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The effects of Sc and Nb substitution in Sr_2FeReO_6 double perovskites. A combined study of X-ray powder diffraction and Mössbauer spectroscopy†

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The structure, magnetic properties and Mössbauer effect on $Sr_2Fe_{1-x}M_xRe_{1-y}M'_yO_6$ ($x=0$, 0.1; $y=0$, 0.1; M = Sc; M′ = Nb) phases with partially ordered double perovskite structures are presented. The Nb and Sc substitutions affect the magnetisation values but the T_c values remain unaltered around 400 K. Mössbauer analysis shows high spin Fe^{3+} ions, except for Sr_2FeReO_6, which shows a mixed valence state at high temperatures.

Much of the interest in double perovskites arises from the prospects of finding half-metallic oxides with high Curie temperatures. It is well known that Curie temperatures of mixed-valence manganites of the type $Ln_{1-x}A_xMnO_3$ cannot be increased above 400 K by any manipulation of the composition or stoichiometry.[1] Many compounds with a double-perovskite structure have been known since 1960.[2–4] Oxides with this structure have a general formula $A_2BB'O_6$ where the A divalent cation is twelve-fold coordinated and the B and B′ cations are six-coordinated to oxygen. The ideal cubic symmetry consists of an ordered rock-salt type arrangement of B and B′ cations and generally occurs in compounds with large charge differences between B and B′ ions.[5]

Recently Kobayashi *et al.*[6] reported that Sr_2FeMoO_6 is a half-metallic ferrimagnet, which exhibits intrinsic tunnelling-type magnetoresistance (MR) at room temperature. The magnetic structure was described as an ordered arrangement of parallel Fe^{3+} ($3d^5$, $S=5/2$) magnetic moments, antiferromagnetically coupled to Mo^{5+} ($4d^1$, $S=1/2$). However, neutron diffraction studies reported by Garcia-Landa *et al.*[7] seemed to discard the existence of a ferrimagnetic state below T_C in this material. This fact suggests an electronic configuration of $Fe^{2+}Mo^{6+}$ instead of $Fe^{3+}Mo^{5+}$, consistent with the ordered magnetic moment observed for Fe (4 μ_B). These results support the itinerant character of the t_{2g} Mo electron, giving no local magnetic moment at the Mo sites. In the case of the Sr_2FeReO_6 phase, it presents a half-metallic ground state,[8] concomitant with the ferrimagnetic coupling of Fe^{3+} and Re^{5+} ($5d^2$, $S=1$) magnetic moments, and shows significant intergrain tunnelling MR at room temperature. There have been only a few studies on this kind of rhenium phase, probably due to the difficulties found in their preparation. We present the study of three compounds of general formula $Sr_2Fe_{1-x}M_xRe_{1-y}M'_yO_6$ ($x=0$, 0.1; $y=0$, 0.1; M = Sc; M′ = Nb).

Polycrystalline powders of Sr_2FeReO_6, $Sr_2Fe_{0.9}Sc_{0.1}ReO_6$ and $Sr_2FeRe_{0.9}Nb_{0.1}O_6$ were prepared under identical conditions by the sol–gel method. Stoichiometric amounts of analytical grade $SrCO_3$, $Fe(NO_3)_2\cdot 9H_2O$ and metallic Re, with the correspondent niobium or scandium oxides, were dissolved in a citric acid solution to which ethylene glycol was added. The gel obtained was dried at 370 K in a sand bath and then fired at 1273 K for 1 h under Ar. Metal ion contents were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis. The results are consistent with the following stoichiometries: Sr_2FeReO_6 (Found: Sr, 33.63; Fe, 10.64; Re, 35.75; Calc.: Sr, 34.14; Fe, 10.88; Re, 36.28%); $Sr_2Fe_{0.9}Sc_{0.1}ReO_6$ (Found: Sr, 33.72; Fe, 9.60; Sc, 0.74; Re, 35.83; Calc Sr, 34.21; Fe, 9.81;Sc, 0.88; Re, 36.35%) $Sr_2FeRe_{0.9}Nb_{0.1}O_6$ (Found: Sr, 33.25; Fe, 10.94; Nb, 1.69; Re, 32.98; Calc.: Sr, 34.77; Fe, 11.08; Nb, 1.84; Re, 33.25%).

