Manganese-mediated ferromagnetism in $\text{La}_2\text{Fe}_{1-x}\text{Mn}_{2x}\text{Cr}_{1-x}\text{O}_6$ perovskite oxides

R M TIWARI^a, MRUDUL GADHVI^b, ABANTI NAG^a, N Y VASANTHACHARYA^a and J GOPALAKRISHNAN^{a,*}

^aSolid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012

^bDepartment of Physics, St. Xavier's College, Ahmedabad 380 009

e-mail: gopal@sscu.iisc.ernet.in

MS received 11 December 2009; revised 8 March 2010; accepted 9 March 2010

Abstract. We have investigated the structure and magnetic properties of the perovskite oxides of the formula $\text{La}_2\text{Fe}_{1-x}\text{Mn}_{2x}\text{Cr}_{1-x}\text{O}_6$ ($0 < x < 1.0$). For $0 < x \leq 0.5$, the members adopt the orthorhombic ($Pbnm$) structure, where the transition metal atoms are disordered at the $4b$ sites and the MO_6 ($M = \text{Fe}, \text{Mn}, \text{Cr}$) octahedra become increasingly distorted with increasing x . For $0.65 \leq x < 1.0$, the members adopt the rhombohedral ($R-3c$) structure that is similar to $\text{LaMnO}_{3+\delta}$ ($\delta \geq 0.1$) where the MO_6 octahedra are undistorted. While the magnetic properties of the latter series are largely similar to the parent $\text{LaMnO}_{3+\delta}$ arising from the double-exchange (DE) between mixed valent $\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$, the magnetic properties of the orthorhombic members show a distinct (albeit weak) ferromagnetism ($T_C \sim 200$ K) that seems to arise from a Mn^{III} -mediated superexchange (SE) between $\text{Fe}^{\text{III}}/\text{Cr}^{\text{III}}$ in the disordered perovskite structure containing Fe^{III} , Mn^{III} and Cr^{III} .

Keywords. $\text{La}(\text{Fe}, \text{Mn}, \text{Cr})\text{O}_3$; orthorhombic and rhombohedral perovskites; ferromagnetism; superexchange; double exchange.

1. Introduction

Among the ferromagnetic perovskite oxides of current interest,¹ $\text{La}_2\text{NiMnO}_6$ is an attractive material that exhibits ferromagnetism near room temperature ($T_C \sim 280$ K).² The magnetism of this oxide is regarded as a typical manifestation of the celebrated Goodenough–Kanamori (G–K) rule,³ where the superexchange (SE) interaction between $\text{Ni}^{\text{II}}(t_{2g}^6 e_g^2) - \text{O} - \text{Mn}^{\text{IV}}(t_{2g}^3 e_g^0)$ in the ordered double perovskite structure causes the ferromagnetism. Perovskite $\text{La}_2\text{FeCrO}_6$ would provide another illustration of ferromagnetic coupling of spins through $\text{Fe}^{\text{III}}(t_{2g}^3 e_g^2) - \text{O} - \text{Cr}^{\text{III}}(t_{2g}^3 e_g^0)$ superexchange according to G–K rule, but ceramic samples of this oxide display only an antiferromagnetic behaviour attributed to a disordered distribution of Fe^{III} and Cr^{III} in the perovskite structure.⁴ However, Ueda *et al*⁵ have achieved a ferromagnetic spin order ($T_C \sim 375$ K) in the superlattices consisting of alternate layers of LaCrO_3 and LaFeO_3 along $[111]$ direction, demonstrating that linear $\text{Fe}^{\text{III}} - \text{O} - \text{Cr}^{\text{III}}$ SE interaction

indeed occurs according to G–K rule. Jahn–Teller distorted high-spin Mn^{III} ($d^4: t_{2g}^3 e_g^1$) is known to couple $\text{Fe}^{\text{III}}/\text{Cr}^{\text{III}}$ ferro/ferrimagnetically in bulk ceramic materials^{6–9} as well as in artificial superlattices.¹⁰ The prediction of G–K rule for SE interactions among Cr^{III} , Mn^{III} and Fe^{III} in the perovskite lattice (table 1) are consistent with the experimental results. In addition, the possibility of double exchange (DE) has been invoked between Mn^{III} and Cr^{III} in $\text{LaMn}_{1-x}\text{Cr}_x\text{O}_3$ and between Mn^{III} and Fe^{III} in $\text{LaMn}_{1-x}\text{Fe}_x\text{O}_3$ perovskites^{11,12} (although this has not been supported for Mn^{III} and Cr^{III} by other investigations).^{8,13} Moreover, a disordered array of Mn^{III} as in

Table 1. Superexchange interactions among $\text{Cr}(\text{III})$, $\text{Mn}(\text{III})$ (hs), and $\text{Fe}(\text{III})$ (hs) in perovskite oxides*

Ion	$\text{Cr}(\text{III}): d^3$	$\text{Mn}(\text{III}): d^4$	$\text{Fe}(\text{III}): d^5$
$\text{Cr}(\text{III}): d^3$	AF	a	c
$\text{Mn}(\text{III}): d^4$	F/AF ^a	F/AF	b
$\text{Fe}(\text{III}): d^5$	F ^c	F/AF ^b	AF

a, b, c denote redundancies

*Based on the results from refs 3, 5, 6, 8, 9 and 10

*For correspondence

$\text{LaMn}_{1-x}\text{Ga}_x\text{O}_3$ and $\text{LaMn}_{1-x}\text{Sc}_x\text{O}_3$ perovskites where the orbital ordering of the parent LaMnO_3 is disrupted, gives rise to long range ferromagnetic order,^{14,15} indicating that isotropic $\text{Mn}^{\text{III}}\text{--O--Mn}^{\text{III}}$ SE interaction could be ferromagnetic.¹⁴

In view of the foregoing, we expected that a disordered array of Cr^{III} , Mn^{III} and Fe^{III} in perovskite lattice would give rise to a ferromagnetic order, unlike the case of disordered Fe^{III} and Cr^{III} in $\text{La}_2\text{FeCrO}_6$ perovskite. We explored the possibility in the solid solution series, $\text{La}_2\text{Fe}_{1-x}\text{Mn}_{2x}\text{Cr}_{1-x}\text{O}_6$, where octahedral-site Mn^{III} indeed mediates the SE interaction between Fe^{III} and Cr^{III} , resulting in a net ferromagnetism with T_C up to 200 K. The results of this investigation are presented in this paper.

