Structure and magnetism in $Sr_2(Fe_{1-x}Al_x)MoO_6$ (0≤x≤0.3) double perovskite compounds

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Abstract
The effect of Fe substitution by Al in $Sr_2(Fe_{1-x}Al_x)MoO_6$ $(0 \leqslant x \leqslant 0.3)$ double perovskites is reported. X-ray diffraction, magnetic measurements and Mössbauer spectroscopy have been used in the investigation. Contrary to other substitutions in similar compounds, Al increases the cationic order up to $x = 0.1$ and beyond. This ordering effect is accompanied by an increase in the magnetic moment per Fe atom, but not by corresponding higher Curie temperatures.

1. Introduction

In the last few years, the possibility to synthesize compounds with high values of room-temperature magnetoresistance has been the scope of much scientific research. Very recently, transition-metal oxides with ordered double perovskite structure $A_2B'B''O_6$ have been found to be suitable materials for this purpose. In these compounds A is usually an alkaline-earth cation that is twelvefold coordinated and B' and B'' are different cations that are six coordinated to oxygen.

Between the many reported compounds [1] of this type already synthesized, Sr_2FeMoO_6 is a promising composition for technical applications due to its high Curie temperature [2] and the existence of room-temperature tunnelling magnetoresistance [3]. The conduction mechanism of this compound has been proposed to arise from the similar energy between the spin-down 3d orbitals of Fe and the 4d orbitals of Mo [4], giving rise to a narrow band. Recent neutron diffraction studies reported by García-Landa *et al* [5] hint at an electronic configuration of $Fe^{2+}Mo^{6+}$, consistent with the ordered magnetic moment observed for $Fe^{2+}(4 \ \mu_B)$. This configuration leads to no local magnetic moment at the Mo sites.

Mössbauer spectroscopy has shown that a mixed valence $Fe^{2+/3+}$ state is likely to occur in these compounds, giving rise to a double exchange mechanism [6, 7] and a metallic state. The mixed valence state has a strong dependence on the cationic order and is very sensitive to any substitution of the cations. Many authors have already reported such substitutions: changing

Fe by Nb and Re by Sc has proved to destroy the $B'B''$ order in Sr_2FeReO_6 [8]. Up to a 70% content of W produces an increase of the order in the $Sr_2Fe(Mo_xW_{1-x})O_6$ composition. This leads to an increase of the Curie temperature and the magnetic moment of the compound. A transition from a ferrimagnetic metal to antiferromagnetic insulator occurs at doping levels around 70–80% of W but any further increase of its content plays the opposite role [9].

However, the substitution of the Fe ion by other cations has not been so extensively studied and has never been observed to increase the cationic order. In this work we present results concerning the Fe substitution by Al in the $Sr_2(Fe_{1-x}Al_x)MoO_6$ double perovskite. It is already well established for perovskites of the $La(Mn_{1-x}Al_x)O_3$ family that low doping levels of Al (up to a 5%) favours the ferromagnetic character via the double exchange mechanism, while for concentrations higher than a 15% the super exchange mechanism is dominant. All this is accompanied by a systematic decrease in the Curie temperature as the Al content increases [10].

As it will be discussed in the following, quite similar behaviour has been found for the double perovskites studied in this work, but Al will increase the $B'B''$ cationic order up to a 10% content and beyond.

2. Experiment

Polycrystalline powders of the family of compounds $Sr_2(Fe_{1-x}Al_x)MoO_6$ were prepared for $0 \leqslant x \leqslant 0.3$, according to the standard solid-state reaction. The starting material was a stoichiometric mixture of $Sr(NO_3)_2$, $Fe(NO_3)_2$, $Al(NO_3)_2$ and MoO_3, calcined at 1573 K for 12 h in a 5% H_2/Ar current flow.

The first crystallographic characterization of these phases was performed by x-ray powder diffraction analysis using a STOE STADI P diffractometer equipped with a Ge III monochromator, working with Cu Kα_1 radiation. The obtained powder diffraction patterns were Rietveld fitted using the GSAS program [11].

Magnetic measurements were conducted in a Quantum Design MPMS-7 SQUID magnetometer. The zero-field cooling (ZFC) and field cooling (FC) curves were performed under an applied field of 10 mT. The ordering temperature, T_c, was determined from the ZFC curves as the temperature where the minimum of the dM/dT derivative occurs. Hysteresis loops measured at 10 K and up to 7 T were also obtained. The value of the low-temperature magnetic moment was determined by Arrott plots.

Mössbauer spectroscopy was performed in the paramagnetic region, well above T_c, using a conventional constant-acceleration spectrometer with a ^{57}Co–Rh source in the transmission geometry. The velocity was calibrated using Fe foil as a standard material. The spectra were fitted using the NORMOS program, developed by Brand *et al* [12].