The powder X-ray diffraction (XRD) patterns at room temperature were taken on a Stoe/Stadi-P powder diffractometer with Ge(III) monochromatized CuKα_1 radiation, in the angular range $5<2\theta<120°$, by steps of 0.02, and were Rietveld analysed[9] using the GSAS program.[10] Magnetic measurements were carried out under an applied field of 0.5 T using a Faraday balance in the temperature range from 300 to 500 K. Mössbauer spectroscopy measurements were performed in transmission geometry using a ^{57}Co–Rh source in the constant acceleration mode. Mössbauer spectra at different temperatures were recorded using either a cryofurnace or a bath cryostat. The velocity was calibrated using an Fe foil. The spectra were fitted using the program Normos developed by Brand *et al.*[11] The isomer shifts are relative to α-Fe. Field dependent resistance measurements were conducted in a MPMS-7 SQUID magnetometer at 8 and 300 K under a variable magnetic field between ±8 T. The resistance and magnetoresistance *versus* field measurements were taken by a dc four-wire system with the current flowing parallel to the applied field. The pellets obtained from the synthesis procedure were cut into a rectangular shape ($4\times 6\times 2$ mm^3) and silver dag contacts were used. The irregularity of these contacts makes it difficult to give accurate values of the resistivity of the sample.

The results of the Rietveld refinements show single double-perovskite phases with tetragonal *I*4/*mmm* and orthorhombic *Immm* symmetries (Table 1). All the observed peaks can be indexed with unit cells: $\sqrt{2}a_p\times\sqrt{2}a_p\times 2a_p$ whose dimensions are related to the primitive cubic perovskite unit cell a_p. The agreement factors for these refinements are $R_{wp}(\%)=4.98$, 3.27

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†Electronic supplementary information (ESI) available: enlarged Rietveld fits. See http://www.rsc.org/suppdata/jm/b0/b007712g/

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Table 1 Refined cell parameters and results from magnetisation measurements for the Sr_2FeReO_6, $Sr_2FeRe_{0.9}Nb_{0.1}O_6$, and $Sr_2Fe_{0.9}Sc_{0.1}ReO_6$ compounds

	Sr_2FeReO_6	$Sr_2FeRe_{0.9}Nb_{0.1}O_6$	$Sr_2Fe_{0.9}Sc_{0.1}ReO_6$
Space group	*I4/mmm*	*I4/mmm*	*Immm*
a/Å	5.5771(2)	5.5707(6)	5.5759(6)
b/Å			5.6089(7)
c/Å	7.8930(3)	7.9055(9)	7.8794(8)
V/Å^3	243.74(2)	245.33(8)	246.42(8)
T_C/K	410	400	426
M_S (300 K) at 0.5 T/emu g^{-1}	21.2	4.3	5.8
Ordering (%)	92	74	78

and 4.28; $R_p(\%) = 3.52$, 2.53 and 3.24; and $\chi^2 = 2.23$, 1.03 and 1.69 for Sr_2FeReO_6, $Sr_2FeRe_{0.9}Nb_{0.1}O_6$ and $Sr_2Fe_{0.9}Sc_{0.1}ReO_6$ respectively. The global fits for two samples are shown in Fig. 1. When substituting Fe by Sc, the symmetry lowers from tetragonal *I4/mmm* to orthorhombic *Immm* as evidenced by the splitting of most peaks. This is consistent with the larger size differences between Fe^{3+} and Sc^{3+} than between Re^{5+} and Nb^{5+}. Thus, the unit cell volume increases by substitution of Re by Nb and Fe by Sc, as expected when introducing larger ions at the octahedral sites (Re^{5+}: 58 pm *vs.* Nb^{5+}: 64 pm, and Fe^{3+} 64.5 pm *vs.* Sc^{3+} 74.5 pm).[12] The partial occupation of Fe sites by Re ions increases with Sc and Nb substitution for these samples and under these synthesis conditions. Rietveld analysis suggests 92.1(2) and 74.1(4)% ordering for the tetragonal Sr_2FeReO_6 and $Sr_2FeRe_{0.9}Nb_{0.1}O_6$ phases, respectively and 78.0(4)% ordering in the orthorhombic $Sr_2Fe_{0.9}Sc_{0.1}ReO_6$. The degree of B-site ordering observed by X-ray powder diffraction is consistent with the results of the Mössbauer study as explained below.

