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Charge and structural ordering in the brownmillerite phases: $La_{1-x}Sr_xMnO_{2.5}$ ($0.2<x<0.4$)

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Abstract

The topotactic reduction of $La_{1-x}Sr_xMnO_3$ ($0.2<x<0.4$) perovskite phases to the corresponding $La_{1-x}Sr_xMnO_{2.5}$ brownmillerite phases with NaH is described. Neutron and electron diffraction data show the $x=0.25$ and 0.2 phases adopt structures with an unusual ordered L–R–L–R alternation of twisted chains of Mn(II) tetrahedra within each anion-deficient layer. This is accompanied by Mn(II)/(III) charge ordering within the remaining MnO_6 octahedral layers. In contrast, the $x=0.4$ phase adopts a structure in which the twisted chains of tetrahedra are disordered.

Keywords: Brownmillerite; Topotactic reduction; Manganese

1. Introduction

Complex manganese oxides have received considerable attention due to the observation of large magnetoresistive ratios in these phases [1–3]. Interest has been sustained by the broader observation of strong coupling between spin, charge and lattice degrees of freedom [4,5]. The report of unusually large magnetoresistive effects in the brownmillerite phase $SrCaMnGaO_{5.04}$ [6] has directed interest towards materials of this structural type.

The brownmillerite structure is one of the most common anion-vacancy ordered structures. It can be viewed as an anion-deficient variant of the ABO_3 cubic perovskite structure in which half the anions have been removed from alternate BO_2 layers. This gives the stacking sequence AO–BO_2–AO–BO–AO– with alternating layers of apex-linked BO_6 octahedra and BO_4 tetrahedra as shown in Fig. 1.

The anion vacancies are arranged within the BO layers in an ordered manner to yield chains of vacancies parallel to the [110] direction of the simple cubic perovskite lattice. The resulting layers consist of chains of apex-linked BO_4 units which also run along the [110] direction. The structure is complicated by the possibility that the chains of tetrahedra can undergo a cooperative twist, which can occur in either a clock-wise or anti-clockwise sense, to yield 'left'- or 'right'-handed chains (Fig. 2)—the two being related by symmetry.

The three-dimensional arrangement of the twisted chains of tetrahedra leads to a number of general structural configurations (Fig. 3): the *Ima*2 configuration in which all the chains are twisted in the same direction; the *Pnma* configuration where all the chains within the same layer are twisted in the same direction, but the twist direction is inverted between adjacent layers; disordered configurations in which there is a random arrangement of twisted chains. A fourth arrangement has also been observed in which an alternating arrangement of 'left'- and 'right'-handed chains of tetrahedra exists within the same layer as shown in Fig. 3 ($P2_1/c$ configuration). Significant efforts have been made to characterise the structural configurations adopted by A_2MnBO_{5+x} ($A=$ Ca, Sr; $B=$ Ga, Al) phases and to relating these with the often complex magnetic behaviour of the materials to gain a better understanding of the magnetic exchange interactions present in these phases [7–11].

In recent work, it has been shown that binary metal hydrides can affect the topotactic deintercalation of oxide

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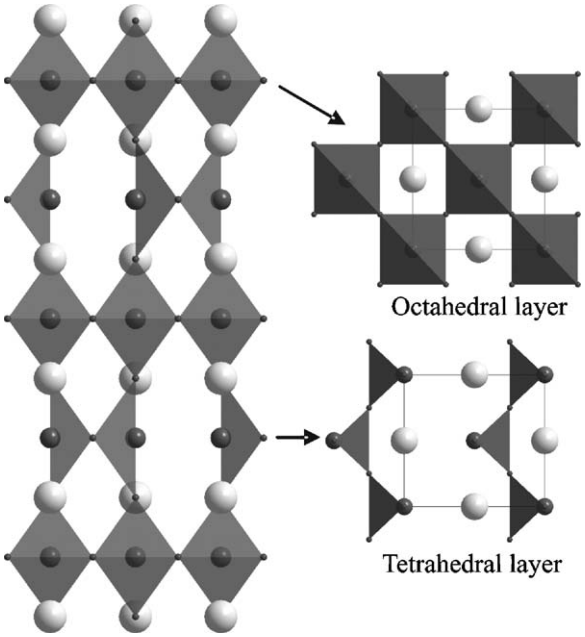

Fig. 1. The brownmillerite structure. Insets show views of the octahedral and tetrahedral layers.

