

Ferrimagnetic order in the insulating $\text{Sr}_3\text{Fe}_2\text{ReO}_9$ double perovskite

E.V. Pannunzio Miner^a, J.M. De Paoli^b, J.A. Alonso^c, M. García-Hernández^c,
R.D. Sánchez^{b,*}, R.E. Carbonio^a

^aINFIQC, CONICET-Departamento de Físicoquímica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000, Córdoba, Argentina

^bCentro Atómico Bariloche, CNEA, Av. E. Bustillo 9500, 8400, San Carlos de Bariloche, Río Negro, Argentina

^cInstituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, E-28049 Madrid, Spain

Abstract

A new iron(III)/rhenium(VI) double perovskite oxide, $\text{Sr}_3\text{Fe}_2\text{ReO}_9$, has been synthesized in polycrystalline form at 1200 °C by solid-state reaction from citrate precursors. The Rietveld analysis of the synchrotron X-ray powder diffraction pattern shows that this compound, at 300 K, has orthorhombic symmetry (S.G.: *Immm*), with $a = 5.56733(1)\text{Å}$, $b = 5.56796(1)\text{Å}$ and $c = 7.90224(2)\text{Å}$. The refinement of the relative Fe/Re occupancies of each B site reveals the presence of a partial cationic order. At high temperatures, the magnetic susceptibility of the $\text{Sr}_3\text{Fe}_2\text{ReO}_9$ is well described as a paramagnet with ferrimagnetic correlations. Below 450 K, the system displays a spontaneous magnetization, and hysteresis loops are observed.

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1. Introduction

In the search for new colossal magnetoresistant (CMR) materials, some members of the family of double perovskites of composition $\text{A}_2\text{BB}'\text{O}_6$ (A = alkali earths and B , B' = transition metals) have been proposed as half-metallic ferromagnets, with T_C 's well above room temperature (RT), as an alternative to perovskite manganites [1–3]. These transition metal double perovskite oxides have a “double” crystalline structure because they exhibit, in an ideal order, the M ions alternated in two different B sites [4].

Also, double perovskites containing transition metals other than Mo, such as A_2FeReO_6 (A = Ca, Sr, Ba), present a half-metallic ground state and show magnetoresistance (MR) at RT [5].

Despite the large number of double perovskites informed up to now, only few reports exist about compounds with stoichiometry $\text{A}_3\text{B}_2\text{B}'\text{O}_9$. These compounds, which we can

call “3219”, are also double perovskites whose crystallographic formula can be re-written as $\text{A}_2[\text{B}^{2a}(\text{B}_{1/3}\text{B}'_{2/3})^{2c}]\text{O}_6$, where $2a$ and $2c$ denote the crystallographic sites in the corresponding space group. This composition gives the possibility of changing the oxidation states of the B and B' ions and consequently changing the electrical and magnetic properties. For the previously mentioned reasons, we focus on preparing and characterizing “3219” double perovskites as potential candidates for CMR materials. In particular, we report on a new double perovskite: $\text{Sr}_3\text{Fe}_2\text{ReO}_9$. We refined its crystal structure and relative Fe/Re occupancies of B sites using synchrotron X-ray powder diffraction (SXRPD). We also performed and show results of electrical resistivity (ρ) vs. temperature (T), magnetization (M) vs. T , hysteresis loops and curves of MR.

2. Experimental

$\text{Sr}_3\text{Fe}_2\text{ReO}_9$ was prepared by the citrate method. Stoichiometric amounts of SrCO_3 , $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and ReO_3 were mixed in citric acid solution, dried and then

*Corresponding author. Tel.: +54 2944 445518; fax: +54 2944 445299.
E-mail address: rodo@cab.cnea.gov.ar (R.D. Sánchez).

treated at 600 °C for 12 h in air. The resulting powders were reground and calcined at 1200 °C for 12 h in Ar.

The high-resolution SXRPD pattern was collected at RT in the D10A diffractometer at Laboratório Nacional de Luz Síncrotron (LNLS), Campinas, Brazil. The wavelength used was 1.61019 Å. The 2θ range was from 21° up to 118°, with increments of 0.02° and a total counting time of 3 h. The FULLPROF program [6] was used to refine the crystal structure by the Rietveld method. A pseudo-Voigt shape function was always adequate to obtain good fits for experimental data. The $\text{Sr}_3\text{Sb}_2\text{NiO}_9$ crystal structure [7] (space group *Immm*, No. 71) was taken as the initial model for this compound.

