High magnetic ordering temperature in the perovskites $\text{Sr}_4-x\text{La}_x\text{Fe}_3\text{ReO}_{12}$ ($x = 0.0, 1.0, 2.0$)

M. Retuerto a, M.-R. Li a, Y.B. Go a, A. Ignatov b, M. Croft b, K.V. Ramanujachary c, R.H. Herber d, I. Nowik d, J.P. Hodges e, W. Dachraoui f, J. Hadermann f, M. Greenblatt a, n

a Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, 610 Taylor Road, Piscataway, NJ 08854, USA
b Department of Physics and Astronomy, Rutgers, The State University of New Jersey, 136 Frelinghuysen Road, Piscataway, NJ 08854, USA
c Department of Chemistry and Physics, Rowan University, 210 Mullica Hill Road, Glassboro, NJ 08028, USA
d Racah Institute of Physics, Hebrew University, Jerusalem, 91904 Israel
e Department of Physics and Astronomy, Rutgers, The State University of New Jersey, 136 Frelinghuysen Road, Piscataway, NJ 08854, USA
f Spallation Neutron Source, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

A series of perovskites $\text{Sr}_4-x\text{La}_x\text{Fe}_3\text{ReO}_{12}$ ($x = 0.0, 1.0, 2.0$) has been prepared by wet chemistry methods. The structure analyses by powder X-ray and neutron diffraction and electron microscopy show that these compounds adopt simple perovskite structures without cation ordering over the B sites; tetragonal ($I4/mmc$) for $x = 0.0$ and $1.0$ and orthorhombic ($Pbnm$) for $x = 2.0$. The oxidation states of the cations in the compound with $x = 0.0$ appear to be $\text{Fe}^{3+}$ and $\text{Re}^{7+}$ and decrease for both with La substitution as evidenced by X-ray absorption spectroscopy. All the compounds are antiferromagnetically ordered above room temperature, as demonstrated by Mössbauer spectroscopy and the magnetic structures, which were determined by powder neutron diffraction. The substitution of Sr by La strongly affects the magnetic properties with an increase of $T_C$ up to $\sim 750$ K.

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1. Introduction

The perovskite and perovskite-related materials are extensively studied due to the huge variety of properties that they can present including magnetism, ferroelectricity, multiferroelectricity, superconductivity and magnetoresistance [1–5]. The complex interplay of electron, charge, spin and lattice interactions and discovery of colossal magnetoresistance (CMR) in manganese perovskites has attracted much attention in search of new materials to understand and control the properties, including the CMR at room temperature (RT) [5–8]. The report of half-metallic properties and RT CMR in $\text{Sr}_2\text{FeMoO}_6$ motivated further interest in the study of complex perovskites [9], and since this discovery many other interesting magnetic perovskites have been found.

Recently, modification of the structural and magnetic properties of $\text{A}_2\text{B}^+\text{B}^-\text{O}_6$ (A=alkaline earth and B$^+$=transition metal cations) double perovskites by substitutions at the A, B$^+$ or B$^-$ sites has been widely studied in attempts to find an optimal candidate for technological applications [10–12]. It has been proposed that the magnetic interactions in $\text{Sr}_2\text{FeMoO}_6$ are mediated by itinerant electrons in $\pi^*$ bands of $\text{Fe}^{3+}$, as trivalent rare earths ions (Ln$^3+$) in a series of general stoichiometry, $\text{Sr}_2\text{Ln}_x\text{FeMoO}_6$ [17,18]. An effective increment of $T_C$ has been described by several groups in La-doped $\text{Sr}_2\text{FeMoO}_6$ [19,20]; however, an increased anti-site disorder effect has been shown to be harmful for the magnetotransport properties of this system. Another double perovskite that presents both ferromagnetism and half-metallic behaviour is $\text{Sr}_2\text{FeReO}_6$, due to the mixed valence of Fe and Re [21]. However, the preparation of the desired mixed valence usually requires synthesis at extreme conditions of reducing or inert environments.

Perovskites with complex formulas of the type $\text{A}_2\text{B}^+\text{B}^-\text{O}_6$ have been demonstrated to be a way to further increase $T_C$ by increasing the amount of the stronger magnetic transition metal cation at the B position of the perovskite. This effect has been previously observed in $\text{A}_2\text{Fe}^2\text{B}^-\text{O}_6$ ($\text{A} = \text{Ca, Sr, Ba}; \text{B}^- = \text{W, Mo, Te, U})$ [22–25].

* Corresponding author. Fax: +1 732 445 5312.
E-mail address: martha@rutchem.rutgers.edu (M. Greenblatt).

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Materials of stoichiometry $A_xB^{2-}B'^{3-}O_{12}$ are also double perovskites (rewritten as $A_xB^{2-}B'^{3-}(O_{a.5}B'^{a.5}O_{a.5})_6$) with intrinsic partial disorder over half of the perovskite B positions ($B'$). We have successfully prepared $Sr_xFe_xReO_{12}$ to study the effect in the magnetic properties of three Fe cations and one Re cation over the B sites, and also increased the charge carriers on the B sublattice by substitution of Sr by La in $Sr_{3-x}La_xFe_xReO_{12}$ ($x=0.0, 1.0$ and $2.0$). We presumed that the electron doping could produce an enhancement of the magnetic properties as it has been observed in many other perovskites [22–25]. The compounds have been prepared by a soft-chemistry procedure and subsequent treatments in air, avoiding the extreme conditions needed for the synthesis of many mixed-valence double perovskites.