2. Experimental

Formation of perovskite oxides for the compositions $\text{La}_2\text{Fe}_{1-x}\text{Mn}_{2x}\text{Cr}_{1-x}\text{O}_6$ for $x = 0.00, 0.10, 0.33, 0.50, 0.65, 0.75$ and 0.90 was explored by reacting stoichiometric mixtures of the starting materials [high purity Cr_2O_3 , $\text{MC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Fe}, \text{Mn}$) and La_2O_3 (pre-dried at 900°C)] at elevated temperatures ($900\text{--}1150^\circ\text{C}$) in air for varying duration. Single phase products were obtained by the reaction at 1150°C with repeated grinding and heating for 2–3 days.

The products were examined by powder X-ray diffraction (XRD) employing a Philips X'Pert Diffractometer (Ni filtered $\text{Cu K}\alpha$ radiation). Lattice parameters were obtained by least-squares refinement of powder XRD data by means of the program PROSZKI¹⁶ and XRD patterns were simulated by the program POWDERCELL.¹⁷ Oxygen stoichiometry of selected samples was determined by thermogravimetry (TG) under hydrogen reduction ($1\text{H}_2 : 3\text{Ar}$ gas mixture, 40 ml/min) on a Cahn TG-131 system, at a heating rate of 3°C/min .

For structure refinement, XRD data were collected on the Philips X'Pert Diffractometer ($\text{Cu K}\alpha$ radiation) in the 2θ range of $3\text{--}100^\circ$ with a step size of 0.02° and a step time of 9 s. Rietveld refinement of powder XRD data was carried out by means of program GSAS.¹⁸ The patterns were refined for the lattice parameters, scale factor, background (shifted Chebyshev background function), pseudo-Voigt profile function (U, V, W and X), atomic coordinates and isothermal temperature factors (U_{iso}).

DC magnetic susceptibility measurements were performed in the temperature range of $300\text{--}15\text{ K}$

employing a Lewis coil force magnetometer (George Associates, model 2000). High field (5 kOe) magnetic measurements were done under FC condition while the low field (100 Oe) magnetic measurements were done under both FC and ZFC conditions. Room temperature electrical resistivities of the sintered pellets were measured by a two-probe method.

3. Results and discussion

3.1 Structural characterization

Polycrystalline samples of $\text{La}_2\text{Fe}_{1-x}\text{Mn}_{2x}\text{Cr}_{1-x}\text{O}_6$ for various values of x ($0 < x \leq 0.9$), prepared by the conventional ceramic route in air showed formation of single-phase perovskite oxides, as revealed by powder XRD patterns (figure 1 and table 2). Rietveld refinement of powder XRD data showed that the phases adopt orthorhombic ($Pbnm$) perovskite structure for $0 \leq x \leq 0.5$. We show the refinement

Figure 1. Powder XRD patterns of $\text{La}_2\text{Fe}_{1-x}\text{Mn}_{2x}\text{Cr}_{1-x}\text{O}_6$, (a) $x = 0.1$, (b) $x = 0.33$, (c) $x = 0.5$, (d) $x = 0.75$ and (e) $x = 0.9$.

Table 2. Structural characterization of $\text{La}_2\text{Fe}_{1-x}\text{Mn}_{2x}\text{Cr}_{1-x}\text{O}_6$ perovskite oxides.

Nominal composition	x	Lattice parameters (Å) a, b, c	c/a	Bond lengths (Å) Fe/Mn/Cr–O	Distortion parameter (Δ) [†]	BVS Fe/Mn/Cr
$\text{La}_2\text{Fe}_{0.9}\text{Mn}_{0.2}\text{Cr}_{0.9}\text{O}_6$	0.1	5.5202(5) 5.5402(6) 7.8177(2)	1.416 O	$1.994(4) \times 2$ $1.992(2) \times 2$ $1.975(4) \times 2$	0.018	3.110
$\text{La}_2\text{Fe}_{0.66}\text{Mn}_{0.66}\text{Cr}_{0.66}\text{O}_6$	0.33	5.5050(1) 5.5368(1) 7.7972(2)	1.416 O	$1.991(2) \times 2$ $1.988(4) \times 2$ $1.963(4) \times 2$	0.040	3.202
$\text{La}_2\text{Fe}_{0.5}\text{Mn}_{1.0}\text{Cr}_{0.5}\text{O}_6^\#$	0.5	5.4932(2) 5.5258(2) 7.850(4)	1.429 O	$1.987(1) \times 2$ $1.976(2) \times 2$ $1.957(3) \times 2$	0.039	3.290
$\text{La}_2\text{Fe}_{0.25}\text{Mn}_{1.5}\text{Cr}_{0.25}\text{O}_6^\#$	0.75	$a = 5.5278(6)$ $c = 13.3432(1)$	$R\text{-}3c$	$1.967(2) \times 6$	0	3.390
$\text{La}_2\text{Fe}_{0.1}\text{Mn}_{1.8}\text{Cr}_{0.1}\text{O}_6^\#$	0.9	$a = 5.5255(4)$ $c = 13.3359(4)$	$R\text{-}3c$	$1.966(1) \times 6$	0	3.410
$\text{LaMnO}_{3.15}^*$	1.0	$a = 5.4759(1)$ $c = 13.222(1)$	$R\text{-}3c$	$1.948(1) \times 6$	0	3.612
LaMnO_3^*	1.0	5.5367(1) 5.7473(1) 7.6929(2)	1.389 O'	$2.178(1) \times 2$ $1.968(3) \times 2$ $1.907(1) \times 2$	3.310	3.130
$\text{La}_2\text{FeCrO}_6^*$	0	5.5314(5) 5.5556(7) 7.831(1)	1.415 O	$1.9937(1) \times 2$ $1.9934(3) \times 2$ $1.9890(3) \times 2$	0.001	3.052

