1–Cr1–O1 × 2 | 178.6(12) | O2–Cr2–O2 | 140.9(8) |
| O1–Cr1–O1 × 2 | 88.9(1) | O2–Cr2–O3 × 2 | 103.7(7) |
| O1–Cr1–O1 | 89.8(12) | O2–Cr2–O3 × 2 | 106.9(7) |
| O1–Cr1–O2 × 2 | 92.5(12) | O3–Cr3–O3 | 106.9(7) |
| O1–Cr1–O2 × 2 | 92.5(12) | O3–Cr3–O3 | 106.9(7) |
| O1–Cr1–O2 × 2 | 92.5(12) | O3–Cr3–O3 | 106.9(7) |
| O1–Cr1–O2 × 2 | 92.5(12) | O3–Cr3–O3 | 106.9(7) |
| O1–Cr1–O2 × 2 | 92.5(12) | O3–Cr3–O3 | 106.9(7) |
| O1–Cr1–O2 × 2 | 92.5(12) | O3–Cr3–O3 | 106.9(7) |
Ga\textsubscript{2}O\textsubscript{4} tetrahedron in isostructural Ca\textsubscript{2}Ga\textsubscript{2}O\textsubscript{5} is far less distorted, with Ga–O distances of 1.82–1.89 Å and O–Ga–O angles of 106–122°. As Cr\textsuperscript{3+} and Ga\textsuperscript{3+} have almost identical ionic radii (0.615 and 0.62 Å for octahedral coordination) this comparison suggests that the excess distortion of Ca\textsubscript{2}Cr\textsubscript{2}O\textsubscript{5} reflects the instability of tetrahedrally-coordinated Cr\textsuperscript{3+}, as this cation generally has a strong preference for octahedral coordination which maximises crystal field stabilisation energy of the 3d\textsuperscript{3} electronic configuration. The Ca\textsuperscript{2+} site coordination is comparable to that in other brownmillerites,\textsuperscript{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 La\textsubscript{1−x}A\textsubscript{x}MnO\textsubscript{2.5} (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 Ca\textsubscript{2}Cr\textsubscript{2}O\textsubscript{5}, against the deviation of the tetrahedral chains from 180°.\textsuperscript{19} The latter angle is defined as 180°(O3–O3–O3 angle) and takes value 50.3(7)° in the 300 K structure of Ca\textsubscript{2}Cr\textsubscript{2}O\textsubscript{5}. The point for Ca\textsubscript{2}Ga\textsubscript{2}O\textsubscript{5} lies within the domain of inverse susceptibility shows linear variation with temperature suggesting that the spin order is antiferromagnetic. The susceptibility shown in Fig. 3. A transition is apparent near 200 K with no divergence between ZFC and FC data, the susceptibility shown in Fig. 3. A transition is apparent near 200 K with no divergence between ZFC and FC data,

The magnetic structure of Ca\textsubscript{2}Cr\textsubscript{2}O\textsubscript{5} consists of antiferromagnetic structures with moments parallel to the magnetic planes of Cr\textsubscript{1} and Cr\textsubscript{2} moments as shown in Fig. 4b. Fits using a single basis vector for the spin order did not account well for the magnetic intensities. However, a good fit (as shown for the 10 K data in Fig. 2) is obtained using a combination of the basis vectors \( \Psi_3(T_3) \) and \( \Psi_4(T_4) \). These describe a \( \text{Cr}_1\text{Cr}_2 \) antiferromagnetic order of spins, following standard convention for magnetic order in perovskites.\textsuperscript{20} Although the \textit{Cr}1 and \textit{Cr}2 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 \( m_y \) and \( m_z \) moment components at 10 K have values of 1.08(5) and 1.33(7) \( \mu_B \), and the resultant moment is \( m = 1.71(1) \mu_B \). Neutron diffraction shows that the Néel temperature for Ca\textsubscript{2}Cr\textsubscript{2}O\textsubscript{5} is >200 K (see inset to Fig. 2), and hence somewhat higher than the susceptibility features observed in Fig. 3. An estimate of \( T_N \approx 220 \text{ K} \) is obtained by fitting the temperature variation of the moment in Fig. 4a with a critical law \( m(T) = m(0)[1 − (T/T_N)^β]^3 \) for an exponent \( β \approx 0.3 \), in keeping with theoretical models such as the three-dimensional XY magnet for which \( β = 0.34 \).