DC magnetization was measured with a commercial superconducting quantum interference device magnetometer on powdered samples, in a 10–300 K temperature range. A vibrating sample magnetometer was used to take the magnetization from RT to 700 K. The electric transport and magnetotransport experiments were performed by the conventional four-probe technique, under magnetic fields up to 90 kOe.

3. Results and discussions

The refined diffractogram using SXRPD for $\text{Sr}_3\text{Fe}_2\text{ReO}_9$ at RT is shown in Fig. 1. An excellent fit was obtained. The discrepancy factors were: $R_p = 15.1\%$, $R_{wp} = 17.1\%$, $R_1 = 5.02\%$ and $\chi^2 = 2.78$. The final cell parameters, atomic coordinates and relative occupancy of each B site are shown in Table 1.

According to the refined occupancies, the crystallographic formula can be written as: $\text{Sr}_2(\text{Fe}_{0.57}\text{Re}_{0.43})^{2a}(\text{Fe}_{0.76}\text{Re}_{0.24})^{2c}\text{O}_6$.

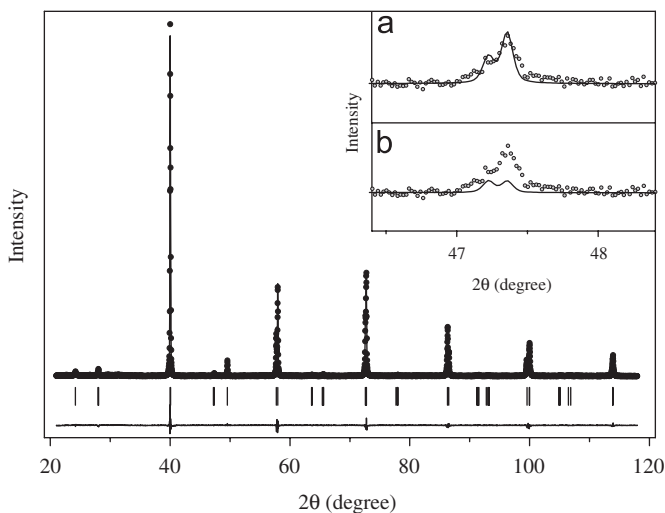


Fig. 1. Rietveld refinement of powder Synchrotron X-ray diffraction pattern for $\text{Sr}_3\text{Fe}_2\text{ReO}_9$, in the space group *Immm* (no. 71). Dots: experimental pattern; solid line: calculated pattern; bottom solid line: difference between observed and calculated patterns; and vertical bars: positions of Bragg reflections. Inset: Rietveld refinement details considering the relative Fe/Re occupancies of each B site (a) with partial Fe/Re order (see Table 1) and (b) with a complete random Fe/Re occupation of each crystallographic site.

Table 1

Refined cell parameters, atomic positions and occupations from rietveld analysis of synchrotron X-ray powder diffraction for $\text{Sr}_3\text{Fe}_2\text{ReO}_9$, in the space group *Immm* (No. 71)

Atom	Wyckoff site	x	y	z	Occ
Sr	4j	$\frac{1}{2}$	0	0.2476(2)	1
Fe1					0.57
Re1	2a	0	0	0	0.43
Fe2					0.76
Re2	2c	$\frac{1}{2}$	$\frac{1}{2}$	0	0.24
O1	8n	0.2295(1)	0.2809(2)	0	1
O2	4i	0	0	0.2509(3)	1

$a = 5.56733(1)$ Å, $b = 5.56796(1)$ Å and $c = 7.90224(2)$ Å.

Table 2

Main interatomic distances and angles for $\text{Sr}_3\text{Fe}_2\text{ReO}_9$

2a site	Distance (Å)	2c site	Distance (Å)
B-O1	$4 \times 1.960(1)$	B-O1	$4 \times 2.044(1)$
B-O2	$2 \times 1.982(2)$	B-O2	$2 \times 1.997(2)$
Angle(degree)		Angle (degree)	
O1-B-O1	78.29(3)	O1-B-O1	78.22(2)
O2-B-O1	90.00	O2-B-O1	90.00

B = Fe or Re.

Thus, this double perovskite presents a partial disorder, and there is no possibility to obtain a complete ordered structure as in the case of the parent compounds A_2FeReO_6 ($\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$) [5]. On the other hand, the Rietveld results, considering random Fe/Re occupation of each B site, have not reproduced the experimental pattern (see inset Fig. 1).