2. Experimental section

The compounds were prepared from stoichiometric amounts of analytical grade SrCO$_3$, La$_2$O$_3$, Fe$_2$O$_3$, 2H$_2$O and ReO$_3$, which were dissolved in citric acid, by adding 5 ml of concentrated HNO$_3$. The citrate + nitrate solution was slowly evaporated, leading to an organic resin containing a statistical distribution of the constituent cations at an atomic level. The resin was first dried at 120 °C, leading to a very porous and voluminous “sponge-like” material, which was ground and slowly decomposed at 600 °C, eliminating all the organic materials and nitrates. This treatment produced highly reactive precursors. The precursors were heated in air at different temperatures and with intermediate grindings between 1000 and 1200 °C to obtain the title compounds as black polycrystalline powders.

The products were initially characterized by powder X-ray diffraction (XRD) ($Cu K_{\alpha}$, $\lambda=1.5406$ Å) for phase identification and to evaluate phase purity. For the structural refinements, powder neutron diffraction (PND) data of selected samples were collected at RT, 60 and 14 K at the POWGEN instrument [26] in the Spallation Neutron Source in Oak Ridge National Laboratory, in Tennessee. About 2 g of sample was contained in a vanadium can; a collecting time of 2 h was required for each PND data set. The PND were refined by the Rietveld method, with the Fullprof refinement program [27,28]. In the final run, the following parameters were refined: scale factor, background coefficients, unit-cell parameters, positional coordinates, isotropic thermal parameters, occupancies and magnitudes of the magnetic moments.

The $dc$ magnetic susceptibility measurements were carried out on a physical properties measurements system (PPMS, Quantum Design). Typical zero field cooling (ZFC) and field cooling (FC) susceptibility curves were recorded under an external field of 1000 Oe in the temperature range of 2.5–400 K and with a furnace setup between 400 and 800 K. The isothermal magnetizations at 5 K and 300 K were measured up to 5 T. Mössbauer studies were performed with a $^{57}$Co: Rh source (50 mCi) and a conventional constant acceleration Mössbauer drive. The absorbers were cooled in a closed-cycle refrigerator (Janis, Model SHI-850-5). X-ray absorption near edge spectroscopy (XANES) was collected simultaneously in both the transmission and fluorescence mode on powder samples on beam line X-19A at the Brookhaven National Synchrotron Light Source.

Samples for electron microscopy were prepared by dispersing the powder in ethanol and depositing it on a holey carbon grid. Selected area electron diffraction (SAED) patterns were obtained on a Philips CM20 transmission electron microscope (TEM). High resolution transmission electron microscopy (HRTEM) was obtained with a Tecnai G2 transmission electron microscope. The composition of the samples was determined with energy dispersive X-ray (EDX) analysis performed with a JEOL JSM55510 scanning electron microscope (SEM) on 50 crystallites for each sample, and with the Philips CM20 TEM on each crystallite studied for electron diffraction; both instruments are equipped with the Oxford INCA system. Derivation of possible tilt systems according to the type of extra reflections observed relative to the perovskite subcell were carried out based on the article of [29].

