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$Ba_7Mn_5Cr_2O_{20}$: charge and chemical order†

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$Ba_7Mn_5Cr_2O_{20}$ adopts a structure containing an ordered array of Mn^{IV}, Mn^{II} and Cr^{V} cations and exhibits complex magnetic behaviour at low temperature.

The structural ordering of two or more transition metal cations, of similar size and charge, in complex oxide structures is a long standing challenge in synthetic solid state chemistry. Typically the thermodynamic competition between different possible structures, or cation ordering schemes, is dominated by entropy and thus statistically disordered structures are strongly favoured. Unless there is a strong enthalpic motivation for the formation of cation ordered structures, driven for example by a large difference in charge or size between the cations to be ordered, disordered structures result. Despite synthetic difficulties strong interest in preparing cation ordered phases has endured due to predictions of exotic physical behaviour in such systems.

One strategy utilized to prepare cation ordered complex oxides is to exploit the differing coordination preferences of transition metals. Anion deficient hexagonal perovskite structures offer a range of different transition metal coordination sites which can differentiate between cations on the basis of both size and coordination number, suggesting they are good host structures for cation ordering studies.

A 5 g sample of $Ba_7Mn_5Cr_2O_{20}$ was prepared from a 7 : 5 : 1 molar ratio of $BaCO_3$ (99.997%), MnO_2 (99.995%) and Cr_2O_3 (99.995%). After being thoroughly mixed in an agate pestle and mortar the sample was heated at 1000 °C in air for 24 hours. The sample was then pressed into 13 mm pellets and heated at 1225 °C for 5 periods of 48 hours under flowing argon. X-ray powder diffraction data collected from the resulting black powder could be indexed on the basis of a rhombohedral unit cell with lattice parameters a = 5.7401(1) Å, c = 50.597(1) Å. These lattice parameters are consistent with a hexagonal perovskite structure with a 21R type stacking sequence. Considering all the possible 7-layer stacking sequences consistent with rhombohedral symmetry, it was determined that a $(hhccccc)_3$ sequence gave the best match to the observed X-ray powder diffraction intensities. This stacking sequence has been previously observed for the phase $Ba_7Mn_5Ca_2O_{20}$[1] which consists of a face sharing trimer of Mn^{IV} stacked with octahedral Ca^{II} and tetrahedral Mn^{V}. The stacking sequence of $Ba_7Mn_5Ca_2O_{20}$ was used as a starting point for the structural model of $Ba_7Mn_5Cr_2O_{20}$, but with the tetrahedral Mn^{V} replaced by Cr^{V} and manganese occupying the remaining octahedral sites (Fig. 1).

This structural model was refined against neutron powder diffraction data collected on the D2b instrument at the ILL, Grenoble (λ = 1.59 Å) (Fig. 2). Structural refinement proceeded smoothly and convergence was achieved rapidly. In the final cycles of refinement the Mn : Cr occupancy ratio of the transition metal coordination sites was refined. All the octahedral sites were found to be fully occupied, within error, by manganese. The tetrahedral site, however, was found to contain a 93 : 7 ratio of Cr : Mn. The large contrast in neutron scattering lengths between Mn and Cr provides a high degree of sensitivity to the transition metal distribution. Final goodness of fit parameters: wRp = 5.28%, Rp = 4.14%. Full structural details are given in the supplementary information.

Close inspection of the refined structure reveals the apex shared octahedral manganese coordination site (Mn(1)) is significantly expanded with respect to the other octahedral coordination sites (Mn(2), Mn(3)). Calculating bond valence sums for the three

