

Structural and magnetic properties of $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeReO}_6$

T. Alamelu and U. V. Varadaraju M. Venkatesan, A. P. Douvalis, and J. M. D. Coey

Citation: *Journal of Applied Physics* **91**, 8909 (2002); doi: 10.1063/1.1451893

View online: <http://dx.doi.org/10.1063/1.1451893>

View Table of Contents: <http://aip.scitation.org/toc/jap/91/10>

Published by the *American Institute of Physics*



Small Conferences. BIG Ideas.

Applied Physics
Reviews

SAVE THE DATE!
3D Bioprinting: Physical and Chemical Processes
May 2–3, 2017 • Winston Salem, NC, USA

The background of the banner features a blue-toned image of a human hand holding a glowing, branching structure that resembles a biological or chemical network, possibly representing a bioprinted structure or a complex material.

Structural and magnetic properties of $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeReO}_6$

T. Alamelu and U. V. Varadaraju

Materials Science Research Centre, Indian Institute of Technology, Madras, India

M. Venkatesan, A. P. Douvalis, and J. M. D. Coey^{a)}

Physics Department, Trinity College, Dublin 2, Ireland

The compounds $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeReO}_6$ ($x=0, 0.2, 0.5, 1.0, 1.5,$ and 2.0) were synthesized by solid state reaction. The resistivity exhibits a metallic behavior for $\text{Sr}_2\text{FeReO}_6$ and insulating behavior for $\text{Ca}_2\text{FeReO}_6$. Structural transformation is observed from tetragonal ($x \leq 1$) to monoclinic ($x \geq 1.5$). The Curie temperature increases from 405 K for $x=0$ to 539 K for $x=2$. The saturation magnetic moment is always less than the $3 \mu_B$ anticipated for a ferrimagnetic configuration of Fe^{3+} and Re^{5+} , suggesting some antisite disorder. All compounds exhibit significant coercivity, which increases with increasing Ca content, from 0.2 T for $x=0$ to 1.1 T for $x=2$. The unexpectedly large coercivity in these compounds is attributed to intrinsic magnetic anisotropy of the Re^{5+} ions. Mössbauer spectra indicate a small admixture of 0.2–0.3 electrons in $3d^1(\text{Fe})t_{2g}$ orbitals. © 2002 American Institute of Physics. [DOI: 10.1063/1.1451893]

I. INTRODUCTION

Current interest in ordered double perovskites is motivated by the desire for half-metallic material with a high Curie temperature T_C in the context of spin polarized transport applications. Kobayashi *et al.*,¹ suggested that $\text{Sr}_2\text{FeMoO}_6$ is a half-metallic ferromagnet¹ with antiferromagnetic coupling of $\text{Fe}^{3+}(3d^5)$ and $\text{Mo}^{5+}(4d^1)$ and a Curie temperature of about 415 K, significantly higher than for any mixed valence manganite.² The objective of the present work is to explore the possible half-metallic behavior in a wide family of ordered double perovskites.^{3–6} $\text{Sr}_2\text{FeReO}_6$ is predicted from band structure calculations⁷ to be a half metal with antiferromagnetic coupling of $\text{Fe}^{3+}(3d^5)$ and $\text{Re}^{5+}(5d^2)$ spins. On the other hand, the compound $\text{Ca}_2\text{FeReO}_6$ (Ref. 8) is a ferrimagnetic oxide with the highest Curie temperature of any double perovskite ($T_C=540$ K). In this article, we studied the crystallographic and magnetic properties of the solid solution $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeReO}_6$, with $x=0, 0.2, 0.5, 1.0, 1.5,$ and 2.0 through x-ray diffraction, magnetization measurements, and Mössbauer spectrometry. The solid solution covers the whole range from low resistivity metallic compounds (Sr rich) to high resistivity insulating compounds (Ca rich) with the ordered perovskite structure.

II. EXPERIMENT

The $\text{Sr}_{2-x}\text{Ca}_x\text{FeReO}_6$ compounds were synthesized by a standard solid state reaction following a procedure reported earlier.⁸ Stoichiometric mixtures of high purity SrO, CaO, Fe_2O_3 , ReO_3 , and Re metal were well mixed, pelletized, and sintered at 900 °C for 24 h in evacuated sealed quartz tubes. The pellets were then reground, repelletized, and sintered at 900 °C for 14 days before quenching into liquid nitrogen. Phase analysis was carried out using x-ray diffraction and Curie temperatures were determined by thermogravim-

etry. The temperature dependence of resistivity was measured using the standard linear four probe method from 5 to 300 K. Magnetization measurements were carried out using a superconducting quantum interference device magnetometer. Mössbauer spectra were recorded in transmission geometry with a $^{57}\text{Co}(\text{Rh})$ source in the constant acceleration mode.