3. Results and discussion

X-ray powder diffraction patterns were fitted by the Rietveld method and show double perovskite structures of the tetragonal $I4/mmm$ symmetry. The spectra show the existence of two peaks at low angles. This is characteristic of a supercell arising from the ordering of Fe/Al and Mo sites alternatingly. Small amounts of impurities in all the Al-containing compositions were also found, being identified as the non-magnetic oxides $SrMoO_4$ and $Sr_8(Al_{12}O_{24})(MoO_4)_2$. These two oxides appear in almost constant percentages of 7 and 3%, respectively. The recalculated double perovskite compositions remain unchanged in all cases. Figure 1 shows the obtained room-temperature experimental diffraction pattern, the calculated one and their difference for the $x = 0.1$ composition.
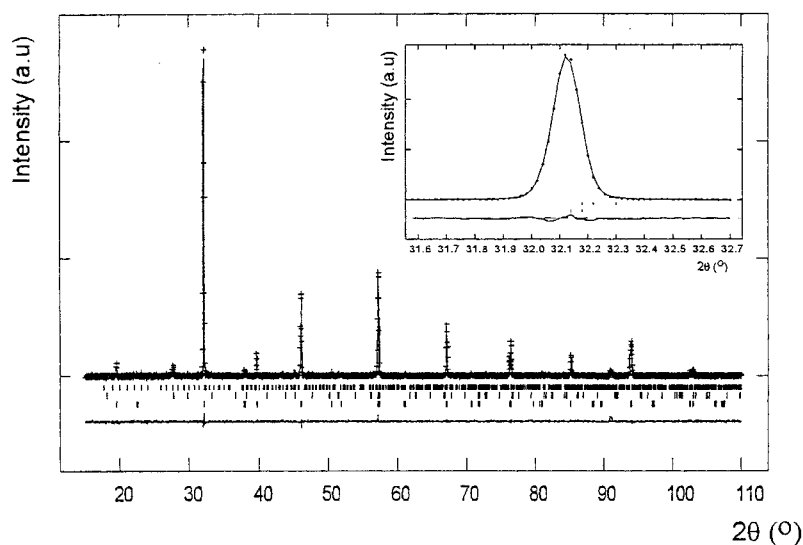
Figure 1. Room-temperature x-ray powder diffraction experimental pattern for the $Sr_2(Fe_{0.9}Al_{0.1})MoO_6$ sample, the calculated one and their difference. The inset shows the obtained fitting for $2\theta = 32.1°$.

Table 1. Refined cell parameters and results from magnetic measurements for the $Sr_2(Fe_{1-x}Al_x)MoO_6$ family of compounds.

	Compound			
	$x = 0$	$x = 0.1$	$x = 0.2$	$x = 0.3$
Space group	$I4/mmm$	$I4/mmm$	$I4/mmm$	$I4/mmm$
a (Å)	5.5728(2)	5.5695(1)	5.5686(1)	5.5771(2)
c (Å)	7.9030(3)	7.8988(2)	7.8940(2)	7.9129(4)
V (Å^3)	245.44(3)	245.01(2)	244.79(2)	246.12(2)
R_{wp}	3.87	4.01	4.18	5.26
R_p	2.53	2.99	3.10	3.75
χ^2	2.76	1.15	1.40	2.66
Per cent ordering	88(1)	91(1)	90(1)	60(3)
$\mu(\mu_B/$formula unit$)$	2.84	3.25	2.52	1.45
$\mu(\mu_B/$Fe atom$)$	2.84	3.61	3.15	2.07
T_c (K)	396	366	358	344