*Data taken from refs 4, 19 and 21

$$^\dagger \Delta = \frac{1}{6} \sum_{i=1}^6 \left[\frac{d_i - \langle d \rangle}{\langle d \rangle} \right]^2 \times 10^3$$
, where d_i is individual bond length and $\langle d \rangle$ is the average bond length

 $^\#$ The apparent oxygen excess parameter (δ) in $\text{La}_2(\text{FeMnCr})_{2-x}\text{O}_{6+\delta}$ determined from TG studies are ~ 0.10 , ~ 0.20 and ~ 0.20 respectively for the $x = 0.50$, 0.75 and 0.90 samples
Figure 2. Rietveld refinement of the structure of $\text{La}_2\text{Fe}_{0.9}\text{Mn}_{0.2}\text{Cr}_{0.9}\text{O}_6$ ($Pbnm$) from powder XRD data. Observed ($\circ$), calculated ($—$) and difference profiles (bottom) are shown. The vertical bars indicate positions of the Bragg reflections.

results for $x = 0.1$, 0.33 and 0.5 in figures 2–4 and tables 3–5. The refinement revealed a rhombohedral ($R\text{-}3c$) structure for $x \geq 0.75$ members. The refinement results are shown in figures 5 and 6 and tables 6 and 7 for $x = 0.75$ and 0.9 , respectively. Also the refinement revealed a disordered distribution of iron, manganese and chromium at the octahedral sites in both the structures ($4b$ for $Pbnm$ and $6b$ for $R\text{-}3c$). We do see several weak reflections (prominent in figure 4) which are not accountable in the refinement, indicating the presence of minor impurity phase (also perovskite-like).

The orthorhombic structure of the $\text{La}_2\text{Fe}_{1-x}\text{Mn}_{2x}\text{Cr}_{1-x}\text{O}_6$ samples for $x \leq 0.5$ is similar to the parent $\text{La}_2\text{FeCrO}_6$, having $c/a > \sqrt{2}$; $a < b$ (O -orthorhombic structure). We do however find that with increasing x (Mn content), the MO_6 ($M = \text{Fe, Mn, Cr}$) octahedral distortion parameter (Δ) increases, consistent

Table 3. Atomic positions, occupancy and isotropic temperature factors for $\text{La}_2\text{Fe}_{0.9}\text{Mn}_{0.2}\text{Cr}_{0.9}\text{O}_6$.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}	Occupancy
La	4 <i>c</i>	−0.0030(7)	0.0228(1)	0.25	0.0184(3)	1
Fe/Mn/Cr	4 <i>b</i>	0.5	0	0	0.0148(6)	0.45/0.10/0.45
O1	4 <i>c</i>	0.0689(2)	0.4894(2)	0.25	0.025(4)	1
O2	8 <i>d</i>	0.7278(3)	0.2748(3)	0.0368(1)	0.0224(2)	1

Space group *Pbnm*: $a = 5.5202(5)$ Å, $b = 5.5402(6)$ Å, $c = 7.8177(2)$ Å, $V = 239.092(2)$ Å³

Reliability factors (%): $R_p = 10.55$, $R_{wp} = 14.95$, $R_F^2 = 6.06$, $\chi^2 = 4.337$

Bond lengths (Å):

La–O(1) = 2.971(1), La–O(1) = 2.606(4), La–O(1) = 2.411(2), La–O(1) = 3.140(2)

La–O(2) = 2.634(2) × 2, La–O(2) = 2.490(3) × 2, La–O(2) = 3.170(2) × 2, La–O(2) = 2.812(3) × 2

Fe/Mn/Cr–O(1) = 1.992(2) × 2, Fe/Mn/Cr–O(2) = 1.975(4) × 2, Fe/Mn/Cr–O(2) = 1.994(4) × 2

Bond angles (°):

Fe/Mn/Cr–O(1)–Fe/Mn/Cr = 157.645(1), Fe/Mn/Cr–O(2)–Fe/Mn/Cr = 160.185(6)

Bond valence sums:

La = 2.929, Fe/Mn/Cr = 3.110

Figure 3. Rietveld refinement of the structure of $\text{La}_2\text{Fe}_{0.66}\text{Mn}_{0.66}\text{Cr}_{0.66}\text{O}_6$ (*Pbnm*) from powder XRD data. Observed (○), calculated (—) and difference profiles (bottom) are shown. The vertical bars indicate positions of the Bragg reflections. **Figure 4.** Rietveld refinement of the structure of $\text{La}_2\text{Fe}_{0.5}\text{Mn}_{1.0}\text{Cr}_{0.5}\text{O}_6$ (*Pbnm*) from powder XRD data. Observed (○), calculated (—) and difference profiles (bottom) are shown. The vertical bars indicate positions of the Bragg reflections.