3. Results

3.1. Crystal structure

EDX analysis of the powders shows a composition of $Sr_xFe_xReO_{12}$ ($x=0.0, 1.0, 2.0$) characteristic of a perovskite-type structure. Within the resolution of XRD there are no observable impurities or superstructure peaks characteristic of an ordering between Fe and Re cations over two independent B sites. The crystal structure refinement was performed from high-resolution PND data collected at RT and 14 K. In a first trial, the crystal structure was refined in the cubic model $Pm-3m$ (No. 221), as it was previously reported for $Sr_xFe_xReO_{12}$ ($x=0.0$). The XRD could be perfectly refined with this cubic space group. This model corresponds to a simple perovskite ($ABO_3$) with one single B position for both Fe and Re cations and no distortions of the structure. However, refinement of the PND structure of $Sr_xFe_xReO_{12}$ in $Pm-3m$, could not index some observed peaks, and the crystal symmetry was lowered to the tetragonal $I4/mcm$ space group (No. 140). The perovskites with this space group belong to a subgroup of the aristotype perovskite space group $Pm-3m$, and may be obtained via the irreducible representations $R^1_2$ for out-of-phase octahedral tilting [31]: along the [001] direction there is an anti-phase cooperative octahedral tilting distortion that may be described as $\delta \phi_{c}^{+} \phi_{c}^{-}$ with the Glazer notation [32]. There are other related perovskites with this space group including $Sr(Mn_{1/2}Ru_{1/2})O_3$ and $Sr(Fe_{12}Nb_{12})O_3$ [33,34]. This model corresponds to a simple perovskite with only one B site for the Fe and Re cations and two nonequivalent oxygen atoms ($O_1$ and $O_2$). Figure 1 illustrates how the cubic model for $x=0.0$ (Fig. 1a) is unable to
account for all the Bragg reflections, whereas the tetragonal space group \( I4/mcm \) (Fig. 1b) is consistent with all the peak intensities of the PND. Electron diffraction (ED) patterns for \( x = 0.0 \) and 1.0 (Fig. 2a, indexed in the parent perovskite cell) indeed show the typical extra reflections \( \{00o\}_p \) (o-odd, subscript p-indexed in perovskite subcell) corresponding to anti-phase tilting in some, but not all of the \( \langle 110 \rangle \) zones. There are no extra reflections that would point to in-phase tilts. This is in agreement with \( a^0a^0c^- \) tilting (note that it is also in agreement with \( a^0b^-b^- \), \( a^-a^-a^- \) and \( a^-b^-b^- \), which were, however, ruled out by PND). This model gives a reasonable fit of PND for \( x = 0.0 \) and 1.0 compounds. However, for \( x = 2.0 \) the splitting of some reflections made it necessary to consider further lowering of the crystal symmetry with respect to the tetragonal one. The structure was successfully refined in the orthorhombic \( Pbnm \) space group, which contains three nonequivalent oxygen atoms (O1, O2 and O3), all in general \((x, y, z)\) positions. In this case, there is an anti-phase octahedral tilting distortion along the \( ab \) plane and an in-phase octahedral tilting distortion along \( c \), described as \( a^-a^-c^+ \) by the Glazer notation. Fig. 1c and d show the splitting of some of the reflections in \( x = 2.0 \), which can only be explained with an orthorhombic symmetry (Fig. 1d) and not using a tetragonal one (Fig. 1c). Electron diffraction patterns of \( x = 2.0 \) (Fig. 2b) show extra reflections typical for antiphase \( \{00o\}_p \) on \([011]^p\) as well as extra reflections typical for in-phase tilting \( \{00o\}_p \) on \([001]^p\). Twinning occurs, impeding the independent observation of the zone \([100]^p\) without overlapping of \([001]^p\) and also of \([110]^p\) without overlap with \([011]^p\). Confirmation of this twinning is given by the HRTEM image in Fig. 3, which shows the domains of \([100]^p\) and \([001]^p\) next to each other in one crystallite. The HRTEM also allows separating the reciprocal lattice images of both domains by Fourier transform. On the ED patterns of \([100]^p\) and \([001]^p\) in Fig. 2b, the black arrow therefore points to an extra reflection of the type \( \{00o\}_p \) present in the \( [100]^p \) zone, the white ones to an extra reflection of the type \( \{00e\}_p \) present in the \( [001]^p \) zone, in a \( 90^\circ \) twin for the horizontal and vertical white arrow. The \( \{00o\}_p \) reflections are present, because of the combined presence of in-phase and anti-phase tilting. On the \([110]^p\) and \([011]^p\) ED pattern, the white arrow points to a \( \{00e\}_p \) reflection present in \([110]^p\) while the black one points to a \( \{00o\}_p \) reflection present in \([011]^p\). As in the ED pattern below it. The observed reflections agree only with the tilt system \( a^-a^-c^+ \) and space group \( Pbnm \), as was also suggested from PND. This symmetry and space group are adopted by other well-known perovskites including \( La_{1-x}Sr_xFeO_3 \), \( La_{1-x}Sr_xMnO_3 \) and \( Ca(Fe_{1/2}Sb_{1/2})O_3 \) with small tolerance factors \([35–37]\). Fig. 4 illustrates the quality of the agreement between the full observed and calculated PND profiles at RT and 14 K for \( x = 0.0, 1.0 \) \((I4/mcm\) space group), and \( 2.0 \) \((Pbnm\) space group). The oxygen content has also been refined with the PND data and a full oxygen stoichiometry has been determined. The structural parameters at RT and 14 K are listed in Tables 1 and 2, respectively. Table 3 contains the main interatomic distances and angles across the series.

The reduction of symmetry when the La content in the structure is large \((x=2.0)\) is understood as a consequence of the

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**Fig. 2.** (a) Electron diffraction patterns of \( Sr_{4-x}La_xFe_3ReO_{12} \) \((x = 1.0)\), indexed in the parent perovskite cell. (b) Electron diffraction patterns of \( Sr_{4-x}La_xFe_3ReO_{12} \) \((x = 2.0)\) indexed in the parent perovskite cell. Explanations of the arrows are given in the main text.

**Fig. 3.** High resolution transmission electron microscopy image of \( Sr_{4-x}La_xFe_3ReO_{12} \) \((x = 2.0)\), showing twin domains. Fourier transforms are given of the areas indicated by the circles.
The Bragg positions correspond to the crystallographic and magnetic reflections.

Table 1
Positional, thermal parameters and agreement factors for Sr4–xLaxFe3ReO12 (x=0.0, 1.0, 2.0) after the Rietveld refinement of PND data collected at RT.

<table>
<thead>
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<th>x</th>
<th>0.0</th>
<th>1.0</th>
<th>2.0</th>
</tr>
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<tr>
<td>(a/\text{Å})</td>
<td>5.56907 (16)</td>
<td>5.56096 (19)</td>
<td>5.57416 (27)</td>
</tr>
<tr>
<td>(b/\text{Å})</td>
<td>5.56907 (16)</td>
<td>5.56096 (19)</td>
<td>5.5713 (25)</td>
</tr>
<tr>
<td>(c/\text{Å})</td>
<td>7.8661 (4)</td>
<td>7.8762 (5)</td>
<td>7.86017 (4)</td>
</tr>
<tr>
<td>(V/\text{Å}^3)</td>
<td>243.963 (17)</td>
<td>243.565 (19)</td>
<td>243.48 (2)</td>
</tr>
<tr>
<td>Sr/La</td>
<td>0.2672 (5)</td>
<td>0.27899 (45)</td>
<td>(\ldots)</td>
</tr>
<tr>
<td>Fe/Re</td>
<td>0.729 (28)</td>
<td>0.629 (29)</td>
<td>0.418 (23)</td>
</tr>
<tr>
<td>Mag. mom./(\mu_B)</td>
<td>2.46 (5)</td>
<td>2.89 (4)</td>
<td>0.0163 (6)</td>
</tr>
<tr>
<td>O1</td>
<td>1.56 (11)</td>
<td>1.07 (11)</td>
<td>0.82 (6)</td>
</tr>
<tr>
<td>(\chi^2)</td>
<td>1.36 (3)</td>
<td>1.41 (3)</td>
<td>0.82 (6)</td>
</tr>
<tr>
<td>(\theta)</td>
<td>0.0377 (15)</td>
<td>0.0121 (12)</td>
<td>0.0307 (3)</td>
</tr>
<tr>
<td>(\lambda/\text{Å})</td>
<td>2.04 (3)</td>
<td>2.04 (3)</td>
<td>0.80 (4)</td>
</tr>
<tr>
<td>(\varsigma)</td>
<td>1.36 (3)</td>
<td>1.41 (3)</td>
<td>0.82 (6)</td>
</tr>
</tbody>
</table>

Table 2
Positional, thermal parameters and agreement factors for Sr4–xLa5Fe3ReO12 (x=0.0, 1.0, 2.0) after the Rietveld refinement of PND data collected at 14 K.