III. RESULTS AND DISCUSSION

$(\text{Sr}_{2-x}\text{Ca}_x)\text{FeReO}_6$ forms a single-phase solid solution throughout the range $0 \leq x \leq 2$. The refined lattice parameters are listed in Table I. The crystal structure changes from tetragonal ($I4/mmm$) for $x \leq 1$ to monoclinic ($P2_1/n$) for $x \geq 1.5$. The lattice parameters a and c decrease monotonically with increasing Ca content.

The variation of resistivity ρ as a function of temperature is shown in Fig. 1. The resistivity increases substantially with increasing Ca content. At room temperature it increases from 3 m Ω cm for $x=0$ to 92 m Ω cm for $x=2.0$. $\rho(T)$ for $\text{Sr}_2\text{FeReO}_6$ exhibits metallic behavior ($d\rho/dT > 0$) with a linear decrease with decreasing temperature. The value of resistivity at 5 K is about 1.8 m Ω cm. This metallic behavior is in agreement with the predicted half-metallic behavior.⁷ The resistivity of $\text{Ca}_2\text{FeReO}_6$ is 5×10^4 times higher than the resistivity of $\text{Sr}_2\text{FeReO}_6$ at 5 K. It should be noted that the room temperature resistivity of half-metallic ferromagnet $\text{Sr}_2\text{FeMoO}_6$ varies from 1 to 100 m Ω cm depending on synthesis conditions.¹ The difference in resistivity between Sr and Ca compounds can be understood on the basis of the difference in their respective crystal structures. The Fe–O–Re bond angle in $\text{Ca}_2\text{FeReO}_6$, with a monoclinic structure, is 154°,⁸ due to the smaller Ca^{2+} ion compared to 180° in tetragonal $\text{Sr}_2\text{FeReO}_6$. The deviation of the Fe–O–Re bond angle from 180° with increasing Ca content reduces the Re–Re overlap and narrows the bandwidth. In addition, Ca also induces monoclinic distortion and lifts the degeneracy of the t_{2g} levels on the Re site. These two factors help to increase the resistivity of Ca substituted compounds.

^{a)} Author to whom correspondence should be addressed; electronic mail: jcoey@tcd.ie

TABLE I. Structural and magnetic properties of $\text{Sr}_{2-x}\text{Ca}_x\text{FeReO}_6$.

Compound	a (Å)	b (Å)	c (Å)	T_C (K)	$\rho(\text{RT})$ (mΩ cm)	m (5 K) ($\mu_B/\text{f.u.}$)	$\mu_0 H_c$ (5 K) (T)
$\text{Sr}_2\text{FeReO}_6$	5.558	—	7.874	405	3	2.67	0.22
$\text{Sr}_{1.8}\text{Ca}_{0.2}\text{FeReO}_6$	5.549	—	7.856	420	19	2.61	0.32
$\text{Sr}_{1.5}\text{Ca}_{0.5}\text{FeReO}_6$	5.538	—	7.836	441	23	2.60	0.33
$\text{Sr}_{1.0}\text{Ca}_{1.0}\text{FeReO}_6$	5.522	—	7.803	473	44	2.43	0.33
$\text{Sr}_{0.5}\text{Ca}_{1.5}\text{FeReO}_6$	5.457	5.532	7.724	509	50	2.40	0.70
$\text{Ca}_2\text{FeReO}_6$	5.404	5.529	7.686	539	92	2.37	1.06

The Curie temperature increases linearly with increasing Ca content from 405 K for $x=0$ to 539 K for $x=2$, as shown in Fig. 2 (inset). The increase in T_C with Ca substitution could be explained by changes in the Fe–O–Re bond. The sum of the Fe–O and Re–O distances in $\text{Sr}_2\text{FeReO}_6$ is 3.98 Å. This sum decreases with increasing Ca content and increases the Curie temperature.

