Selective deintercalation of apex over face-shared oxide ions in the topotactic reduction of $Sr_7Mn_4O_{15}$ to $Sr_7Mn_4O_{12}$†

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Sodium hydride selectively deintercalates the apex rather than face-shared oxide ions within the structure of $Sr_7Mn_4O_{15}$ leading to the formation of the structurally related reduced phase $Sr_7Mn_4O_{12}$.

Recent interest in complex manganese oxides, stemming from the observation of colossal magnetoresistance (CMR) in $La_{1.2}Sr_{1.8}Mn_2O_7$,[1] has focused almost entirely on phases with the cubic perovskite or the related layered Ruddlesden-Popper (RP) type structures. In these materials MnO_6 octahedra share apices to form 3D manganese-oxygen networks in the case of the $AMnO_3$ perovskites or layered 2D structures for the more complex $A_{n+1}Mn_nO_{3n+1}$ RP phases. By substituting the A cations for those with differing charge and/or size the effects of manganese oxidation state and distortions to the Mn–O–Mn angles on the transport and magnetic behaviour of these phases have been studied.[2] Despite the wide variety of studies performed on these materials revealing a wealth of complex physical behaviour, the exact roles of double exchange and super-exchange in the coupling of spins in these phases is unresolved. Furthermore no materials which exhibit large magnetoresistances at ambient temperature in technologically relevant magnetic fields have been reported to date.

In order to better understand the interactions responsible for the behaviour of complex manganese oxides, attention has turned from materials which are constructed exclusively from apex-shared MnO_6 octahedra to those which include both apex and face sharing connectivities. This change in the manganese-oxygen connectivity allows competition between the $\sim 90°$ and $\sim 180°$ super-exchange pathways offered by face and apex sharing respectively and offers another parameter by which we may tailor the complex transport and magnetic behaviour observed in manganese oxides.

Vente *et al.* recently reported the detailed structure and magnetic properties of the Mn(IV) oxide $Sr_7Mn_4O_{15}$.[3] This phase has a complex structure in which pairs of face-sharing octahedra form Mn_2O_9 units which share three out of six apical oxide ions to form columns which are cross linked approximately every 10 Å (Fig. 1B). Attempts to chemically substitute the strontium ions in this material have been restricted to isovalent substitutions, preventing the manipulation of the manganese oxidation state.

An alternative method of changing the manganese oxidation state is to remove or substitute the oxide ions in the structure by low temperature topotactic reduction/anion substitution. Binary metal hydrides have been demonstrated to be effective low temperature reducing agents for both perovskite and RP phases.[4] Here the topotactic reduction of $Sr_7Mn_4O_{15}$ with sodium hydride to the Mn(II)/Mn(III) phase $Sr_7Mn_4O_{12}$ is described.

A 5g sample of $Sr_7Mn_4O_{15}$ was prepared by firing a suitable ratio of $SrCO_3$ and MnO_2 according to the method described by Vente *et al.*[3] The well crystallized brown powder was then mixed with six mole equivalents of NaH, in an argon filled glove box, and the mixture was then sealed in an evacuated pyrex ampoule ($p < 2 \times 10^{-4}$ torr) and heated at 190 °C (2 days), 200 °C (2 days) and 210 °C (2 days) with intermediate regrindings under argon. X-ray powder diffraction data showed the sample contained 5 phases: a

reduced phase which could be readily indexed on the basis of the $Sr_7Mn_4O_{15}$ cell (lattice parameters: $a = 6.954(1)$ Å, $b = 9.674(2)$ Å, $c = 10.041(2)$ Å, $\beta = 93.317(4)°$), NaH, NaOH and small quantities of SrO and MnO produced as a result of mild sample decomposition. The sample was then washed with 6×40 ml aliquots of methanol under dry nitrogen in a filter Schlenk apparatus to remove the sodium containing phases and MnO (confirmed by X-ray powder diffraction) before being pumped to dryness. Full synthetic details are available in the supplementary information.