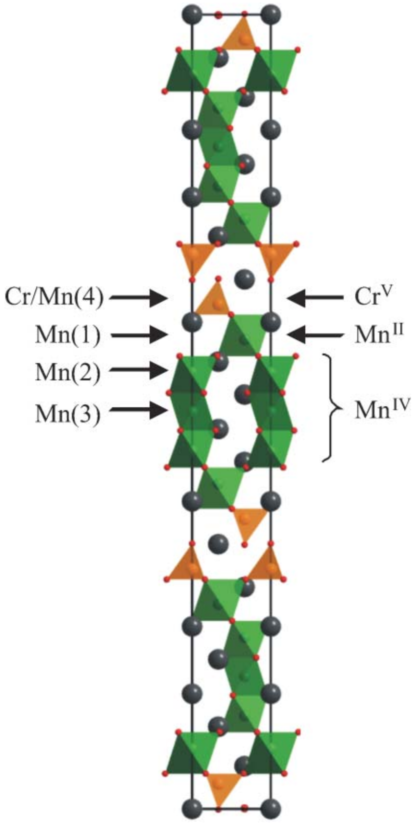

Fig. 1 The refined structure of $Ba_7Mn_5Cr_2O_{20}$.

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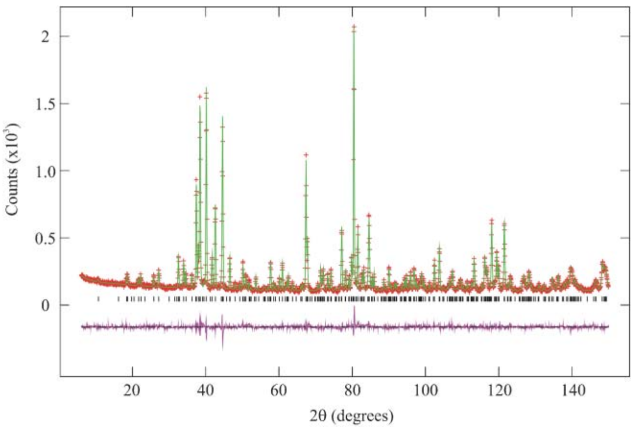

Fig. 2 Observed, calculated and difference plots for the structural refinement of $Ba_7Mn_5Cr_2O_{20}$ against neutron powder diffraction data.

manganese coordination polyhedra yields values consistent with Mn^{II} on site Mn(1) (mean Mn–O = 2.17 Å, BVS = 2.26) and Mn^{IV} on sites Mn(2) and Mn(3) (mean Mn–O = 1.92 and 1.89 respectively, BVS = 3.75 and 4.06 respectively). Bond valence sums calculated for the tetrahedral site Cr(4) are consistent with Cr^{V} (BVS = 5.05) giving an overall formulation of $Ba_7Mn^{IV}{}_3Mn^{II}{}_2Cr^{V}{}_2O_{20}$. In addition it can be seen that the manganese cation in the Mn(1) site is displaced away from the neighbouring Cr/Mn(4) site, consistent with a high charge (Cr^{V}) on this tetrahedral site.

The comparison to the structurally analogous phase $Ba_7Mn_5Ca_2O_{20}$ is obvious,[1] particularly when considered as the formulation $Ba_7Mn^{IV}{}_3Ca^{II}{}_2Mn^{V}{}_2O_{20}$. However the balance of oxidation states in $Ba_7Mn_5Cr_2O_{20}$ is much more delicate. The presence of both Mn(II) and Mn(IV) indicates an effective disproportionation of Mn(III) which, while normal in solution, is highly unusual in the solid state.

Magnetisation data collected as a function of temperature from a 50 mg powder sample using a Quantum Design MPMS SQUID magnetometer are plotted in Fig. 3. Data in the temperature range $100 < T/\mathrm{K} < 300$ obey the Curie–Weiss law (see inset to Fig. 3), yielding values of $C = 10.67\ \mathrm{cm^3\ K\ mol^{-1}}$ and $\theta = 43.6$ K. Below this temperature there is a sharp rise in the magnetisation at $\sim$50 K suggestive of the onset of ferromagnetic order. The magnitude of the paramagnetic moment extracted for $Ba_7Mn_5Cr_2O_{20}$ is inconsistent with a simple weakly interacting paramagnetic model. The observed Curie constant of $10.67\ \mathrm{cm^3\ K\ mol^{-1}}$ is significantly less than the value expected for $2 \times s = ½$ (Cr^{V}) + $3 \times s = {}^3/_2$ (Mn^{IV}) + $2 \times s = {}^5/_2$ (Mn^{II}) which gives a $C_{\mathrm{expected}} = 15.12\ \mathrm{cm^3\ K\ mol^{-1}}$. $BaMnO_{3-x}$ phases have been observed to have similarly reduced magnetic moments[2] which is thought to be the result of strong antiferromagnetic coupling between neighbouring Mn^{IV} centres at room temperature. Given the strong structural similarity between $BaMnO_{3-x}$ phases and $Ba_7Mn_5Cr_2O_{20}$ it is likely that a similar coupling interaction is responsible for the reduced moment observed here. Magnetisation–field data collected at 5 K are plotted in Fig. 4 and appear consistent with the assignment of ferromagnetic order, yielding a saturated ferromagnetic moment of $\sim$7.5 μ_B per formula unit. This value is also considerably smaller than would be expected from a phase in which all the magnetic centres ordered ferromagnetically ($\mu_{\mathrm{sat\text{-}expected}} = 21\ \mu_B$), further indicating complex behaviour.