Interatomic distances and angles are shown in Table 2. The 2a and 2c MO_6 octahedra ($\text{M} = \text{Fe}$ or Re) are slightly distorted. These octahedra are also rotated by 12° around [001] direction.

The electrical resistivity (ρ) as a function of temperature shows a semiconducting behaviour. The experimental data were obtained from room temperature to 220 K; below this temperature, the resistance was inaccessible in our experimental set-up. In Fig. 2 we plot $\ln \rho$ vs. $10^3/T$ and a linear behaviour is observed. This can be associated with a thermal activated electronic conduction mechanism ($\rho = A \exp(-\Delta/kT)$), given $\Delta = 0.2$ eV. This Δ value could show the gap between the valence and the conduction bands.

At high T , we compute the magnetic susceptibility (χ) as the ratio between the magnetization (M) and the magnetic field (H). M was taken at a constant magnetic field of $H = 1$ kOe. We plot χ^{-1} vs. T , and a linear behaviour is observed at high temperature (see Fig. 3). However, when T is decreased, χ^{-1} diminishes abruptly to zero, which can be associated with the appearance of ferrimagnetic order at low temperature. The data can be fitted with the susceptibility obtained by the mean field theory of ferrimagnetism (MFTF) [8], $\chi^{-1} = (T-\theta)/C-\xi/(T-\theta')$. The parameters

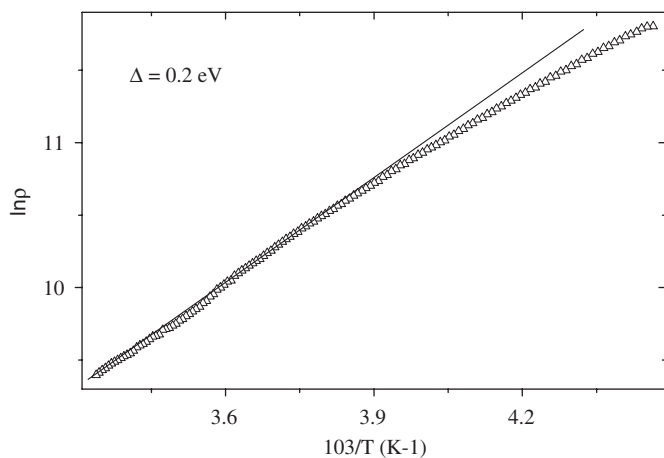


Fig. 2. Logarithm of electrical resistivity vs. inverse of temperature.

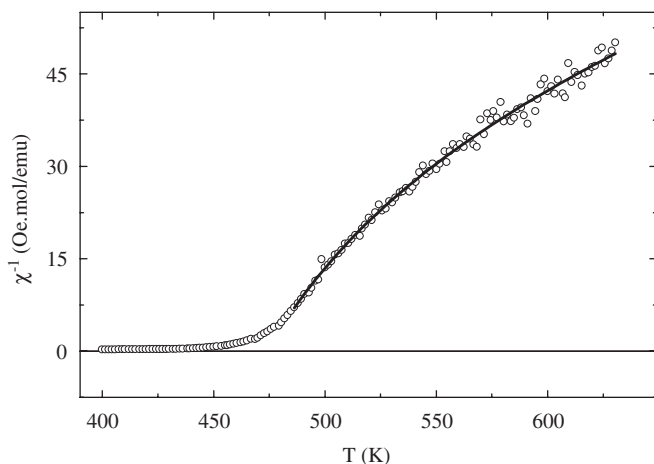


Fig. 3. Open circles show the inverse of magnetic susceptibility vs. temperature data. Solid line is the fit using the Mean Field Theory of Ferrimagnetism.

obtained are $\theta = 9$ K, $\theta' = 374$ K, $C = 9.2$ Oe mol/emu K and $\xi = 5072$ Oe mol K/emu. $\text{Sr}_3\text{Fe}_2\text{ReO}_9$ presents two Fe^{3+} ($S = 5/2$) and one Re^{6+} ($S = 1/2$) as the only magnetic ions, and we would expect $C = 9.125$ Oe mol/emu K. This value is in agreement with the obtained C value from the fit with MFTF.