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<tr>
<td>(a/\text{Å})</td>
<td>5.55142 (11)</td>
<td>5.54898 (13)</td>
<td>5.56440 (21)</td>
</tr>
<tr>
<td>(b/\text{Å})</td>
<td>5.55142 (11)</td>
<td>5.54898 (13)</td>
<td>5.55033 (20)</td>
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<tr>
<td>(c/\text{Å})</td>
<td>7.8670 (3)</td>
<td>7.8630 (4)</td>
<td>7.8472 (3)</td>
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<tr>
<td>(V/\text{Å}^3)</td>
<td>242.448 (11)</td>
<td>242.112 (14)</td>
<td>242.354 (16)</td>
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<tr>
<td>Sr/La</td>
<td>0.93 (3)</td>
<td>1.00 (3)</td>
<td>(\ldots)</td>
</tr>
<tr>
<td>Fe/Re</td>
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<td>0.458 (22)</td>
<td>0.246 (16)</td>
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<td>Mag. mom./(\mu_B)</td>
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<tr>
<td>O1</td>
<td>1.03 (31)</td>
<td>1.01 (31)</td>
<td>0.82 (6)</td>
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<td>(\chi^2)</td>
<td>0.729 (28)</td>
<td>0.629 (29)</td>
<td>0.418 (23)</td>
</tr>
<tr>
<td>(\theta)</td>
<td>0.0377 (15)</td>
<td>0.0121 (12)</td>
<td>0.0307 (3)</td>
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<tr>
<td>(\lambda/\text{Å})</td>
<td>2.04 (3)</td>
<td>2.04 (3)</td>
<td>0.80 (4)</td>
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</table>

Reliability factors
Pattern 1
\(\chi^2\) | 3.43 | 3.58 | 2.64 |
\(\theta\) | 3.02 | 2.78 | 2.65 |
\(R_p\) | 2.82 | 2.47 | 2.40 |
\(R_f\) | 1.52 | 1.67 | 1.48 |
\(R_{max}\) | 3.41 | 4.67 | 2.07 |
Pattern 2
\(\chi^2\) | 3.62 | 3.76 | 3.25 |
\(\theta\) | 5.04 | 4.92 | 4.90 |
\(R_p\) | 5.34 | 5.29 | 5.01 |
\(R_f\) | 2.80 | 2.73 | 2.78 |
\(R_{max}\) | 1.95 | 5.27 | 12.9 |

The decrease of the tolerance factor, \(t\), of the ABO3 perovskite, defined as \(t = \frac{r_A + r_B}{\sqrt{r_A^2 + r_B^2}}\) [38], where \(r_A\), \(r_B\), and \(r_O\) are the ionic radii of A, B, and O. The tolerance factor decreases due to the smaller effective ionic radius of \(\text{Sr}^{2+}\) (\(r_s = 1.36\ \text{Å}\)) ions compared to \(\text{La}^{3+}\) (\(r_L = 1.44\ \text{Å}\)), and the \(\sqrt{r_A^2 + r_B^2}\) factor increases due to the electron injection over this sublattice, since some \(\text{Re}^{6+}\) (\(r_{\text{Re}^6} = 0.53\ \text{Å}\)) are reduced to \(\text{Re}^{5+}\). The observed decrease in symmetry from tetragonal-to-orthorhombic space group is mainly due to the subtle tilting of the BO6 octahedra, involving small shifts of the oxygen positions, which can be well detected by neutron diffraction. Fig. 5a plots the evolution of lattice parameters with La-doping. The variation of unit-cell parameters with Sr/La–O distances. In the case of Sr2La2–Fe3ReO12, the highly distorted polyhedron makes it necessary to consider the effective coordination of these cations as eightfold, only considering the bond-lengths below 2.82 Å. Fig. 5b shows the evolution of the \(\langle\text{Sr}^2\rangle\) and \(\langle\text{Fe}/\text{Re}\rangle\) distances. The \(\langle\text{Sr}^2\rangle\) decreases with increasing La content as do the cell parameters, as expected, due to the smaller effective size of La3+ compared to Sr2+. However, while \(\langle\text{Sr}^2\rangle\) decreases, the \(\langle\text{Fe}/\text{Re}\rangle\) increases; this expansion of the B-O distances is attributed to an injection of electrons into the B sublattice; when the A sublattice changes from...
Table 3
The space group Pbnm is only for x = 2.0 (RT and 14 K) NOT for x = 1.0 at 14 K.

