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Fluorine insertion reactions of the brownmillerite materials $Sr_2Fe_2O_5$, Sr_2CoFeO_5, and $Sr_2Co_2O_5$

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The brownmillerite structure provides an ordered vacancy lattice into which fluorine anions should easily be accommodated, with full occupation of the vacant sites resulting in a simple perovskite structure. Low-temperature fluorine insertion reactions with the brownmillerite $Sr_2Co_2O_5$ and related materials Sr_2CoFeO_5 and $Sr_2Fe_2O_5$ have been investigated with a view to using fluorine insertion reactions to fill the oxygen vacancies in these materials, thus forming cubic perovskite-type phases with mixed 3+/4+ B cation oxidation states. The synthesis and magnetic properties of the new perovskite materials $SrCoO_{2.5}F_{0.5}$ and $SrCo_{0.5}Fe_{0.5}O_{2.5}F_{0.5}$ are presented here, supplemented by a consideration of Madelung energy calculations in order to explain the dissimilar fluorination behaviour of $Sr_2Fe_2O_5$.

1. Introduction

Ordered vacancy perovskite-related materials such as brownmillerites $A_2BB'X_5$ (where B = transition metal cation with octahedral co-ordination and B′ = transition metal cation with tetrahedral coordination) are good candidates for anion insertion studies due to their inherent anion vacancies. Materials adopting the brownmillerite structure (see Fig. 1) can consist of a single B cation or of two different B cations, which are commonly disordered over both octahedral and tetrahedral sites or may be ordered according to transition metal cation preference for a particular co-ordination environment. Therefore, fluorine incorporation could be used as a facile route to instigate mixed cation oxidation states in the B cation sites, with the possibility that any existing cation ordering may be retained.

The first brownmillerite system shown to be amenable to low-temperature fluorine insertion reactions was $La\mathit{A}CuGaO_5$ (*A* = Ca, Sr) [1–3]; which adopts a brownmillerite structure formed by alternating layers of corner-sharing CuO_6 octahedra and GaO_4 tetrahedra stacked along the long axis, with the La and A cations statistically occupying the 10-fold cavities within the structure.

The brownmillerite Sr_2MnGaO_5 consists of alternating MnO_2 and GaO layers [4–6], although the best description of the ordering of the tetrahedral chains within a layer is unclear: disordered (*Imma*) [6], all chain orientations identical (*I2mb*) [5] or a L–R–L–R– alternation of chain rotation (*Pcmb*) [7]. The latter order is increasingly being observed in brownmillerite materials over short length scales [8]. This intralayer ordering results in a superstructure whereby one of the shorter orthorhombic axes is doubled, consistent with the assignment of the space group *Pcmb*. Rigorous structural re-examination of Ca_2FeCoO_5 has shown that brownmillerites may simultaneously exhibit this intralayer ordering of chain orientations necessitating the use of a *Pcmb* supercell alongside adopting a NaCl–type ordering of mixed B cations between octahedral and tetrahedral sites to a certain extent [9].

Antipov et al. [10] demonstrated that Sr_2MnGaO_5 is amenable to fluorine insertion, producing a tetragonal phase where $a \approx a_p$ and $c \approx 2a_p$. The structure was found to consist of alternating layers of MnO_2, SrO and $GaO_{0.78}F_{1.22}$ ($GaO_{1-x}F_{1+x}$) with the Ga atoms situated in slightly elongated octahedral and the MnO_6 octahedra apically compressed [10,11]. The atomic coordinates were transformed from perovskite structure and full occupancy assigned to all anion positions with the formation of an octahedral environment around the Ga atoms, giving the general composition $Sr_2MnGa(O,F)_6$ with the structure being described by the space group *P4/mmm*.

$Sr_2Fe_2O_5$ crystallises with a brownmillerite structure, with disordered, *Imma* [12], or ordered, *Ima*2 [13], vacancies. However, an electron diffraction study suggests that L–R–L–R– ordering of tetrahedral chains within any given layer occurs over short distances [14].