The magnetization vs. T data at $H = 1$ kOe, in the 5–700 K temperature range, are shown in Fig. 4. On decreasing T , a spontaneous magnetization appears at $T_N = 450$ K. Below this, M increases to reach a saturation value. Nevertheless, this saturation magnetization continuously increases when the magnetic field is increased. This can be appreciated in the inset of Fig. 4 where the hysteresis loop measured at 5 K is plotted. At the higher H and the lower T measured, we take the maximum M value as the saturation magnetization $\mu_{\text{sat}} = 1.10 \mu_{\text{B}}/\text{mol}$. This value is in good agreement with the expected $\mu_{\text{sat}}^T = 1.14 \mu_{\text{B}}/\text{mol}$, which comes from considering an antiparallel coupling between the Fe and Re spins occupying the 2a and 2c, with the different relative occupations obtained by SXRPD experiment. MR vs. H was measured in a

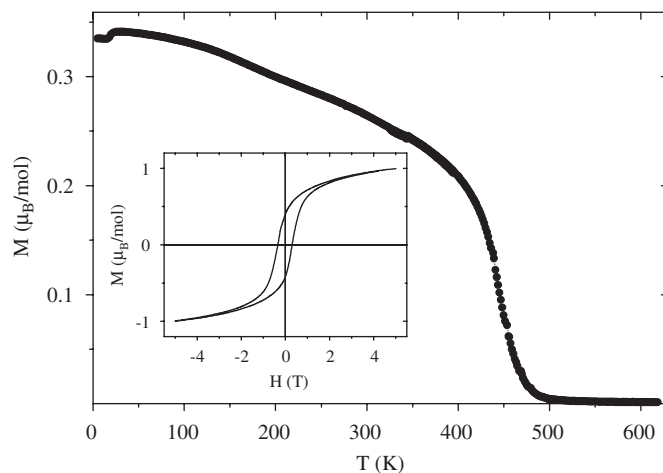


Fig. 4. Magnetization vs. temperature at 1 kOe. Inset: Hysteresis loop at 5 K.

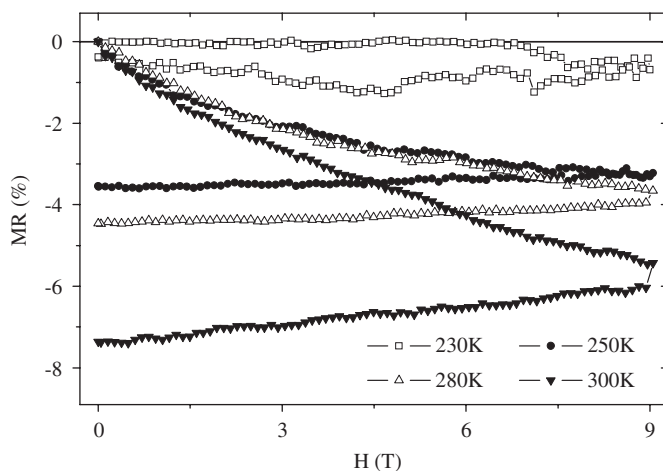


Fig. 5. Curve of magnetoresistance vs. magnetic field at different temperatures.

0–90 kOe magnetic field range at different temperatures. In Fig. 5, MR presents a complex and non-reversible behaviour. The maximum value (8%) occurs at RT, and the effect is reduced when T is decreased. This can be associated with irreversible relaxations of the magnetic domains inside the sample. The temperature can help to reverse the magnetization mechanism of magnetic clusters or ferrimagnetic regions. On the contrary, at low temperature, these ferrimagnetic regions could be perfectly correlated.

4. Conclusion

Double perovskite $\text{Sr}_3\text{Fe}_2\text{ReO}_9$ has been synthesized by the citrate method. Its crystal structure has been refined from synchrotron X-ray powder diffraction data by Rietveld method and was found to be orthorhombic $\text{SG} = \text{Immm}$, with $a = 5.56733(1)$ Å, $b = 5.56796(1)$ Å and $c = 7.90224(2)$ Å. The crystallographic formula can be written as $\text{Sr}_2(\text{Fe}_{0.57}\text{Re}_{0.43})^{2a}(\text{Fe}_{0.76}\text{Re}_{0.24})^{2c}\text{O}_6$.

This compound is a semiconductor with a band gap of $\Delta = 0.2$ eV. The magnetization behaviour shows that $\text{Sr}_3\text{Fe}_2\text{ReO}_9$ presents ferrimagnetic order below 450 K. At low T , the saturation moment can be explained with an antiferromagnetic ordering between 2a and 2c crystallographic sites, considering the relative occupations obtained by Rietveld refinement of synchrotron X-ray powder diffraction pattern. The paramagnetic regime can be described by the mean field theory of ferrimagnetism.

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