A structural model based on that of the unreduced starting material (space group: $P2_1/c$) was refined against three room-temperature, high resolution, neutron powder diffraction data sets (d-spacing ranges : $1 \leq d/\text{Å} \leq 8$, $0.8 \leq d/\text{Å} \leq 4$, $0.5 \leq d/\text{Å} \leq 3.5$) collected using the POLARIS diffractometer at ISIS, UK. Atomic thermal parameters were modelled as isotropic ellipsoids and were constrained by element. The size of the manganese thermal ellipsoid was fixed at 0.004 Å² to prevent it taking an un-physical negative value. On refinement the occupancy factors of the apex-shared oxide ions rapidly approached zero, while all other oxygen occupancies remained within ± 2% of full occupation. A minority phase corresponding to approximately 10 mass percent strontium
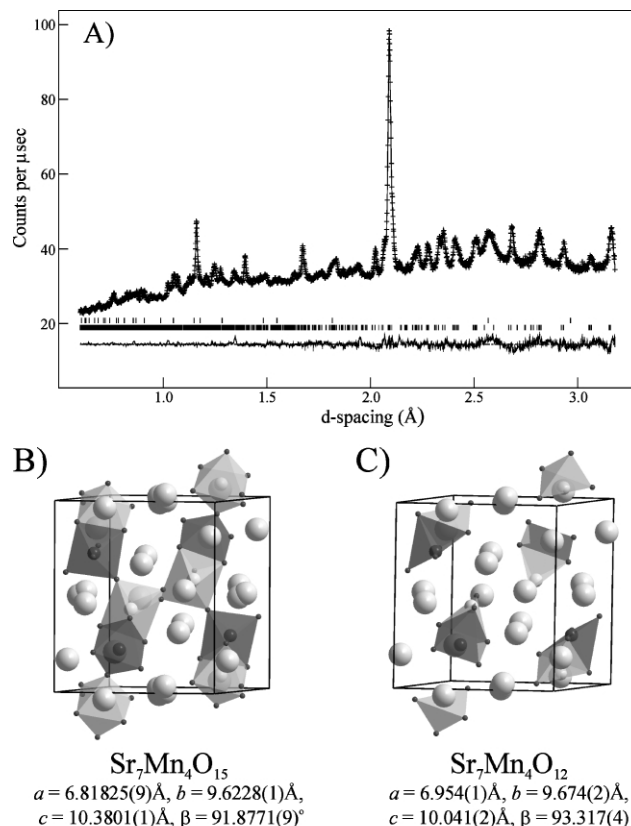
Fig. 1 (A) Observed (crosses) calculated (line) and difference (lower line) plots for the structural refinement of $Sr_7Mn_4O_{12}$ from powder neutron diffraction data. Illustration of the topotactic nature of the transformation of (B)$Sr_7Mn_4O_{15}$ to (C) $Sr_7Mn_4O_{12}$.

$Sr_7Mn_4O_{15}$
$a = 6.81825(9)$Å, $b = 9.6228(1)$Å,
$c = 10.3801(1)$Å, $\beta = 91.8771(9)°$

$Sr_7Mn_4O_{12}$
$a = 6.954(1)$Å, $b = 9.674(2)$Å,
$c = 10.041(2)$Å, $\beta = 93.317(4)$

† Electronic Supplementary Information (ESI) available: synthetic, thermogravimetric and crystallographic details for $Sr_7Mn_4O_{12}$. See http://www.rsc.org/suppdata/cc/b3/b312792c/

oxide was required in order to achieve an acceptable fit to the data. The final refinement cycle optimised 127 variables against 5880 reflections to yield fitting statistics : $\chi^2 = 2.598$, wRp = 0.94%, Rp = 1.3%. The refined stoichiometry of $Sr_7Mn_4O_{12}$ was confirmed by thermogravimetric re-oxidation to $Sr_7Mn_4O_{15}$ in oxygen.‡

Fig. 2 shows the topotactic and highly selective nature of the reduction. All three apex-shared oxide ions have been deintercalated from the structure leaving isolated Mn_2O_6 dimers consisting of a distorted square based pyramid sharing a triangular face with a highly distorted tetrahedron. Comparison of the four equivalent Mn_2O_6 units in $Sr_7Mn_4O_{12}$ with the Mn_2O_9 units in $Sr_7Mn_4O_{15}$ (Fig. 2) shows the isolated dimer units have undergone a degree of structural relaxation in order to increase the spherical symmetry of their co-ordination polyhedra and thus reduce excessive bond strain. The newly four-coordinate Mn(2) has moved towards the plane of the three shared oxide ions (O(1), O(2) and O(4)) and the non-bridging oxide ion has also moved to try to reduce some of the distortion in the newly formed MnO_4 'tetrahedron'. In order to maintain the Mn-Mn distance Mn(1) has been pushed towards one of the edges of the shared triangular face which in turn causes O(7) and O(8) to move to maintain the approximately square plane (Mn(1), O(1), O(2), O(7), O(8)).

Bond valence sums for Mn(1) and Mn(2) yield values of +3.09 and +2.29 respectively.[5] These values, along with the differing co-ordination numbers of the two manganese sites suggest charge ordering within the material. The mean manganese oxidation state of +2.5 can be readily accounted for by a 1 : 1 ratio of Mn^{3+} and Mn^{2+} located at Mn(1) and Mn(2) respectively.