<table>
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<th></th>
<th>SrO₆</th>
<th>Sr–O₁ (x 4)</th>
<th>Sr–O₂ (x 4)</th>
<th>Fe/Re–O</th>
<th>(Fe/Re)–O₂–(Fe/Re)</th>
<th>Sr–O₁–(Fe/Re)</th>
<th>(Fe/Re)O₆</th>
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</table>

1Sr⁴⁺ in SrₓFe₃ReO₁₂ to Sr₂La₂Fe₃ReO₁₂, the cations in the B sublattice are forced to reduce. The reduction of the cations over the B position would lead to the expansion of the octahedra and thus to the enlargement of the mean B–O distances. To determine the evolution of Fe and Re oxidation states we carried out XANES. Fe/Re–O–Fe/Re bond angles tend to become smaller with increasing La³⁺ content (Fig. 5d) due to the tilting of the Fe/ReO₆ octahedra. The transition from tetragonal-to-orthorhombic structure gives rise to an angle closer to 170° defined in the ab plane. Typically, in the perovskites the reduction of the super exchange B–O–B angles leads to less perfect orbital overlapping, a narrowing of the π° bands and a weakening of the magnetic interactions. However, the effect of the distortion found in this series is unexpected—the magnetic ordering temperature (T_N) increases with increasing La content and octahedral BO₆ distortion. Below we will attempt to explain the observed behaviour.

3.2. X-ray absorption near edge spectroscopy (XANES)

XANES was used to further characterize the formal oxidation state of the transition metal ions. The L₂,₃ edges of transition metals (T) manifest intense “white line” (WL) features due to dipole allowed transitions into unoccupied final d states [40]. The octahedral O-ligand coordination around the T sites in perovskite based compounds induces a crystal electric (or ligand) field, CEF, splitting of the d states, into a lower energy, 6X degenerate, eg multiplets. This CEF splitting can be clearly observed at the T(5d–L₃) edges as split WL in A (t₂g related) and B (e_g related) features (Fig. 6a). The A-feature peak height is comparable, or greater than that of the B-feature, which is consistent with a –d⁰ state, as illustrated in Fig. 6a for Ta⁵⁺ in TaNd₂₋ₓCeₓSr₂Cu₂O₁₀₋₀.₅ (x = 0.6) and W⁶⁺ in Sr₃W₈O₂₃ standards [41,42]. On the other hand, in the Re–L₃ spectrum of –Re⁶⁺(d⁵) in Sr₂MnReO₆, the A-feature is an unresolved low-intensity shoulder of the B-feature. This A-feature intensity reduction is consistent with the loss of a t₂g hole state.

In Fig. 6b, the A-feature in Ba₂MnReO₆ (~Re⁶⁺(d⁵)) is an unresolved lower intensity shoulder on the B-feature [42]. The centrum of the Ba₂MnReO₆ spectrum is chemically shifted downward in energy, relative to the other spectra. The SrFe₃ReO₆ spectrum, by contrast, has a large A-feature intensity placing Re in the d⁰ configuration similar to Ta⁵⁺ and W⁶⁺. Moreover, the centrum of WL of SrFe₃ReO₆ is also chemically shifted to higher energy relative to ~Re⁶⁺(d⁵) in Ba₂MnReO₆. Thus both the A–B
spectral intensity ratio and the chemical shift are consistent with a $\sim \text{Re}^{7+}(d^0)$ state in Sr$_4$Fe$_3$ReO$_6$. It should be noted that the A–B CEF splitting in Sr$_4$Fe$_3$ReO$_{12}$ is $\sim 3.3$ eV.

The substitution of Sr$^{2+}$ by La$^{3+}$ in Sr$_2$La$_2$Fe$_3$ReO$_{12}$ greatly reduces the A-feature intensity, along with the A–B CEF splitting (Fig. 6b). Sr$_2$La$_2$Fe$_3$ReO$_{12}$ is clearly chemically shifted to lower energy relative to Sr$_4$Fe$_3$ReO$_{12}$. This is particularly apparent comparing the high energy side of the WL features of both compounds. Thus, there is clear evidence for a decrease of Re valence state (d-electron count increase) in response to the La$^{3+}$-substitution-induced electron addition. Comparison to the chemical shift of $\sim \text{Re}^{4+}(d^1)$ in Ba$_2$MnReO$_6$ suggests that the La substituted material is however, not fully reduced to the $\sim \text{Re}^{5+}$ state.

Fig. 6a shows the comparison of the L$_3$ edges of 5d$^0$ and 5d$^1$ Ta/W/Re compounds. The zero of energy has been assigned at the A-feature in order to compare the spectra. (b) Re–L$_3$ edges of Sr$_4$Fe$_3$ReO$_{12}$ and Sr$_2$La$_2$Fe$_3$ReO$_{12}$. The Re$^{6+}$ standard Ba$_2$MnReO$_6$ spectrum is displayed twice: superimposed with the other spectra to illustrate the chemical shift and displaced downward to make A–B features more visible.

Fig. 7a shows the Fe–K main edge spectra for the following corner-sharing octahedrally coordinated Fe standards: Fe$^{2+}$, LiFePO$_4$; Fe$^{3+}$, La$_2$VFeO$_6$; and $\sim \text{Fe}^{4+}$, SrFeO$_{1-x}$ [43–46]. The upward chemical shift of the edge and main edge peak, with increasing valence, is clear from the standard spectra. Moreover, the main edge peak degrades between Fe$^{3+}$ and Fe$^{4+}$ standards so much that $\sim \text{Fe}^{4+}$ standard peak is almost imperceptible. This is presumably due to strong configuration mixing/covalency causing broadened, split 4p-feature in the Fe$^{4+}$ standard. Indeed the clearest signature of the pulling of the formal Fe valence above 3+, toward 4+, is the degradation of the main peak at the edge.