The obtained structural parameters from the refinements are summarized in table 1. We observed a first increase of the $B'B''$ cationic order (compared with the undoped composition) being 90% even for the 20% Al sample. We also estimated a continuous decrease of the cell volume consistent with the smaller radius of the aluminium ions (Al^{3+}: 53.5 pm) as compared with the iron ions (Fe^{3+}: 64.5 pm) [13]. However, this tendency is broken for the corresponding $x = 0.3$ composition, most probably because this sample shows the highest degree of cationic disorder. The fact that increasing disorder leads to a higher volume cell has been previously reported for other ABO_3 perovskite-like compounds [14]. The degree of ordering deduced from x-ray diffraction patterns is, however, very close for all compounds with $x \leqslant 0.2$. Further confirmation of the role of Al must be given by magnetic and Mössbauer measurements.
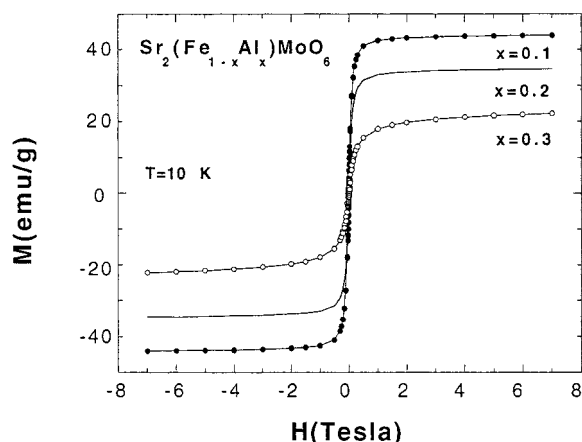
Figure 2. Hysteresis loops measured at 10 K and up to 7 T, for the Al-doped samples.
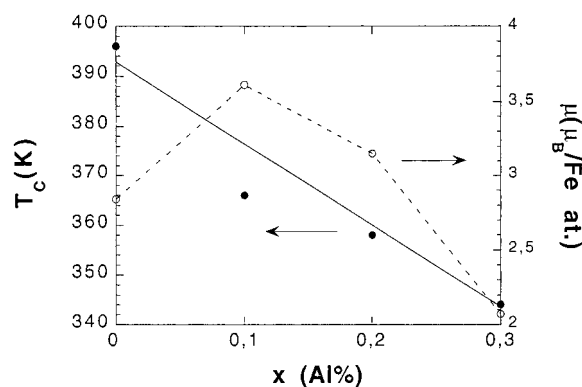

Figure 3. Evolution of T_c and $\mu(\mu_B/\text{Fe}$ atom) with temperature, for the $Sr_2(Fe_{1-x}Al_x)MoO_6$ studied family of compounds. The lines are guides for the eyes.

From magnetic measurements we estimated a Curie temperature of 396 K and a magnetic moment of 2.85 μ_B for the Sr_2FeMoO_6 parent compound, in good agreement with the values reported in the literature [2–5]. A continuous decrease on the Curie temperature from this value is observed as the Al content increases in the samples. However, this is accompanied by a first increase, with respect to the undoped composition, of the measured low-temperature magnetic moment. The measured hysteresis loops for the Al-containing samples are shown in figure 2. For the $x = 0.1$ compound, we measured 3.25 μ_B/formula unit and 3.61 μ_B/Fe atom, if they are assumed to be the only magnetic atoms in the compound. With such an assumption the Fe moment is still larger than in the parent compound for the 20% Al substitution, but a decrease of the moment is found for higher Al content (see table 1). Figure 3 shows this behaviour of T_c and $\mu(\mu_B/\text{Fe}$ atom) with temperature.

Some of the Mössbauer spectra obtained in the paramagnetic region are displayed in figure 4. All the spectra were fitted using two components: a single line and a quadrupolar doublet with isomer shifts ranging between 0.47–0.50 and 0.26–0.32 mm s^{-1} respectively. The obtained hyperfine parameters for the studied compositions are shown in table 2. The isomer shift value of the main component (the singlet) is consistent with the presence of a
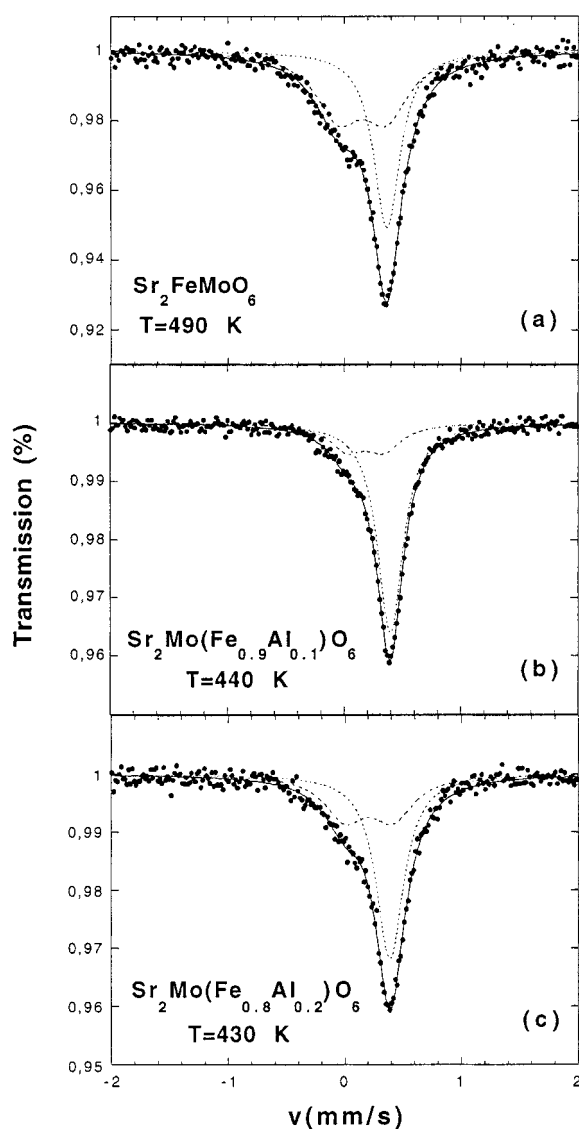
Figure 4. Mössbauer spectra obtained in the paramagnetic region for some of the samples studied in this work.