The temperature dependences of the magnetisation under an applied magnetic field of 0.5 T are shown in Fig. 2 for all the phases. No significant changes are observed in the ordering temperatures but appreciable changes were observed in the magnetisation values (Table 1). Around 415 K, there is a sharp change in the magnetisation indicating a transition from a paramagnetic to a ferromagnetic state. Thus, the ferromagnetic transition temperature (T_c) of Sr_2FeReO_6 was estimated to be 410 K, which is comparable to the value reported in the literature.[8] $Sr_2FeRe_{0.9}Nb_{0.1}O_6$ exhibits a lower T_c, above 400 K, and higher values are observed for the $Sr_2Fe_{0.9}Sc_{0.1}ReO_6$ phase.

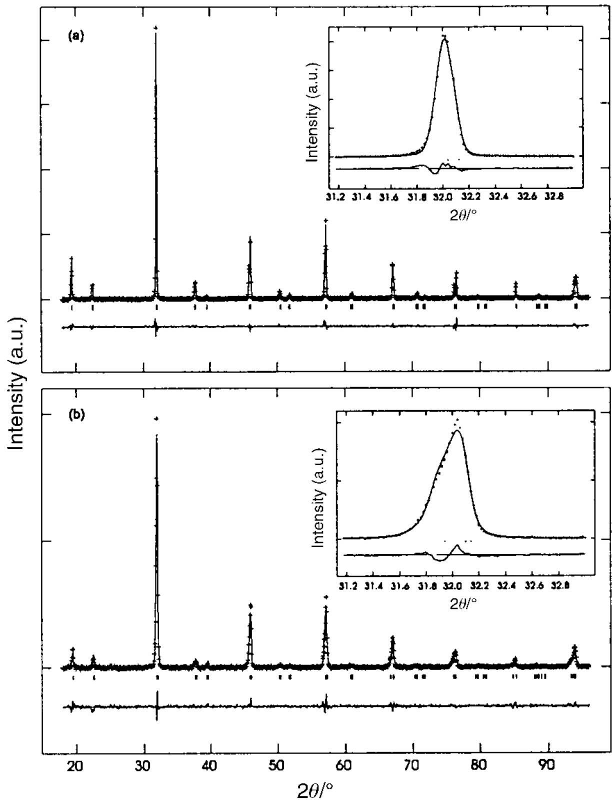

Fig. 1 Rietveld plots from room temperature X-ray powder diffraction data for tetragonal *I4/mmm* Sr_2FeReO_6 (a) and orthorhombic *Immm* $Sr_2Fe_{0.9}Sc_{0.1}ReO_6$ (b).

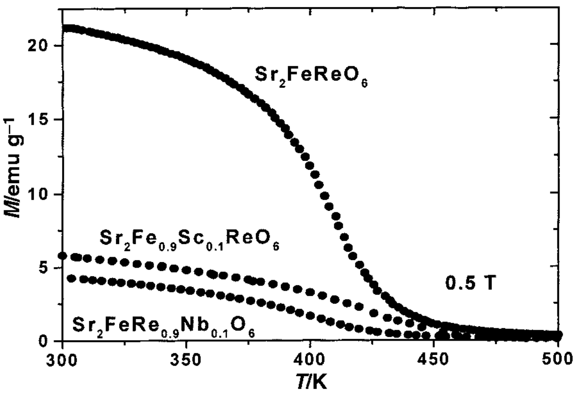

Fig. 2 Magnetisation measurements for the studied compounds in a 0.5 T field.