with the expected Jahn–Teller distortion of $\text{Mn}^{\text{III}}\text{O}_6$ octahedron. Accordingly, we find that the bond lengths progressively become unequal with increasing Mn content, giving rise to three sets of (M–O) × 2 bonds, somewhat similar to the stoichiometric LaMnO_3 (table 2).¹⁹ However, the distortion in $\text{La}_2\text{Fe}_{1-x}\text{Mn}_{2x}\text{Cr}_{1-x}\text{O}_6$ is much smaller than in LaMnO_3 . The distortion of MnO_6 octahedra in stoichiometric LaMnO_3 is much higher (distortion parameter $\Delta = 3.31$) because the $\text{Mn}^{\text{III}}\text{O}_6$ octahedra are strongly distorted due to the Jahn–Teller effect and the structure orbitally ordered. The rhombohedral structure of $\text{La}_2\text{Fe}_{1-x}\text{Mn}_{2x}\text{Cr}_{1-x}\text{O}_6$ members for $x \geq 0.75$ is similar to the oxidized/nonstoichiometric

$\text{LaMnO}_{3+\delta}$, having six equal octahedral M–O bonds ($\Delta = 0$). The formation of rhombohedral structure for Mn-rich members of $\text{La}_2\text{Fe}_{1-x}\text{Mn}_{2x}\text{Cr}_{1-x}\text{O}_6$ suggests that Mn is partially oxidized to Mn^{IV} and is consistent with a larger BVS (bond valence sum) for MO_6 octahedra of these members (table 2). The larger BVS is a clear indication of an apparent oxygen excess non-stoichiometry of these samples similar to $\text{LaMnO}_{3+\delta}$. Indeed our TG studies in hydrogen show an apparent oxygen excess of $\delta \approx 0.20$ in $x = 0.90$ and 0.75 samples and $\delta \approx 0.10$ in $x = 0.50$ sample, while a sample of nominal LaMnO_3 prepared under similar conditions showed $\delta \approx 0.125$ in our TG experiments.

Table 4. Atomic positions, occupancy and isotropic temperature factors for $\text{La}_2\text{Fe}_{0.66}\text{Mn}_{0.66}\text{Cr}_{0.66}\text{O}_6$.

Atom	Site	x	y	z	U_{iso}	Occupancy
La	4c	-0.0060(2)	0.0203(1)	0.25	0.0256(3)	1
Fe/Mn/Cr	4b	0.5	0	0	0.0212(4)	0.33/0.33/0.33
O1	4c	0.0739(2)	0.4839(2)	0.25	0.055(5)	1
O2	8d	0.7320(2)	0.2714(2)	0.0349(1)	0.0190(1)	1

Space group $Pbnm$: $a = 5.5050(1)$ Å, $b = 5.5368(1)$ Å, $c = 7.7972(2)$ Å, $V = 237.666(13)$ Å³

Reliability factors (%): $R_p = 6.81$, $R_{wp} = 9.30$, $R_F^2 = 6.91$, $\chi^2 = 3.409$.

Bond lengths (Å):

La–O(1) = 2.985(2), La–O(1) = 2.590(4), La–O(1) = 3.150(3), La–O(1) = 2.401(1)

La–O(2) = 2.613(4) $\times$ 2, La–O(2) = 2.501(3) $\times$ 2, La–O(2) = 2.825(2) $\times$ 2, La–O(2) = 3.132(2) $\times$ 2

Fe/Mn/Cr–O(1) = 1.991(2) $\times$ 2, Fe/Mn/Cr–O(2) = 1.988(4) $\times$ 2, Fe/Mn/Cr–O(2) = 1.963(4) $\times$ 2

Bond angles (°):

Fe/Mn/Cr–O(1)–Fe/Mn/Cr = 155.76(3), Fe/Mn/Cr–O(2)–Fe/Mn/Cr = 161.81(2)

Bond valence sums:

La = 2.966, Fe/Mn/Cr = 3.202

Figure 5. Rietveld refinement of the structure of $\text{La}_2\text{Fe}_{0.25}\text{Mn}_{1.5}\text{Cr}_{0.25}\text{O}_6$ ($R\text{-}3c$) from powder XRD data. Observed (○), calculated (—) and difference profiles (bottom) are shown. The vertical bars indicate positions of the Bragg reflections.

Figure 6. Rietveld refinement of the structure of $\text{La}_2\text{Fe}_{0.1}\text{Mn}_{1.8}\text{Cr}_{0.1}\text{O}_6$ ($R\text{-}3c$) from powder XRD data. Observed (○), calculated (—) and difference profiles (bottom) are shown. The vertical bars indicate positions of the Bragg reflections.

3.2 Magnetic properties

We have investigated the magnetic properties of $\text{La}_2\text{Fe}_{1-x}\text{Mn}_{2x}\text{Cr}_{1-x}\text{O}_6$ members in the temperature range 300–15 K. Measurements have been carried out at 100 Oe (ZFC and FC) and 5 kOe (FC). The Curie–Weiss plots for orthorhombic $\text{La}_2\text{Fe}_{1-x}\text{Mn}_{2x}\text{Cr}_{1-x}\text{O}_6$ ($x = 0, 0.1, 0.33$ and 0.5) samples are given in figures 7–10.