The main edge peak height and chemical shift of the Fe–K edge of Sr$_4$Fe$_3$ReO$_6$ (Fig. 7a) are intermediate between Fe$^{3+}$ and $\sim \text{Fe}^{4+}$.
indicating a mixed Fe valence closer to $3^+$. The spectrum of Sr$_2$La$_2$Fe$_3$ReO$_{12}$ is also intermediate between Fe $3^+$ and $4^+$, but it clearly shows a shift toward $3^+$ relative to Sr$_4$Fe$_3$ReO$_{12}$. Thus the Fe–K main edge results clearly evidence a reduction in the Fe-site valence state in response to La for Sr substitution in analogy to the Re valence response. In order to reinforce the Fe–K main edge observations the pre-edges are considered. Since the main edge peak features are related to dipole transitions into final p states; the pre-edge features are related to transitions into final 3d-states via quadrupole and p/d-hybridization, dipole matrix elements. The attractive final state 3d–electron/core-hole interaction shifts these transitions down in energy into the pre-edge region. As it is shown in Fig. 7b, the pre-edge spectra have been displaced vertically for clarity with the higher Fe valence compound being displaced downward. The pre-edges of the sequence of Fe$^{2+}$, Fe$^{3+}$, and $\sim$Fe$^{4+}$ standards manifest, with increasing valence: an overall shift in spectral weight toward higher energy, an increase (in most cases) in spectral intensity, and a change in spectral shape. It should be noted that the integrated spectral weight of the LiFePO$_4$ appears relatively enhanced because of the prominent A1 feature. The non-centrosymmetric distortion of the FeO$_6$ octahedra in this compound could introduce p/d mixing and enhance dipole transitions to the pre-edge features [43]. The Sr$_4$Fe$_3$ReO$_{12}$ pre-edge shape, integrated area, and chemical shift all

Fig. 7. (a) Sr$_4$Fe$_3$ReO$_{12}$ and Sr$_2$La$_2$Fe$_3$ReO$_{12}$ Fe–K main edges with several corner shared octahedral standards. (b) Sr$_4$Fe$_3$ReO$_{12}$ and Sr$_2$La$_2$Fe$_3$ReO$_{12}$ Fe–K pre-edges with the standards.
provide support for some admixture of Fe$^{4+}$ into its configuration. Moreover, the same spectral signatures again support the decreased Fe$^{4+}$ admixture in the La for Sr substituted compound. Thus the Fe–K pre-edge results are in qualitative agreement with those of the main edge discussed above.

Some consideration of the overall charge state balance in Sr$_4$Fe$_2$ReO$_6$ is warranted at this juncture. Given the $\sim$Re$^{7+}$(d$^0$) state and the stoichiometry of the compound, a Fe valence of 3+ would be expected. The XAS results, however, indicate that the Fe valence is in fact somewhat elevated above 3+. The notion of a pure integral valence state for the transition metals in such solid state compounds is a first step simplified approximation. Cluster model interpretations of 3d row compounds invariably involve superpositions of different d-occupancy configurations [46,47]. In the case of a 5d-row compound (e.g., like Re) the spatial extent and band width of the 5d-orbitals further reduces the validity of the integral valence approximation. One possibility for the charge balance in this compound is that the effective Re configuration is Re$^{7+}$=(d$^0$) not exactly Re$^{6+}$, and this would account for a Fe$^{3+}$$\sim$$3z/3$ state. The notion of an internal Fe$^{3+}$ admixture is further supported by the Fe$^{3+}$-$\gamma$ admixture in the La for Sr substituted compound.

Also the chemical valences in Sr$_2$La$_2$Fe$_3$ReO$_{12}$ have to be rationalized; XAS indicates Fe$^{3+}$ and Re$^{6+}$ or even somewhat higher oxidation states. As it has been observed by EDX analysis of the compounds doped with La are not completely stoichiometric and present some Re vacancies (e.g., Sr$_{1.8(2)}$La$_{2.18(8)}$Fe$_{3.2(2)}$Re$_{0.69(6)}$O$_{12}$ instead of Sr$_2$La$_2$Fe$_3$ReO$_{12}$). These vacancies are originated by the partial volatilization of Re at the relatively high annealing temperature, due to the high volatility of ReO$_3$. This possibility was already proposed for similar perovskites, e.g., Sr$_2$FeMoO$_6$, annealed at 1200 °C, with partial volatilization of Mo cations [48,49]. If the Re content is reduced to Re$_{1-y}$ one would observe a formal Fe$^{3+}$+$y$(3$z$) even if a full Re$^{7+}$=(d$^0$) is assumed. We believe that the above noted hybridization induced 5$d^0$ effect is probably present, but that a Re-vacancy population contribution is also present. For Sr$_{1.8(2)}$La$_{2.18(8)}$Fe$_{3.2(2)}$Re$_{0.69(6)}$O$_{12}$ and assuming Re$^{6+}$, the formal Fe valence could increase to 3.24+. As is shown later, the room temperature M"ossbauer effect isomer shift, IS, values (averaged over all sites) are in the 0.34–0.35 mm/s range. From previous work by our group, this value at least should be reconcilable with a Fe valence in the 3.2–3.3 range [45,46].