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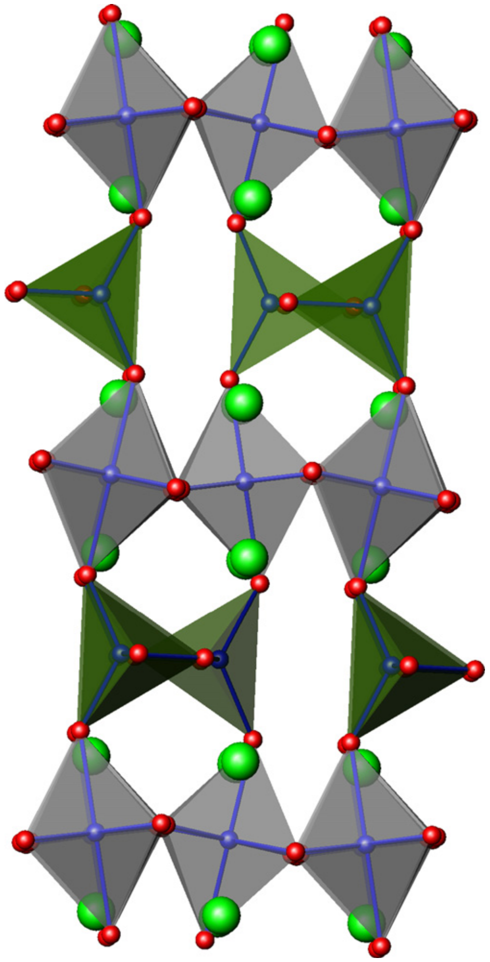

Fig. 1. The crystallographic structure of brownmillerite $A_2BB'X_5$ where A cations are shown in light green, B cations are shown in blue and X anions are shown in red. BX_6 octahedra are highlighted in grey whilst $B'X_4$ tetrahedra are highlighted in khaki. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

In their study of the fluorinated materials $Sr_3Fe_2O_6F_{0.87}$, Sr_2FeO_3F and $Ba_2InFeO_5F_{0.68}$, Case et al. [15] also briefly reported that the fluorination of $Sr_2Fe_2O_5$ resulted in the formation of 2 cubic perovskite phases formed in an approximately 1:1 ratio with the respective lattice parameters $a = 3.95$ Å and $a = 3.87$ Å. The compositions of the phases were not known nor were any reasons identified for the formation of a 1:1 mixture of these 2 phases upon fluorination of $Sr_2Fe_2O_5$.

The study by Berry et al. [16] found that the novel Fe^{3+} perovskite $SrFeO_2F$ can be formed via the low-temperature fluorination of the oxygen-deficient perovskite-related material $SrFeO_{3-\delta}$ (a mixed Fe^{3+}/Fe^{4+} perovskite). Fluorination of this phase produced a material with the cubic unit cell parameter $a = 3.956(1)$ Å. Upon comparing the primitive perovskite subcells for each sample, fluorination leads to a significant increase in cell parameter. The larger unit cell was attributed to the partial replacement of O^{2-} anions by F^- anions and hence a reduction of the Fe oxidation state and lengthening of the bond distances.

This raises the question of whether it is possible to use the low-temperature fluorination of $Sr_2Fe_2O_5$ (as first proposed by Case et al. [15]) to form a cubic perovskite $Sr_2Fe_2O_5F$ phase with an average oxidation state of $Fe^{3.5+}$ as opposed to the purely Fe^{3+}-containing phase $SrFeO_2F$, or if formation of the $Fe^{3.5+}$ phase is unfeasible. A further study of the fluorination of $Sr_2Fe_2O_5$ has therefore been conducted.