Magnetoresistance measurements for the Sr_2FeReO_6 phase were carried out at 8 and 300 K with variable field. The MR (8 K, 8 T) and MR (300 K, 8 T) values obtained are 27.4 and 8% respectively. These values are similar to those reported by Kobayashi *et al.*[8] The low-field rapid variation in MR of the sample may arise from a long-range ordering, leading to the half-metallic ferromagnetic state. The hysteresis effects agree with the coercive force observed in the *M*(*H*) curves at the same temperature. The magnitude of the MR is larger at lower

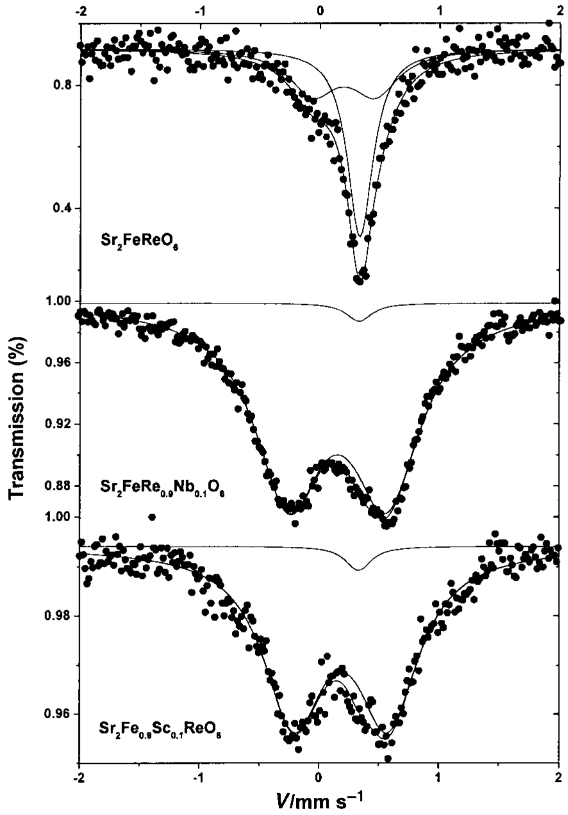

Fig. 3 Mössbauer spectra obtained on the paramagnetic region for the Sr_2FeReO_6, $Sr_2FeRe_{0.9}Nb_{0.1}O_6$, and $Sr_2Fe_{0.9}Sc_{0.1}ReO_6$ compounds.

Table 2 Mössbauer data for the Sr_2FeReO_6, $Sr_2FeRe_{0.9}Nb_{0.1}O_6$, and $Sr_2Fe_{0.9}Sc_{0.1}ReO_6$ compounds in the paramagnetic region

Compound	T/K	δ/mm s^{-1}	Δ/mm s^{-1}	Γ/mm s^{-1}	%
Sr_2FeReO_6	490	0.44(3)	0.0	0.26(2)	54(2)
		0.30(1)	0.52(1)	0.47(2)	46(2)
$Sr_2FeRe_{0.9}Nb_{0.1}O_6$	480	0.44(5)	0.0	0.26(5)	2(2)
		0.26(1)	0.81(2)	0.69(2)	98(2)
$Sr_2Fe_{0.9}Sc_{0.1}ReO_6$	500	0.44(5)	0.0	0.26(5)	3(2)
		0.29(1)	0.78(1)	0.61(2)	97(2)
Sr_2FeMoO_6[15]	475	0.48(2)	0.09(2)	0.28(2)	63(2)
		0.38(2)	0.48(2)	0.34(2)	37(2)

temperature due to the field suppression of the spin dependent scattering, namely field enhancement of carrier tunnelling, at the grain or domain boundaries.