3.3. Magnetic measurements

The dc susceptibility vs. temperature data of Sr$_{4-x}$La$_x$Fe$_3$ReO$_{12}$ ($x=0.0, 1.0, 2.0$) are displayed in Fig. 8. The onset of an antiferromagnetic-like (AFM) ordering is observed at high temperatures of $T_N \sim 600 \text{ K}$ for $x=0.0$ and $T_N \sim 750 \text{ K}$ for $x=2.0$. Surprisingly the magnetic ordering temperatures are much higher than RT. The high $T_N$ of Sr$_2$La$_2$Fe$_3$ReO$_{12}$ is a significant result since there are not many compounds with such high magnetic transitions. The temperature dependence of the susceptibility has been measured under zero field cooled (ZFC) and field cooled (FC) conditions. For temperatures below 200 K, we observe thermomagnetic irreversibility between the ZFC and FC curves, suggesting a very frustrated magnetic state. This divergence has been reported before in analogous perovskite-type compounds and has been attributed to the formation of spin-glass-like compound states [50]. The spin-glass behaviour is believed to arise due to the competition between different magnetic interactions, or due to geometric frustration that intrinsically involves a high degree of magnetic frustration. The isothermal magnetization curves are displayed in the insets of Fig. 8. All the compounds show an antiferromagnetic response with a small hysteresis, characteristic of a weak ferromagnetic (FM) component, which could be also ascribed to the presence of some canting of the spins, produced due to magnetic frustrations inside the oxides.

![Fig. 8](image-url) Thermal evolution of the field cooling (FC) and zero field cooling (ZFC) dc susceptibility of (a) Sr$_4$Fe$_2$ReO$_{12}$, and (b) Sr$_2$La$_2$Fe$_3$ReO$_{12}$. Upper insets: Magnetization vs. magnetic field isotherms for (a) Sr$_4$Fe$_2$ReO$_{12}$ and (b) Sr$_2$La$_2$Fe$_3$ReO$_{12}$ at 5 and 300 K.

![Fig. 9](image-url) Mössbauer spectrum of Sr$_{4-x}$La$_x$Fe$_3$ReO$_{12}$ ($x=0.0, 1.0, 2.0$) taken at RT and around 90 K.
The Mössbauer parameters of Sr$_{4-x}$La$_x$Fe$_3$ReO$_{12}$ series at RT and 90 K.

<table>
<thead>
<tr>
<th>$x$</th>
<th>T (K)</th>
<th>IN (%)</th>
<th>IS (mm/s)</th>
<th>EQ (mm/s)</th>
<th>HF (kOe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>RT</td>
<td>34</td>
<td>0.40</td>
<td>−0.03</td>
<td>391 dis.</td>
</tr>
<tr>
<td></td>
<td>33</td>
<td>0.33</td>
<td>−0.07</td>
<td>242 dis.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>33</td>
<td>0.32</td>
<td>0.4 dis.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>45</td>
<td>0.45</td>
<td>−0.02</td>
<td>507</td>
<td></td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>0.55</td>
<td>0.08</td>
<td>464</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.42</td>
<td>0.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>RT</td>
<td>48</td>
<td>0.36</td>
<td>0</td>
<td>394 dis.</td>
</tr>
<tr>
<td></td>
<td>34</td>
<td>0.35</td>
<td>0</td>
<td>350 dis.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>0.36</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>100</td>
<td>0.45</td>
<td>−0.02</td>
<td>534 dis.</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>RT</td>
<td>100</td>
<td>0.34</td>
<td>−0.02</td>
<td>558 dis.</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>0.46</td>
<td>−0.03(1)</td>
<td>541</td>
<td></td>
</tr>
</tbody>
</table>

The errors on IN is 5%, on IS 0.03 mm/s, on EQ is 0.02 mm/s and HF in case of distributions is the value at maximum probability and the error is 10 kOe.

3.4. Mössbauer spectroscopy

The Mössbauer spectrum of $x$=0.0, 1.0 and 2.0 samples, taken at RT are shown in Fig. 9. At RT all the samples are below the magnetic ordering temperature with a poorly resolved magnetic Zeeman sextet for $x$=0.0 and 1.0 and a well resolved magnetic Zeeman sextet for $x$=2.0. The better resolution of the sextet for higher $x$, indicates that the magnetic ordering temperature increases when La content increases. For $x$=0.0, although at RT it is possible to see the sextet, it is not well defined, which indicates either dynamic spin fluctuations, or the presence of inequivalent Fe sites.

For Sr$_2$La$_2$Fe$_3$ReO$_{12}$ the spectrum at 94 K (Fig. 9) clearly shows that all Fe ions are equivalent; this suggests that the RT “smeared” spectra result from spin fluctuations, frequently observed in magnetically ordered materials [51]. The parameters of the fitted Mössbauer spectra in terms of inequivalent sites, are summarized in Table 4. Both, the values of the isomer shifts, and the hyperfine magnetic fields close to saturation (at ~90 K) show that in all three samples the iron is very close to a trivalent state.

3.5. Magnetic structures

The PND data show magnetic contribution in some low-angle reflections at both RT and 14 K (Fig. 10a and b). These peaks could be ascribed to the establishment of a long range magnetic ordering between Fe/Re spins on the B site. The Fe and Re cations could not be distinguished since they are disordered over the same structural position. The magnetic intensities have been refined in a model that considers an AFM coupling of Fe$^{3+}$ spins over the B sites along the [100] direction. A schematic view of the magnetic structure of Sr$_2$Fe$_3$ReO$_{12}$ is illustrated in Fig. 10c, highlighting only the Fe/Re cations. The three compounds, $x$=0.0, 1.0 and 2.0, present the same type of magnetic structure, even for $x$=2.0, which has a different crystallographic structure.