The magnetic property of parent $\text{La}_2\text{FeCrO}_6$ is consistent with the disordered distribution of Fe and Cr atoms at the octahedral sites, showing a large negative Weiss constant ($\theta = -490$ K) in the Curie–Weiss plot (figure 7). The experimental μ_{eff} obtained

from the high temperature linear region is $6.41 \mu_{\text{B}}$, while the calculated μ_{eff} for a non-interacting array of Fe^{3+} and Cr^{3+} is $7.06 \mu_{\text{B}}$. The slightly smaller μ_{eff} and the large negative Weiss constant are a clear indication of an overall antiferromagnetic correlation in the solid. The magnetic ordering temperature (T_{N}) estimated from the FC and ZFC data at 100 Oe is ~ 200 K. The results are largely in agreement with the earlier report on this oxide.⁴ Interestingly, there is a positive deviation of the susceptibility/magnetization from the Curie–Weiss behaviour at $T < 200$ K. The susceptibility enhancement corresponds to a small $\mu_{\text{B}} \sim 0.027$ per formula unit which likely indicates a weak short range ferromagnetic

Table 5. Atomic positions, occupancy and isotropic temperature factors for $\text{La}_2\text{Fe}_{0.5}\text{Mn}_{1.0}\text{Cr}_{0.5}\text{O}_6$.

Atom	Site	x	y	z	U_{iso}	Occupancy
La	4c	-0.0012(1)	0.0171(4)	0.25	0.0075(5)	1
Fe/Mn/Cr	4b	0.5	0	0	0.0033(2)	0.25/0.50/0.25
O1	4c	0.062(5)	0.493(4)	0.25	0.011(7)	1
O2	8d	0.734(5)	0.270(5)	0.0353(2)	0.019(4)	1

Space group $Pbnm$: $a = 5.4932(2) \text{ \AA}$, $b = 5.5258(2) \text{ \AA}$, $c = 7.850(4) \text{ \AA}$, $V = 236.308(2) \text{ \AA}^3$

Reliability factors (%): $R_p = 9.29$, $R_{wp} = 13.97$, $R_F^2 = 6.78$, $\chi^2 = 2.961$

Bond lengths ($\text{\AA}$):

La–O(1) = 2.901(2), La–O(1) = 2.636(2), La–O(1) = 3.103(1), La–O(1) = 2.429(1)

La–O(2) = 2.652(2) $\times 2$, La–O(2) = 2.507(1) $\times 2$, La–O(2) = 2.825(1) $\times 2$, La–O(2) = 3.099(1) $\times 2$

Fe/Mn/Cr–O(1) = 1.976(2) $\times 2$, Fe/Mn/Cr–O(2) = 1.987(1) $\times 2$, Fe/Mn/Cr–O(2) = 1.957(3) $\times 2$

Bond angles ($^\circ$):

Fe/Mn/Cr–O(1)–Fe/Mn/Cr = 159.83(2), Fe/Mn/Cr–O(2)–Fe/Mn/Cr = 161.95(1)

Bond valence sums:

La = 2.864, Fe/Mn/Cr = 3.290

Figure 7. Inverse molar magnetic susceptibility ($1/\chi_m$) versus temperature (T) plot for $\text{La}_2\text{FeCrO}_6$ measured at 5 kOe. Inset shows the experimental and theoretical molar magnetic susceptibility (χ_m) versus temperature (T) plot for $\text{La}_2\text{FeCrO}_6$ at 5 kOe.

Figure 8. Inverse molar magnetic susceptibility ($1/\chi_m$) versus temperature (T) plot for $\text{La}_2\text{Fe}_{0.9}\text{Mn}_{0.2}\text{Cr}_{0.9}\text{O}_6$ measured at 5 kOe. Inset shows the temperature dependence of magnetization at 5 kOe.

correlation due to a finite fraction of $\text{Fe}^{\text{III}}\text{--O--Cr}^{\text{III}}$ interaction in the disordered structure. It is known that artificially engineered superlattices of $\text{La}_2\text{FeCrO}_6$ gives rise to a ferromagnetic ordering ($T_C = 375 \text{ K}$) attributed to $\text{Fe}^{\text{III}}(t_{2g}^3 e_g^2)\text{--O--Cr}^{\text{III}}(t_{2g}^3 e_g^0)$ SE interaction according to the G–K rule.⁵

Manganese-substituted $\text{La}_2\text{Fe}_{1-x}\text{Mn}_{2x}\text{Cr}_{1-x}\text{O}_6$ oxides with the orthorhombic structure show a clear enhancement of the magnetization below 200 K. The magnetic moment per formula unit increases with

increasing Mn-content (table 8) reaching a maximum of $1.5 \mu_B$ for the $x = 0.5$ sample. We also see that the Weiss constant becomes positive ($\theta \sim 120 \text{ K}$). These changes signal a ferromagnetic ordering with $T_C \sim 200 \text{ K}$, most likely arising from Mn(III)-mediated SE interaction in $\text{La}_2\text{Fe}_{1-x}\text{Mn}_{2x}\text{Cr}_{1-x}\text{O}_6$ oxides. While in the parent $\text{La}_2\text{FeCrO}_6$, the disorder precludes a long range ferromagnetic ordering due to $\text{Fe}^{\text{III}}\text{--O--Cr}^{\text{III}}$ SE, introduction of Mn^{III} in the lattice would provide new ferromagnetic SE

Table 6. Atomic positions, occupancy and isotropic temperature factors for $\text{La}_2\text{Fe}_{0.25}\text{Mn}_{1.5}\text{Cr}_{0.25}\text{O}_6$.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}	Occupancy
La	6 <i>a</i>	0	0	0.25	0.0264(7)	1.0
Fe/Mn/Cr	6 <i>b</i>	0	0	0	0.0182(5)	0.125/0.75/0.125
O	18 <i>e</i>	0.4464(8)	0	0.25	0.0228(3)	1.0

Space group: $R\bar{3}c$; $a = 5.5278(6)$, $c = 13.3432(1)$ Å, $V = 353.188(8)$ Å³