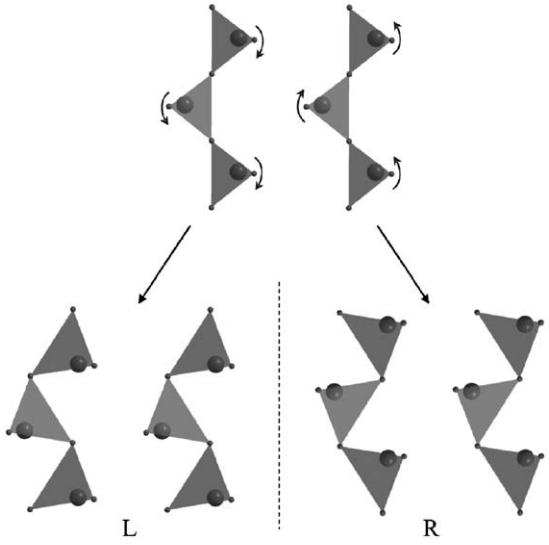

Fig. 2. Cooperative twisting of the chains of tetrahedra leads to two, symmetry-related, distorted chains.

ions from complex manganese oxides to yield phases with mean manganese oxidation states between Mn(II) and Mn(III) [12]. The topotactic reduction of $Ln_{1-x}A_xMnO_3$ (Ln = lanthanide, A = Ca, Sr) perovskites by this method offers a route to prepare the 'all-manganese' brownmillerite phases $Ln_{1-x}A_xMnO_{2.5}$ thus enabling a direct comparison with the A_2MnBO_{5+x} phases.

2. Experimental

Five-gram samples of $La_{1-x}Sr_xMnO_3$ ($x = 0.2$, 0.25, 0.4) were prepared via a citrate gel method. Suitable ratios of

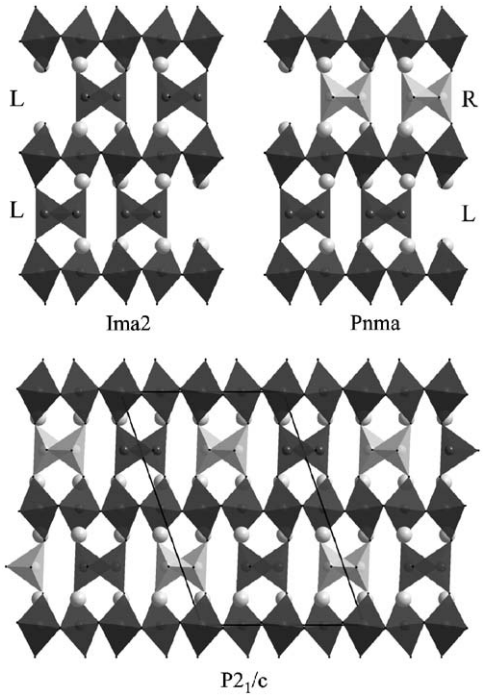

Fig. 3. Ordered arrangements of the two types of twisted chains of tetrahedra.

La_2O_3 (99.999%, dried at 900 °C), $SrCO_3$ (99.994%) and MnO_2 (99.999%) were dissolved in a minimum quantity of a 1:1 mixture of 6 M nitric acid and distilled water. Two mole equivalents of citric acid and 5 ml of analar ethylene glycol were added and the solution heated with constant stirring. The gel thus formed was subsequently ground into a fine powder, placed in an alumina crucible and heated at 1 °C min^{-1} to 1000 °C in air. Samples were then reground and pressed into 13 mm pellets under 5 tonne pressure and heated in air for three periods of 2 days at 1300 °C with regrinding between heating periods. Samples were observed to be phase pure, by laboratory X-ray powder diffraction with lattice parameters in good agreement with published values [13].

The reduction of samples was performed using NaH (Aldrich >95%). $La_{1-x}Sr_xMnO_3$ samples were thoroughly ground in an Argon filled glove box (O_2 and H_2O <1 ppm) with a double stoichiometric quantity of NaH. The resulting mixtures were then sealed in evacuated Pyrex tubes and heated for three periods of 3 days at 210 °C with grinding between heating periods. Samples were then washed with 4 × 100 ml of methanol under nitrogen to remove sodium containing phases (NaOH and NaH) before being dried under vacuum.

Thermogravimetric data were collected from powdered samples heated under flowing oxygen using a Rheometric Scientific STA 1500 thermal analyser. Neutron powder diffraction data were collected from samples contained in vanadium cans sealed with an indium washer under an argon atmosphere. Data were collected at room temperature from the $x = 0.25$ and 0.4 samples using the D2b