The Mössbauer spectra obtained in the paramagnetic region for Sr_2FeReO_6, $Sr_2FeRe_{0.9}Nb_{0.1}O_6$, and $Sr_2Fe_{0.9}Sc_{0.1}ReO_6$ are displayed in Fig. 3. The spectrum of the Sr_2FeReO_6 phase has been fitted by means of two components: a single line and a quadrupolar doublet with isomer shifts of 0.44 and 0.30 mm s^{-1} respectively (see Table 2). The quadrupole splitting was found to be 0.52 mm s^{-1}. The different hyperfine parameters are compared to those of Sr_2FeMoO_6 in Table 2. One observes that the isomer shifts for the singlets (majority spectrum) are consistent with values previously reported for related compounds, suggesting an intermediate state $Fe^{2+/3+}$ for the iron ions.[13–15] The minority subspectrum corresponding to about 46% of the total absorption is attributed to some disorder of the Fe and Re ions.[16] Each misplaced iron influences the spectrum of a further six iron ions. The spectrum is consistent with approximately 8% of iron ions located at the Re sites, in good agreement with the data obtained from the X-ray analysis. The paramagnetic spectra of the substituted oxides show an asymmetric doublet, which can be also interpreted as a combination of a single line and a quadrupolar doublet (see Fig. 3). The values of both the isomer shift and quadrupole splitting are listed in Table 2. The linewidths observed for the doublets are broad. This fact is due to a decrease in the cationic ordering caused by substitutions of either Sc or Nb ions, being higher for the Nb phase. However, these data are not unreasonable and similar values were found in disorder oxides where fluctuations in the local environment tend to result in a distribution of quadrupole splittings.[16,17] In this case, the spectra are more difficult to fit on account of line broadening of the hyperfine pattern. The contribution of the singlet components is within the statistical error (2–3%). The isomer shift values of the main component are consistent with the presence of high spin Fe^{3+} ions, excluding an intermediate state of valence by Fe as encountered in non-substituted compounds.

The Mössbauer spectra at 77 K show the existence of a magnetic order, as illustrated in Fig. 4. They exhibit rather broad and weakly asymmetric lines because of the existence of several magnetic environments of Fe sites within the structures. It is concluded that Fe–Re cationic disorder occurs in Sr_2FeReO_6. Moreover the substitution of either Nb or Sc causes an increasing number of magnetic Fe sites. In the case of Sr_2FeReO_6, the spectrum can be reasonably modelled by means of at least three magnetic sextets, with different values of hyperfine fields and isomer shifts. In addition a small paramagnetic contribution was present in all phases. We also tried to fit the spectra by means of a discrete distribution of hyperfine fields correlated to that of isomer shift but the results were unsuccessful. For the substituted phases, the magnetic part of the spectra was finally well reproduced using at least four magnetic components. Different values of hyperfine field, isomer shift and quadrupolar shift were obtained. The mean values are listed in Table 3 and compared to those of Sr_2FeMoO_6.

Table 3 Mössbauer data for the Sr_2FeReO_6, $Sr_2FeRe_{0.9}Nb_{0.1}O_6$, and $Sr_2Fe_{0.9}Sc_{0.1}ReO_6$ compounds at 77 K

Compound	Sr_2FeReO_6	$Sr_2FeRe_{0.9}$-$Nb_{0.1}O_6$	$Sr_2Fe_{0.9}Sc_{0.1}$-ReO_6	Sr_2FeMoO_6[15]
$\langle\delta\rangle$/mm s^{-1}	0.48	0.54	0.50	0.67
$\langle 2\varepsilon\rangle$/mm s^{-1}	−0.03	−0.03	0.02	0.01
$\langle B\rangle$/T	52.5	49.6	50.2	47.2