$Sr_2Co_2O_5$ has recently been shown in the bulk phase to display similar disorder to $Sr_2Fe_2O_5$ and is best described using the space group *Imma*. The mixed phase Sr_2CoFeO_5 also has the brownmillerite structure and is reported to have disordered vacancies [17]. Although samples quenched from 1200 °C contained Fe and Co cations randomly distributed over the octahedral and tetrahedral sites, annealing under flowing argon at 800 °C induced a partial ordering whereby Co^{3+} showed a slight preference (57:43) for the tetrahedral sites.

It is interesting to note that for both $Sr_2Fe_2O_5$ and Sr_2CoFeO_5, the use of the disordered space group *Imma* (with half-occupied 8i sites) has been necessary to describe the bulk phase, but it has been acknowledged that there is most likely some degree of additional order over smaller length scales. These observations are similar to previous findings [18], where a higher degree of order was observed in $Sr_2Co_2O_5$ using electron microscopy techniques, but was shown not to be applicable on the length scale pertinent to neutron powder diffraction.

This paper reports an examination of the fluorination behaviour of the three related brownmillerite phases $Sr_2Fe_2O_5$, Sr_2CoFeO_5, and $Sr_2Co_2O_5$. Particular attention is paid to the possible production of mixed valency transition metal cations.

2. Experimental

All fluorinated brownmillerite samples synthesised during the course of this study were prepared via low-temperature solid–gas fluorine insertion reactions.

$Sr_2Fe_2O_5$ was prepared from stoichiometric amounts of dried $SrCO_3$ and Fe_2O_3, ground together and subjected to 2 separate heat treatments of 12 h at 1300 °C under $N_{2(g)}$ with intermediate grinding, then an additional 12 h at 800 °C under $N_{2(g)}$ with no grinding. All fluorinated samples produced were approximately 1:1 mixtures of 2 cubic perovskite phases with lattice parameter $a \approx 3.87$ Å and $a \approx 3.95$ Å. Varying the reaction conditions had no effect on the ratio of the product phases. The optimum conditions for sample crystallinity and minimising SrF_2 in the sample were 2 h at 250 °C under static $10\%F_{2(g)}/90\%N_{2(g)}$ with intermediate grinding of the sample, followed by another 2 h at 265 °C under static $10\%F_{2(g)}/90\%N_{2(g)}$.

Sr_2CoFeO_5 was prepared from stoichiometric amounts of dried $SrCO_3$, Co_3O_4 and Fe_2O_3 ground together and pressed into a pellet. This was then subjected to 2 heat treatments of 12 h at 1200 °C each followed by immediately quenching in liquid nitrogen. The optimum conditions for fluorination of this phase were found to be heat treatments of 2 h at 220 °C and 230 °C followed by an additional 2 heat treatments of 2 h at 250 °C, all carried out under static $10\%F_{2(g)}/90\%N_{2(g)}$ with intermediate grinding.

$Sr_2Co_2O_5$ was prepared by solid-state reaction of stoichiometric quantities of high purity $SrCO_3$ and Co_3O_4 for two 12-h heat treatments at 1150 °C in air, with the second heat treatment followed immediately by quenching from 1150 °C into liquid nitrogen.

The optimum conditions for preparing fluorinated samples was found to be a 15 min pulse of $10\%F_{2(g)}/90\%N_{2(g)}$ at 200 °C followed by grinding and annealing for 90 min in static $10\%F_{2(g)}/90\%N_{2(g)}$ at 220 °C.

Powder X-ray diffraction (XRD) data were collected on a Siemens D5000 diffractometer operating in transmission mode with $\theta - 2\theta$ geometry fitted with a curved primary beam germanium monochromator in order to select only the $K_{\alpha 1}$ line ($\lambda = 1.5406$ Å). The diffracted X-ray radiation was detected using a position sensitive detector with $\Delta 2\theta = 8°$ and a step size of 0.02°.

Neutron powder diffraction (NPD) was carried out at the Institut Laue-Langevin, Grenoble using the high-resolution, two-axis powder diffractometer D2B (Ge monochromator, $\lambda = 1.59432$ Å)