Reliability factors (%): $R_F^2 = 4.62$, $R_p = 7.53$, $R_{wp} = 10.79$, $\chi^2 = 5.13$

Bond lengths (Å):

La–O = $3.060(3) \times 3$, La–O = $2.467(2) \times 3$, La–O = $2.753(2) \times 6$

Fe/Mn/Cr–O = $1.967(2) \times 6$

Bond angles (°):

Fe/Mn/Cr–O–Fe/Mn/Cr = $162.667(1)$

Bond valence sums:

La = 2.874, Fe/Mn/Cr = 3.390

Table 7. Atomic positions, occupancy and isotropic temperature factors for $\text{La}_2\text{Fe}_{0.1}\text{Mn}_{1.8}\text{Cr}_{0.1}\text{O}_6$.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}	Occupancy
La	6 <i>a</i>	0	0	0.25	0.0285(2)	1.0
Fe/Mn/Cr	6 <i>b</i>	0	0	0	0.0211(3)	0.05/0.9/0.05
O	18 <i>e</i>	0.4461(6)	0	0.25	0.0260(1)	1.0

Space group: $R\bar{3}c$; $a = 5.5255(4)$, $c = 13.3359(4)$ Å, $V = 352.622(6)$ Å³

Reliability factors (%): $R_F^2 = 4.35$, $R_p = 6.29$, $R_{wp} = 9.00$, $\chi^2 = 5.734$

Bond lengths (Å):

La–O = $3.060(2) \times 3$, La–O = $2.465(2) \times 3$, La–O = $2.752(2) \times 6$

Fe/Mn/Cr–O = $1.966(1) \times 6$

Bond angles (°):

Fe/Mn/Cr–O–Fe/Mn/Cr = $162.584(1)$

Bond valence sums:

La = 2.79, Fe/Mn/Cr = 3.410

Figure 9. Inverse molar magnetic susceptibility ($1/\chi_m$) versus temperature (T) plot for $\text{La}_2\text{Fe}_{0.66}\text{Mn}_{0.66}\text{Cr}_{0.66}\text{O}_6$ measured at 5 kOe. Inset shows the temperature dependence of magnetization at 5 kOe.

pathways between $\text{Fe}^{\text{III}}/\text{Mn}^{\text{III}}$ and $\text{Cr}^{\text{III}}/\text{Mn}^{\text{III}}$ even in the disordered perovskite lattice according to the G–K rule: thus $\text{Fe}^{\text{III}}(t_{2g}^3 e_g^2) - \text{O} - \text{Mn}^{\text{III}}(t_{2g}^3 e_g^1)$ SE would be ferromagnetic for a Jahn–Teller distorted octahedral Mn^{III} site, for the interaction between half-filled $\text{Fe}^{\text{III}}(e_g^2)$ and empty $\text{Mn}^{\text{III}}([d_{x^2-y^2}]^0)$. Similarly, the $\text{Cr}^{\text{III}}(t_{2g}^3 e_g^0) - \text{O} - \text{Mn}^{\text{III}}(t_{2g}^3 e_g^1)$ SE would also be ferromagnetic for the interaction between empty $\text{Cr}^{\text{III}}(e_g^0)$ and half-filled $\text{Mn}^{\text{III}}([d_{z^2}]^1)$. Moreover, it is known that the $\text{Mn}^{\text{III}} - \text{O} - \text{Mn}^{\text{III}}$ SE interaction for orbitally disordered perovskites such as $\text{LaMn}_{1-x}\text{Sc}_x\text{O}_3$ and $\text{LaMn}_{1-x}\text{Ga}_x\text{O}_3$ is ferromagnetic due to fluctuating e_g electrons.¹⁴ A similar situation would arise in $\text{La}_2\text{Fe}_{1-x}\text{Mn}_{2x}\text{Cr}_{1-x}\text{O}_6$ perovskites providing an additional ferromagnetic $\text{Mn}^{\text{III}} - \text{O} - \text{Mn}^{\text{III}}$ pathway. Accordingly, Mn(III) substitution provides several ferromagnetic pathways for the SE interaction between $\text{Fe}^{\text{III}}/\text{Mn}^{\text{III}}$, $\text{Mn}^{\text{III}}/\text{Cr}^{\text{III}}$ and $\text{Mn}^{\text{III}}/\text{Mn}^{\text{III}}$ in the disordered perovskites containing all the three ions. The Mn(III)-mediated ferromagnetism at the orthorhombic $\text{La}_2\text{Fe}_{1-x}\text{Mn}_{2x}\text{Cr}_{1-x}\text{O}_6$ oxides showing a maximum magnetic moment of $1.5 \mu_B/\text{f.u.}$ for the $x = 0.5$ sample is however much smaller than the

Table 8. Magnetic properties of $\text{La}_2\text{Fe}_{1-x}\text{Mn}_{2x}\text{Cr}_{1-x}\text{O}_6$ perovskite oxides.