The refinement of the low-temperature (14 K) magnetic structures allowed us to determine the ordered magnetic moments on the magnetic sites. The magnetic moments are listed in Table 1 (at RT) and Table 2 (at 14 K). A net magnetic moment of 3.12(4) $\mu_B$ is obtained for Sr$_2$La$_2$Fe$_3$ReO$_{12}$ at 14 K compared to 2.63(5) $\mu_B$ at RT. In the other samples the magnetic moments are smaller but they are still significant at RT, 2.21(5) $\mu_B$ for Sr$_3$LaFe$_3$ReO$_{12}$ and 1.73(5) $\mu_B$ for Sr$_3$LaFe$_3$ReO$_{12}$ indicating the higher magnetic character of all the samples at RT. The enhancement of the net magnetic moments with increasing La content indicates the stronger magnetic character of the substituted compounds. For all the samples the net magnetic moment decreases with increasing temperature as expected. Since all the compounds have the magnetic transition above room temperature, high temperature neutron diffraction would be necessary to confirm the magnetic transitions.

One would be tempted to ascribe the onset of AFM ordering, at high temperatures (~750 K) to the presence of Fe-containing impurities. FeO$_4$ (magnetite) is the most probable impurity in this system (involving a thermal treatment in air) which exhibits a very distinct $T_C$ of about 850 K [52]. $\alpha$-Fe$_2$O$_3$ (hematite) is a canted antiferromagnet with a still higher $T_N$ of 950 K. $\gamma$-Fe$_2$O$_3$ (hemimelite) has a $T_C$=920 K [53], and converts to hematite when heated in air above 1023 K. However, Sr$_3$LaFe$_3$ReO$_{12}$ is the only product with a ~5% of impurity, of a different chemical composition, as observed by EDX. PND and Mössbauer confirm that the magnetism is arising for the compounds and not from impurity phases. Thus, we conclude that the magnetic response of these compounds is intrinsic to the perovskites. The high ordering magnetic temperatures could be well understood taking into account that LaFeO$_3$ is an antiferromagnetic compound with a $T_N$ around 750 K [54]. We have very carefully determined the absence of LaFeO$_3$ as an impurity. Also there is another related
compound, SrFeO$_{2.5}$, with very similar $T_N \sim 700$ K [55], however, its crystal structure is very different from our materials with a brownmillerite structure, where some octahedra switch into tetrahedra. The compound of the Sr–Fe–O system most similar to our materials is SrFeO$_3$, with a very different magnetic ordering temperature, $\sim 130$ K [56].

We have a series of compounds analogous to La$_{1-x}$Sr$_x$FeO$_3$, but in La$_1$–Sr$_x$FeO$_3$ series, the magnetic order is weakened by substitution of trivalent La by divalent Sr, decreasing the values of the magnetic ordering temperatures even below RT [54]. In this work we introduce one atom of Re in the B sublattice seems to reinforce the magnetic properties increasing the value of $T_N$ to very high values for highly doped samples.

The observed magnetic results are similar to perovskites of formula A$_3$B$_x$B'O$_{3-x}$, where the content of magnetic B cations with high net magnetic moment was larger than those existing in LnFeO$_3$ ferrites (above, the Fe–O–Fe super-exchange AFM interactions are comparable to those existing in LnFeO$_3$ ferrites [22–24]; in all these cases there is a significant magnetic contribution to the scattering in the low-temperature PND patterns, which arises from the long-range AFM arrangement of Fe$^{3+}$ spins, as in our compounds. In the A$_3$B$_x$B'O$_{3-x}$ compounds above, the Fe–O–Fe super-exchange AFM interactions are comparable to those existing in LnFeO$_3$ ferrites (in rare earths), exhibiting an AFM coupling between near-neighbour Fe–O–Fe cations. In Sr$_x$Fe$_{4-x}$ReO$_{12}$, as in RFeO$_3$, the existence of only one B site for Fe cations favours the long range magnetic ordering involving the full set of Fe$^{3+}$ ions in the crystal structure, thus implying a virtual complete magnetic coherence across the crystal [22]. In case of the substitution of Sr by La$^{3+}$, some Fe and Re cations reduce their oxidation states creating mixed valence states, which reinforce the magnetic interactions. The magnetic interactions in Sr$_x$Fe$_{4-x}$ReO$_{12}$ occur only along the Fe–O–Fe paths while the La containing samples allow the creation of new Fe–O–Re$^{6+}$–O–Fe magnetically active paths that appear to reinforce the magnetism of the system and increases the magnetic transition temperature. We have successfully confirmed an enhancement of the magnetic properties of a perovskite with electron injection in the magnetic B sublattice, even though a distortion of the symmetry is produced.

4. Conclusions

A series of perovskites Sr$_{1-x}$La$_x$Fe$_{4-x}$ReO$_{12}$ ($x=0.0, 1.0, 2.0$) has been prepared and characterized, and their magnetic properties has been investigated. Their crystal structures are simple perovskite types with tetragonal space group (I4/mcm) for $x=0.0$ and 1.0 and orthorhombic (Pbnm) for $x=2.0$. The formal oxidation states of Fe$^{3+}$, Re$^{7+}$ in Sr$_x$Fe$_{4-x}$ReO$_{12}$ decrease with La substitution. This change in the oxidation states has a critical effect on the magnetic properties with an increase of $T_N$ as the quantity of La increases. All the samples present an AFM coupling of the spins over the B sites along the [100] direction as determined by analysis of the powder neutron diffraction data. The magnetic interactions in Sr$_x$Fe$_{4-x}$ReO$_{12}$ occur only along Fe–O–Fe paths while La containing samples have new Fe–O–Re$^{6+}$–O–Fe magnetic paths that appear to reinforce the magnetism of the system with increasing magnetic transition temperature. Thus, we have successfully increased the magnetic ordering temperature in these perovskites by an effective electron injection in the magnetic B sublattice.

Acknowledgments

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