mixed valence state $Fe^{3+/2+}$, and that of the doublets indicates the existence of high-spin Fe^{3+} ions in distorted sites. On the other hand, the linewidths observed for the doublets are broad. This indicates a somewhat disordered site for the Fe^{3+} ions, which can be ascribed to sites with a cationic disorder. The relative amount of each component is then a measure of the cationic order in the compound. Note, however, that a disordered Mo–Fe pair affects to a maximum of six neighbour atoms, so that the disordered observed by x-ray diffraction experiments turns out to be more increased than in Mössbauer spectra. As it is evident at first sight in figure 4, the data in table 2 indicates a first increase and then a decrease in the cationic order caused by the substitution of Fe by Al atoms. The increase in order (again compared with the undoped

Table 2. Mössbauer data for the $Sr_2(Fe_{1-x}Al_x)MoO_6$ family of compounds obtained in the paramagnetic region.

Compound	T (K)	δ (mm s^{-1})	Δ (mm s^{-1})	Γ (mm s^{-1})	Fraction per cent
$x = 0$	490	0.26	0.41	0.47	44
		0.47	—	0.27	56
$x = 0.1$	440	0.29	0.31	0.36	15
		0.50	—	0.26	85
$x = 0.2$	430	0.30	0.41	0.43	23
		0.49	—	0.28	77
$x = 0.3$	430	0.32	0.43	0.49	51
		0.50	—	0.32	49
Sr_2FeMoO_6[a]	475	0.38	0.48	0.34	37
		0.48	—	0.28	63

[a] Data taken from [6].

composition) is evident up to a 20% Al substitution, and is accompanied by the increase in the magnetic moment per Fe atom, but not by a corresponding one in the Curie temperature. These results strongly confirm those obtained by means of x-ray powder diffraction and magnetic characterization.

In conclusion, we have shown that small amounts of light atoms, such as Al, strongly contribute to stabilize the Sr_2FeMoO_6 double perovskite structure and to improve the magnetic properties of these compounds. When characterizing their structural and magnetic properties, x-ray powder diffraction and Mössbauer spectroscopy have demonstrated that they are powerful tools that give consistent and complementary results.

Acknowledgments

References

[1] Anderson M T, Greewood K B, Taylor G A and Poeppelmier K R 1993 *Prog. Solid State Chem.* **22** 197
[2] Kobayashi K I, Kimura T, Sawada H, Terakura K and Tokura Y 1998 *Nature* **395** 677
[3] Kobayashi K I, Kimura T, Sawada H, Terakura K and Tokura Y 1999 *Phys. Rev.* B **59** 11 159
[4] Sleight A W and Weiher J F 1972 *J. Phys. Chem. Solids* **33** 679
[5] García-Landa B, Ritter C, Ibarra M R, Blasco J, Algarabel P A, Mahendiran R and García J 1999 *Solid State Commun.* **110** 435
[6] Greneche J M, Venkatesan M, Surynarayanan R and Coey J M D 2001 *Phys. Rev.* B **63** 174403
[7] Moussa D E A *Thesis* Université du Maine
[8] Blanco J J, Hernández T, Rodríguez-Martínez L M, Insausti M, Barandiarán J M, Grenèche J M and Rojo T 2001 *J. Mater. Chem.* **11** 253
[9] Ray S, Kumar A, Majumdar S, Sampathkumaran E V and Sarma D D 2001 *J. Phys.: Condens. Matter* **13** 607
[10] Krishnan R V and Banerjee A 2000 *J. Phys.: Condens. Matter* **12** 3835
[11] Larson A C and von Dreele R B 1994 *General Structure Analysis System* (Los Alamos, NM: Los Alamos National Laboratory)
[12] Brand R A, Lauer J and Harlach D M 1984 *J. Phys. F: Met. Phys.* **14** 555
[13] Shannon R D 1976 *Acta Crystallogr.* A **32** 751
[14] Rodríguez-Martínez L M and Attfield J P 1996 *Phys. Rev.* B **54** R15 622