Figure 2 shows the hysteresis loops at 5 K. The magnetization is unsaturated at low temperatures, even in a 5 T magnetic field. The saturation magnetic moment obtained by extrapolating to $1/H^2=0$ is always less than the $3\mu_B$ anticipated for a ferrimagnetic configuration of $\text{Fe}^{3+}(3d^5)$ and $\text{Re}^{5+}(5d^2)$. The extrapolated value is $2.37\mu_B$ for $\text{Ca}_2\text{FeReO}_6$ and $2.67\mu_B$ for $\text{Sr}_2\text{FeReO}_6$. The saturation magnetic moment observed in the present study is greater than reported earlier.^{8,9} The lack of saturation of magnetic moment could be attributed to either antisite defects^{10,11} or the presence of antiphase boundaries which were reported recently in double perovskite thin films¹² and polycrystalline ceramics.¹³ All compounds exhibit significant coercivity both at room temperature and low temperature. The coercivity of all the compounds increases with decreasing temperature. Coercivity at 5 K increases with increasing Ca content, from 0.22 T for $x=0$ to 1.06 T for $x=2$. The remanent magnetization of $\text{Ca}_2\text{FeReO}_6$, the compound with the highest coercivity, is

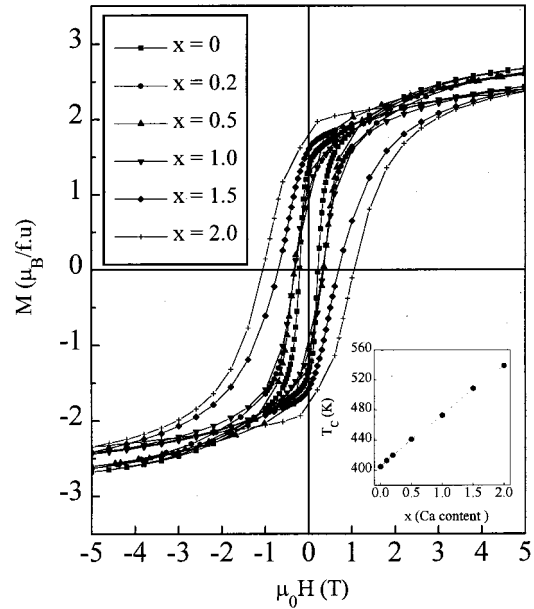


FIG. 2. Hysteresis loops of $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeReO}_6$ at 5 K. Inset shows the variation of T_C with Ca content.

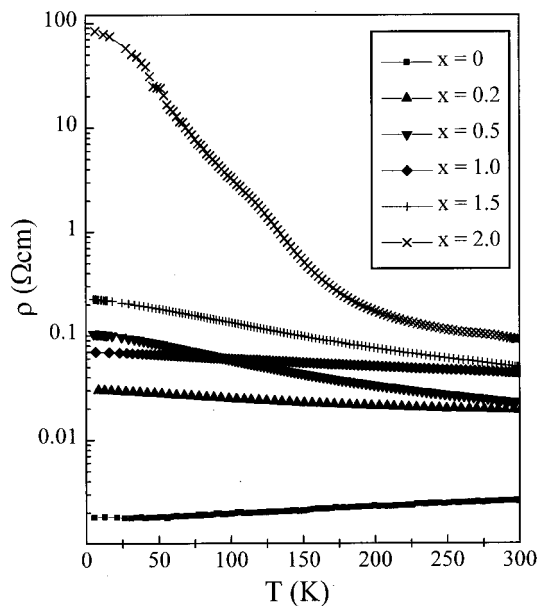


FIG. 1. Resistivity as a function of Ca content in $(\text{Sr}_{2-x}\text{Ca}_x)\text{FeReO}_6$.

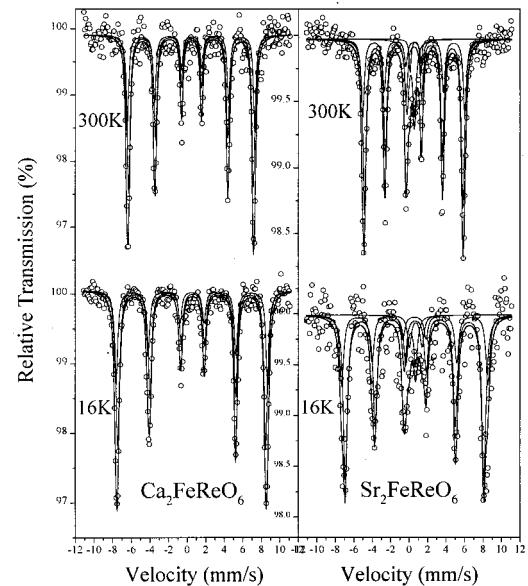


FIG. 3. Mössbauer spectra of $\text{Sr}_2\text{FeReO}_6$ and $\text{Ca}_2\text{FeReO}_6$ at room temperature and 16 K.

TABLE II. Hyperfine parameters of $\text{Ca}_2\text{FeReO}_6$ and $\text{Sr}_2\text{FeReO}_6$ at 300 and 16 K.