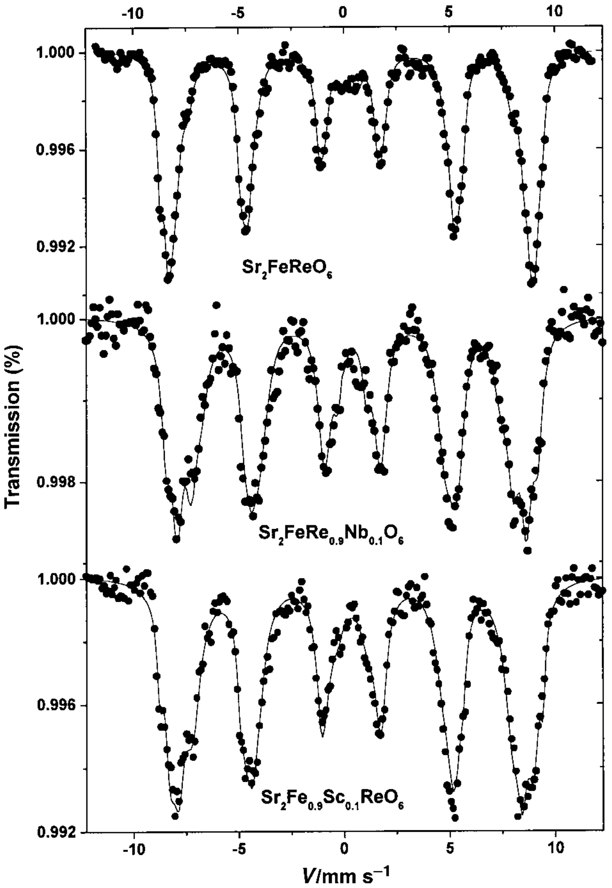

Fig. 4 Mössbauer spectra at 77 K magnetically ordered for the Sr_2FeReO_6, $Sr_2FeRe_{0.9}Nb_{0.1}O_6$, and $Sr_2Fe_{0.9}Sc_{0.1}ReO_6$ compounds.

The spectrum of Sr_2FeReO_6 recorded at 4.2 K is shown in Fig. 5. This spectrum is better resolved than that obtained at 77 K and no small paramagnetic contribution occurs. One clearly observes the presence of non-lorentzian and broadened lines, consistent with Fe–Re cationic disorder as previously suggested. The magnetic sextet was fitted using four principal components with hyperfine fields ranging from 49 to 54 T. The mean hyperfine data are compared to those given for Sr_2FeMoO_6 in Table 4.

The isomer shift values of the hyperfine components in Sr_2FeReO_6 remain close to 0.50 mm s^{-1} at 4.2 K, as typically observed in Fe oxides, being significantly lower than that of Sr_2FeMoO_6.[15] They are unambiguously characteristic of only high spin state Fe^{3+} ions. Such a situation is opposite to that observed in Sr_2FeMoO_6 which displays an intermediate valence state at any temperature.[15] However, it is important to

Table 4 Mössbauer data for Sr_2FeReO_6 at 4.2 K

Compound	T/K	$\langle\delta\rangle$/mm s^{-1}	$\langle 2\varepsilon\rangle$/mm s^{-1}	$\langle B\rangle$/T	%
Sr_2FeReO_6	4.2	0.50(2)	−0.01(2)	52.7(5)	
Sr_2FeMoO_6[15]	4.2	0.63(2)	0.04(2)	49.7(5)	32(2)
		0.72(2)	−0.02(2)	47.7(5)	68(2)

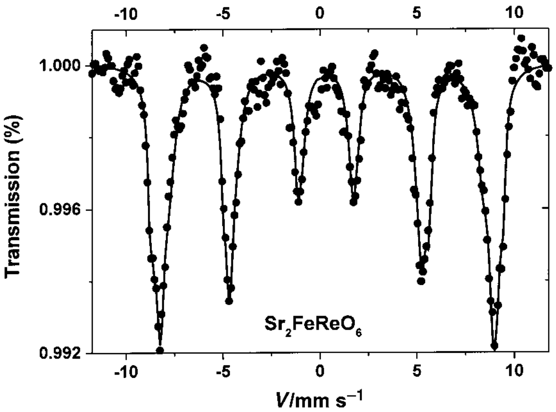

Fig. 5 Mössbauer spectrum at 4.2 K for Sr_2FeReO_6.

emphasize that an intermediate valence also occurs at high temperature for Sr_2FeReO_6, suggesting some temperature dependent electron transfer. The mean hyperfine field of Sr_2FeReO_6 is typical of those encountered in ferric Fe oxides while a significant reduction is noted in the substituted compounds, according to the diamagnetic character of Nb^{5+} and Sc^{3+}. But the present values remain larger than that of Sr_2FeMoO_6.

Consequently, the Mössbauer spectra provide relevant information on both the electronic configuration of iron, the magnetic behaviour and the degree of cationic disorder. It is observed that the degree of disorder of $Sr_2FeRe_{0.9}Nb_{0.1}O_6$ is larger than that of $Sr_2Fe_{0.9}Sc_{0.1}ReO_6$, which is consistent with the results obtained by means of X-ray diffraction.

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