The magnetic structure of Ca\textsubscript{2}Cr\textsubscript{2}O\textsubscript{5} consists of antiferromagnetic planes of \textit{Cr}1 and \textit{Cr}2 moments as shown in Fig. 4b. Spins lie in the \textit{bc}-plane and are tilted by 51(4)° from the \textit{b}-axis. Neighbouring \textit{Cr}1 and \textit{Cr}2 spins connected through \textit{Cr}1–O–\textit{Cr}2 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 \textit{Cr}1 and \textit{Cr}2, and that \textit{Cr}1–O–\textit{Cr}2 Heisenberg exchange interactions are weak or frustrated. This reduction in the low temperature ordered moment of 1.7 \( \mu_B \) from the ideal value of 3 \( \mu_B \) for 3d\textsuperscript{3} Cr\textsuperscript{3+} 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 \textit{a} or \textit{b}.

| Irreps   | Basis vectors | \( m_{x_1} \), \( m_{x_2} \), \( m_{y_2} \) | \( \{0, 1/2, 0\} \), \( \{x, 1/4, z\} \), \( \{x, 3/4, −z\} \) |
|---------|---------------|------------------------------------------|------------------------------------------|
| \( \Gamma_1 \) | \( \Psi_1 \)   | 1, 0, 0 –1, 0, 0 0, 1, 0 0, −1, 0   | (0, 0, 0) \( \{0, 1/2, 0\} \) \( \{x, 1/4, z\} \) \( \{x, 3/4, −z\} \) |
| \( \Gamma_2 \) | \( \Psi_2 \)   | 1, 0, 0 0, −1, 0 1, 0, 0 1, 0, 0   | (0, 0, 0) \( \{0, 1/2, 0\} \) \( \{x, 1/4, z\} \) \( \{x, 3/4, −z\} \) |
| \( \Gamma_3 \) | \( \Psi_3 \)   | 0, 0, 1 0, 0, 1 0, 1, 0 0, 1, 0   | (0, 0, 0) \( \{0, 1/2, 0\} \) \( \{x, 1/4, z\} \) \( \{x, 3/4, −z\} \) |
| \( \Gamma_4 \) | \( \Psi_4 \)   | 0, 0, 0 0, 1, 0 1, 0, 0 0, 1, 0   | (0, 0, 0) \( \{0, 1/2, 0\} \) \( \{x, 1/4, z\} \) \( \{x, 3/4, −z\} \) |
| \( \Gamma_5 \) | \( \Psi_5 \)   | 0, 0, 0 0, 1, 0 1, 0, 0 0, 1, 0   | (0, 0, 0) \( \{0, 1/2, 0\} \) \( \{x, 1/4, z\} \) \( \{x, 3/4, −z\} \) |
| \( \Gamma_6 \) | \( \Psi_6 \)   | 0, 0, 0 0, 1, 0 1, 0, 0 0, 1, 0   | (0, 0, 0) \( \{0, 1/2, 0\} \) \( \{x, 1/4, z\} \) \( \{x, 3/4, −z\} \) |
| \( \Gamma_7 \) | \( \Psi_7 \)   | 0, 0, 0 0, 1, 0 1, 0, 0 0, 1, 0   | (0, 0, 0) \( \{0, 1/2, 0\} \) \( \{x, 1/4, z\} \) \( \{x, 3/4, −z\} \) |

Fig. 3 ZFC and FC magnetic susceptibilities for Ca\textsubscript{2}Cr\textsubscript{2}O\textsubscript{5}, and the inverse ZFC susceptibility showing a Curie–Weiss fit to the 240 < \( T < 300 \text{ K} \).
actions determine spin directions.

The unusual tetrahedral coordination of Cr$^{3+}$ results in local structural distortions. The observation of Cr$^{3+}$ 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 SrCrO$_2$. 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 (La$_{1-x}$Sr)$_x$CrO$_3$.

Conclusions

This study confirms that Ca$_2$Cr$_2$O$_5$ synthesised by reduction of the high pressure perovskite phase CaCrO$_3$ is a brownmillerite and adopts the ordered $I2mb$ superstructure at ambient temperature. The unusual tetrahedral coordination of Cr$^{3+}$ results in local structural distortions. The observation of Cr$^{3+}$ 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 SrCrO$_2$. 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 (La$_{1-x}$Sr)$_x$CrO$_3$.

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.