Three of the four crystallographically independent strontium sites have their coordination numbers reduced from ten to eight with the remaining site reduced from eight to seven. The mean strontium-oxygen bond length contracts from 2.71(2) Å[3] to 2.66(3) Å to compensate for this.

Magnetisation data collected as a function of temperature (Figure 3) show no indication of long range magnetic order. The data in the temperature range 35 < T/K < 300 can be approximately fitted to
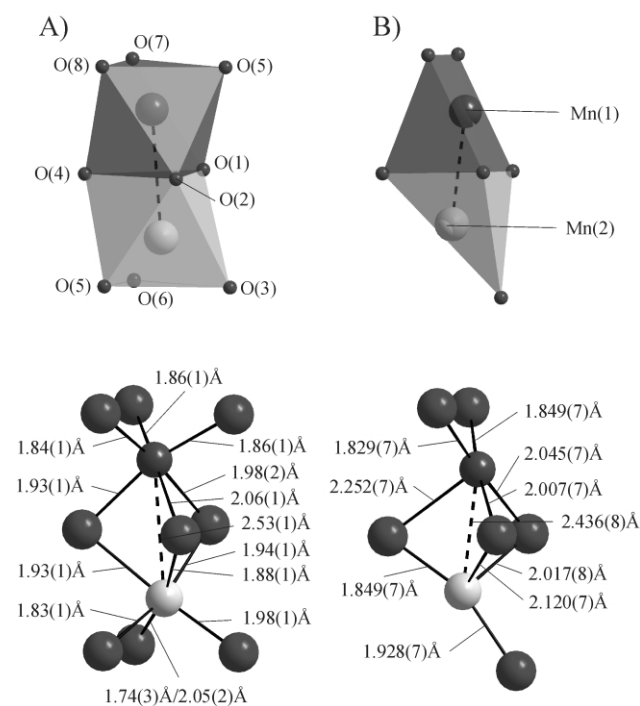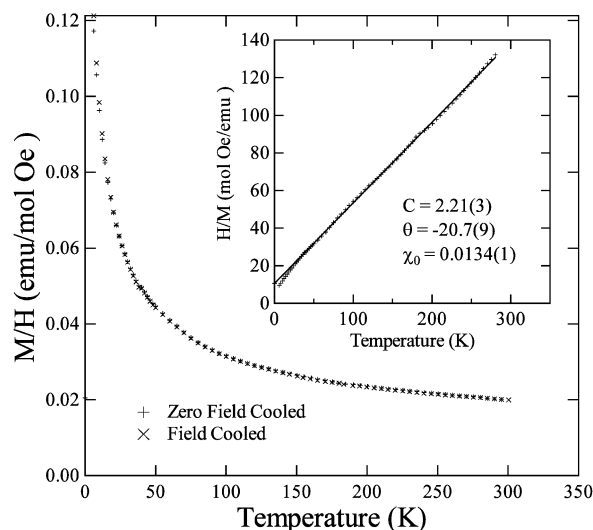
Fig. 3 Zero-field cooled and field cooled magnetisation data collected from $Sr_7Mn_4O_{12}$. Inset plots the inverse of the normalized magnetization against temperature.

a Curie–Weiss + temperature independent model. The physical values extracted from this fit do not provide much detail about the magnetic behaviour of the material as the molar susceptibility is the sum of the magnetic response of all four manganese centres in the formula unit. The small magnitude of the average manganese moment ($2.1\mu_B$) does suggest either low spin configurations are adopted§ or that strong antiferromagnetic intra-dimer couplings exist across the whole temperature range studied resulting in the small average moment observed. It should be stressed that there is no suggestion of metal-metal bonding in the Mn_2O_6 unit as the Mn(1)–Mn(2) distance is too great to support such an interaction. The presence of Mn_3O_4 in some samples (confirmed by X-ray powder diffraction) led to the observation of weak ferromagnetic behaviour, however the data in Fig. 3 clearly show $Sr_7Mn_4O_7$ does not order magnetically in the temperature range studied.

The conversion of $Sr_7Mn_4O_{15}$ to the Mn(II)/Mn(III) phase $Sr_7Mn_4O_{12}$ described above demonstrates that simple binary hydrides are effective reagents for the low-temperature topotactic reduction of complex manganites. The selective deintercalation of apex over face-shared oxide ions may be a widely applicable feature of the reduction chemistry of phases with mixed metal-oxygen connectivities which can be exploited to prepare materials with complex anion vacancy ordering schemes.

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Notes and references

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Fig. 2 A comparison of the coordination polyhedra of manganese in (A) $Sr_7Mn_4O_{15}$ and (B) $Sr_7Mn_4O_{12}$.