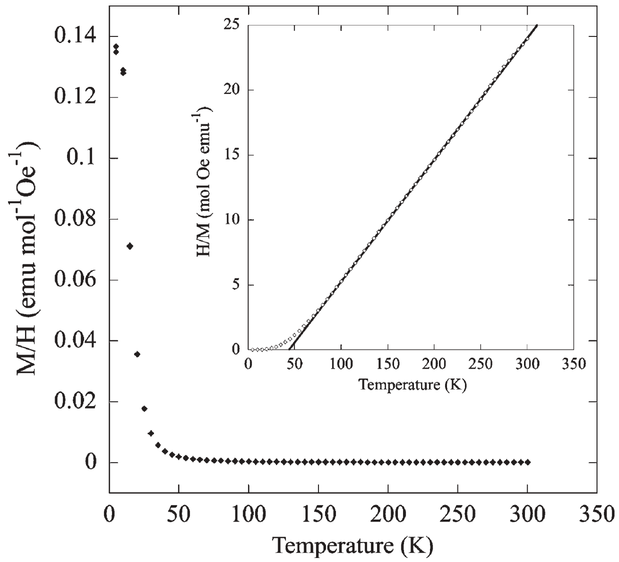

Fig. 3 Zero-field cooled and field cooled magnetisation of $Ba_7Mn_5Cr_2O_{20}$. Inset shows a Curie–Weiss fit to a plot of *H*/*M* giving extracted values of $C = 10.67\ \mathrm{cm^3\ K\ mol^{-1}}$, $\theta = 43.6$ K.

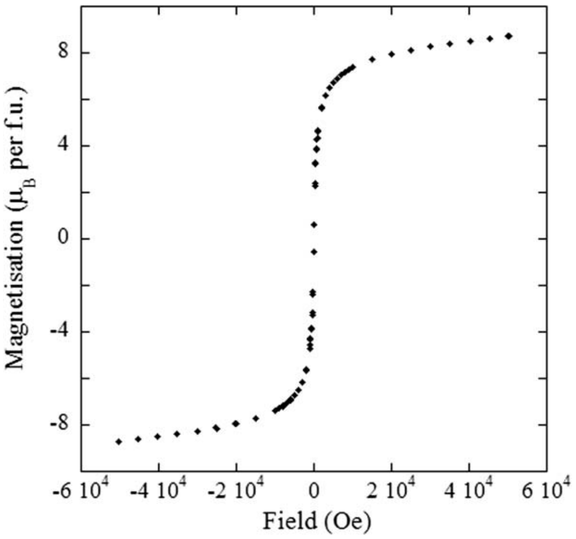

Fig. 4 Plot of magnetisation against field collected from $Ba_7Mn_5Cr_2O_{20}$ at 5 K.

The rigorous ordering of Mn^{IV}, Mn^{II} and Cr^{V} centres within the structure of $Ba_7Mn_5Cr_2O_{20}$ demonstrates the ability of anion deficient hexagonal perovskites to organise transition metal ions into ordered arrays. The fact that these ions are all paramagnetic and that charge ordering is also observed suggests a series of structurally related phases can be prepared which would be expected to exhibit complex magnetic behaviour.

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Notes and references

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