Composition	Structure	$\mu_{\text{eff}} (\mu_B)$ (Experimental) from C-W plot	$\mu_{\text{eff}} (\mu_B)$ (spin-only) (Calculated)	θ (K)	Saturation magnetization (M) at 5 kOe, 20 K (emu/mol)	Saturation magnetic moment/ f.u. at 5 kOe, 20 K ($\mu_B/\text{f.u.}$)
$\text{La}_2\text{FeCrO}_6$	<i>Pbnm</i>	6.41	7.06	−490	155	0.027
$\text{La}_2\text{Fe}_{0.9}\text{Mn}_{0.2}\text{Cr}_{0.9}\text{O}_6$	<i>Pbnm</i>	5.54	7.05	−295	275	0.049
$\text{La}_2\text{Fe}_{0.66}\text{Mn}_{0.66}\text{Cr}_{0.66}\text{O}_6$	<i>Pbnm</i>	5.02	6.98	45	1860	0.333
$\text{La}_2\text{Fe}_{0.5}\text{Mn}_{1.0}\text{Cr}_{0.5}\text{O}_6$	<i>Pbnm</i>	5.75	6.99	120	8350	1.495
$\text{La}_2\text{Fe}_{0.35}\text{Mn}_{1.3}\text{Cr}_{0.35}\text{O}_6$	<i>R-3c</i>	6.39	6.97	140	20050	3.591
$\text{La}_2\text{Fe}_{0.25}\text{Mn}_{1.5}\text{Cr}_{0.25}\text{O}_6$	<i>R-3c</i>	6.72	6.96	145	41650	7.459
$\text{La}_2\text{Fe}_{0.1}\text{Mn}_{1.8}\text{Cr}_{0.1}\text{O}_6$	<i>R-3c</i>	7.53	6.94	180	35570	6.371
$[\text{LaMnO}_{3.10}]_2^*$	<i>R-3c</i>	6.00	6.93	170	34092	6.100

*Data taken from ref. 21

Figure 10. (a) Inverse molar magnetic susceptibility ($1/\chi_m$) versus temperature (T) plot for $\text{La}_2\text{Fe}_{0.5}\text{Mn}_{1.0}\text{Cr}_{0.5}\text{O}_6$ measured at 5 kOe. Inset shows the temperature dependence of magnetization at 5 kOe. (b) The temperature dependence of FC and ZFC magnetizations for $\text{La}_2\text{Fe}_{0.5}\text{Mn}_{1.0}\text{Cr}_{0.5}\text{O}_6$ at 100 Oe. Inset shows M - H hysteresis loop for $\text{La}_2\text{Fe}_{0.5}\text{Mn}_{1.0}\text{Cr}_{0.5}\text{O}_6$ at 10 K.

expected magnetic moment of $4.0 \mu_B/\text{f.u.}$; the smaller magnitude of the magnetic moment is clearly attributable to the disordered distribution of $\text{Fe}^{\text{III}}/\text{Mn}^{\text{III}}/\text{Cr}^{\text{III}}$ ions in the lattice. Given that BVS sums indicate an increasing Mn^{IV} content with x (table 2), presence of a ferromagnetic component arising from $\text{Mn}^{\text{III}}\text{--O--Mn}^{\text{IV}}$ DE interaction cannot be neglected in the orthorhombic oxides.

$\text{La}_2\text{Fe}_{1-x}\text{Mn}_{2x}\text{Cr}_{1-x}\text{O}_6$ oxides with the rhombohedral structure ($x \geq 0.65$) show a different magnetic behaviour as compared to the orthorhombic mem-

bers ($0 < x \leq 0.5$). All the rhombohedral members show a strong ferromagnetism ($T_C \sim 150\text{--}200$ K) with a large magnetization that progressively increases with increasing Mn content reaching a maximum of $7.5 \mu_B/\text{f.u.}$ for the $x = 0.75$ sample (figures 11–13; table 8). The corresponding Curie–Weiss plots for the high temperature magnetic susceptibility data show a positive $\theta = 140\text{--}180$ K that appears to increase with increasing x . Also, the paramagnetic moment (μ_{eff}) obtained from the Curie–Weiss plots are 6.39 , 6.72 and $7.53 \mu_B$ for the $x = 0.65$, 0.75 and

0.90 samples, respectively. Magnetization versus temperature plots at 100 Oe for all the rhombohedral oxides (figure 14) show a clear divergence between the ZFC and FC data. The magnetic properties of the rhombohedral oxides of the $\text{La}_2\text{Fe}_{1-x}\text{Mn}_{2x}\text{Cr}_{1-x}\text{O}_6$ are by and large similar to those of $\text{LaMnO}_{3+\delta}$ ($\delta \geq 0.1$).^{20–22} The latter series of oxides showing apparent oxygen excess non-stoichiometry are indeed formulated as $\text{La}_{1-y}\text{Mn}_{1-y}\text{O}_3$ ($y = \delta/3 + \delta$), where manganese exists in the mixed-valent ($\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$) state.^{20–22} It is the latter that actually causes the ferromagnetic properties of $\text{LaMnO}_{3+\delta}$ ($\delta > 0.1$) through the DE between $\text{Mn}^{\text{III}}(t_{2g}^3 e_g^1) - \text{O} - \text{Mn}^{\text{IV}}(t_{2g}^3 e_g^0)$. For the Mn-rich rhombohedral oxides of the $\text{La}_2\text{Fe}_{1-x}\text{Mn}_{2x}\text{Cr}_{1-x}\text{O}_6$ members, it is likely that both the DE between $\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$ and the SE between $\text{Fe}^{\text{III}}/\text{Mn}^{\text{IV}}$, $\text{Cr}^{\text{III}}/\text{Mn}^{\text{III}}$ and $\text{Mn}^{\text{III}}/\text{Mn}^{\text{III}}$ contribute to the observed magnetic behaviour. Although it is difficult to disentangle the different contributions to the magnetism from the limited data presented here, we surmise that the DE is likely to be a major contributor to the magnetism of the rhombohedral oxides. This conclusion is reinforced by the observation that the rhombohedral oxides show a much lower resistivity ($\rho \sim 10^2$ ohm cm) than the orthorhombic members of the $\text{La}_2\text{Fe}_{1-x}\text{Mn}_{2x}\text{Cr}_{1-x}\text{O}_6$ series ($\rho \sim 10^4 - 10^5$ ohm cm) at room temperature.

Figure 11. Inverse molar magnetic susceptibility ($1/\chi_m$) versus temperature (T) plot for $\text{La}_2\text{Fe}_{0.35}\text{Mn}_{1.3}\text{Cr}_{0.35}\text{O}_6$ measured at 5 kOe. Inset shows the temperature dependence of magnetization at 5 kOe.

4. Conclusions

$\text{La}_2\text{Fe}_{1-x}\text{Mn}_{2x}\text{Cr}_{1-x}\text{O}_6$ perovskite oxides crystallize in the orthorhombic ($Pbnm$) structure for $0 < x \leq 0.5$ and rhombohedral ($R-3c$) structure for $0.65 \leq x < 1.0$. Unlike the parent $\text{La}_2\text{FeCrO}_6$, the oxygen-stoichiometric orthorhombic oxides exhibit a distinct ferromagnetism ($T_C \sim 200$ K) that appears to

Figure 12. (a) Inverse molar magnetic susceptibility ($1/\chi_m$) versus temperature (T) plot for $\text{La}_2\text{Fe}_{0.25}\text{Mn}_{1.5}\text{Cr}_{0.25}\text{O}_6$ measured at 5 kOe. Inset shows the temperature dependence of magnetization at 5 kOe. (b) M - H hysteresis loop for $\text{La}_2\text{Fe}_{0.25}\text{Mn}_{1.5}\text{Cr}_{0.25}\text{O}_6$ at 10 K.

Figure 13. Inverse molar magnetic susceptibility ($1/\chi_m$) versus temperature (T) plot for $\text{La}_2\text{Fe}_{0.1}\text{Mn}_{1.8}\text{Cr}_{0.1}\text{O}_6$ measured at 5 kOe. Inset shows the temperature dependence of magnetization at 5 kOe.

Figure 14. The temperature dependence of FC and ZFC magnetizations for $\text{La}_2\text{Fe}_{0.25}\text{Mn}_{1.5}\text{Cr}_{0.25}\text{O}_6$ at 100 Oe.

be due to Mn^{III} -mediated superexchange between $\text{Fe}^{\text{III}}/\text{Cr}^{\text{III}}$ in the disordered structure. The rhombohedral members with an apparent oxygen excess non-stoichiometry display a strong ferromagnetism ($T_C \sim 150\text{--}200$ K) that is similar to the magnetism of $\text{LaMnO}_{3+\delta}$ ($\delta \geq 0.1$). The M–H hysteresis data (figures 10(b)-inset and 12(b)) are consistent with this conclusion.

Acknowledgements

J G thanks the Department of Science and Technology, New Delhi for the award of a Ramanna Fellowship and the Indian National Science Academy for the award of a Senior Scientist position. A N thanks the University Grants Commission, New Delhi for the award of a D S Kothari Postdoctoral Fellowship.

References

1. Serrate D, De Teresa J M and Ibarra M R 2007 *J. Phys. Condens. Matter* **19** 023201
2. Rogado N S, Li J, Sleight A W and Subramanian M A 2005 *Adv. Mater.* **17** 2225
3. Goodenough J B 2008 *Scholarpedia* **3**(10) 7382
4. Azad S K, Møllergård A, Eriksson S-G, Ivanov S A, Yunus S M, Lindberg F, Svensson G and Mathieu R 2005 *Mater. Res. Bull.* **40** 1633
5. Ueda K, Tabata H and Kawai T 1998 *Science* **280** 1064
6. Jonker G H 1956 *Physica* **22** 707
7. Vasanthacharya N Y, Singh K K and Ganguly P 1981 *Revue de Chimie Minerale* **18**(4) 333
8. Gundakaram R, Arulraj A, Vanitha P V, Rao C N R, Gayathri N, Raychaudhuri A K and Cheetham A K 1996 *J. Solid State Chem.* **127** 354
9. Karpinsky D V, Troyanchuk I O and Sikolenko V V 2007 *J. Phys. Condens. Matter.* **19** 036220
10. Ueda K, Tabata H and Kawai T 1999 *Phys. Rev. B* **60** R12561
11. Sun Y, Tong W, Xu X and Zhang Y 2001 *Phys. Rev. B* **63** 174438
12. Tong W, Zhang B, Tan S and Zhang Y 2004 *Phys. Rev. B* **70** 014422
13. Deisenhofer J, Paraskevopoulos M, Krug von Nidda H-A and Loidl A 2002 *Phys. Rev. B* **66** 054414
14. Goodenough J B, Dass R I and Zhou J 2002 *Solid State Sciences* **4** 297
15. Blasco J, García J, Campo J, Sánchez M C and Subías G 2002 *Phys. Rev. B* **66** 174431
16. Lasocha W and Lewinski K J 1994 *J. Appl. Cryst.* **27** 437
17. Kraus K and Nolze G 1996 *J. Appl. Cryst.* **29** 301
18. Larson A C and von Dreele R B 1990 *General structure analysis system*, Report LAUR 86-748, Los Alamos National Laboratory, Los Alamos, NM
19. Rodríguez-Carvajal J, Hennion M, Moussa F, Moudén A H, Pinsard L and Revcolevschi A 1998 *Phys. Rev. B* **57** R3189
20. Töpfer J and Goodenough J B 1997 *Solid State Chem.* **130** 117
21. Ritter C, Ibarra M R, De Teresa J M, Algarabel P A, Marquina C, Blasco J, García J, Oseroff S and Cheong S-W 1997 *Phys. Rev. B* **56** 8902
22. Prado F, Sánchez R D, Caneiro A, Causa M T and Tovar M 1999 *J. Solid State Chem.* **146** 418