Compound	T (K)	δ^a (mm/s)	2ϵ (mm/s)	B (T)	$3d^n$	p (%)
$\text{Ca}_2\text{FeReO}_6$	300	0.52	-0.06	42.2
	16	0.63	-0.07	50.0	5.2	5
$\text{Sr}_2\text{FeReO}_6$	300	0.59	-0.01	33.5
	16	0.71	-0.03	47.4	5.3	6

^aRelative to α -Fe at 300 K.

around $1.78\mu_B$, 75% of saturation. The surprising magnetic anisotropy in these compounds is attributed to intrinsic magnetic anisotropy of the $\text{Re}^{5+}(5d^2)$ ions since little anisotropy is to be expected from the Fe^{3+} ions with a half-filled d shell and no orbital moment in octahedral coordination. The anisotropy field estimated from the magnetization curve on oriented powders of $\text{Ca}_2\text{FeReO}_6$ is 4 T.

Mössbauer spectra of $\text{Sr}_2\text{FeReO}_6$ and $\text{Ca}_2\text{FeReO}_6$ at room temperature and 16 K are compared in Fig. 3. The spectra show hyperfine sextets with narrower lines than the corresponding Mo analogs. The $\text{Ca}_2\text{FeReO}_6$ sample was a single-phase sample, but $\text{Sr}_2\text{FeReO}_6$ showed a small paramagnetic component in the center of the spectra both at 300 and 16 K, which is attributed to a secondary phase produced during the preparation. In order to fit the experimental data we used two components for each spectrum, plus the paramagnetic component in the case of $\text{Sr}_2\text{FeReO}_6$. For each spectrum the component with the large absorption area (main component) is attributed to iron ions, which have a well ordered first neighbor Re environment in the B crystallographic sites. The component with the lower absorption area (secondary component) also has a lower isomer shift and higher hyperfine field than the main component for each compound both at 300 and 16 K. This component is attributed to iron ions with a disordered first-neighbor Re environment in the crystallographic B sites.¹³ The percentage of misplaced Fe ions (p) in the B sites is found to be 5% and 6% for $\text{Sr}_2\text{FeReO}_6$ and $\text{Ca}_2\text{FeReO}_6$, respectively, quite similar to that observed in $\text{Sr}_2\text{FeMoO}_6$.¹³ The misplaced atoms correspond to the antisite defects, which can explain the low temperature spontaneous magnetization of $\text{Sr}_2\text{FeReO}_6$ and $\text{Ca}_2\text{FeReO}_6$. The magnetic moment per formula unit is given by $M = (3 - 6p)\mu_B$, where p is the percentage of misplaced iron ions. The values of p deduced from the intensity of the secondary component in the spectra, assuming only antisite defects leads to moments of 2.70 and 2.64 μ_B for $\text{Sr}_2\text{FeReO}_6$ and $\text{Ca}_2\text{FeReO}_6$, respectively, compared to the measured value of 2.67 and 2.37 μ_B . The experimentally observed magnetization value is in good agreement with the value obtained from this model for $\text{Sr}_2\text{FeReO}_6$. The discrepancy for $\text{Ca}_2\text{FeReO}_6$ suggests that in addition to antisite defects, some antiphase boundaries might also exist there, as found in $\text{Ca}_2\text{FeMoO}_6$.¹³

The weighted average values of δ , B_{hf} , and quadrupole shift (2ϵ) are listed in Table II. We find that the δ values (taking a value of 0.52 mm/s for Fe^{3+} and 1.20 mm/s for Fe^{2+} , as in Sr_2FeWO_6)¹⁴ and the B_{hf} values for both compounds are intermediate between the characteristic values of high spin Fe^{2+} and Fe^{3+} in oxides. However the isomer shift of the Ca compound is smaller than that of the Sr compound. Our results are in accordance with other Mössbauer measurements in these materials.^{8,9} The nonintegral $3d$ electronic configurations deduced for the iron ions in both compounds ($3d^{5.2}$ for $\text{Ca}_2\text{FeReO}_6$ and $3d^{5.3}$ for $\text{Sr}_2\text{FeReO}_6$) can be explained by admixture of electronic charge caused by the hybridization of $\text{Fe } 3d(t_{2g})^{\downarrow}$ and $\text{Re } 5d(t_{2g})$ states.⁷ Judging from the δ and B_{hf} values we can see that the degree of this admixture is smaller for the Ca compound, which is close to a $\text{Fe}^{3+} 3d^{5.2}$ configuration, but greater for the Sr compound, which is metallic, but has a lower Curie temperature.

ACKNOWLEDGMENT

This work forms part of the AMORE Project, supported by the EU Growth Program.

- ¹K.-I. Kobayashi, T. Kimura, H. Sawada, K. Terakura, and Y. Tokura, *Nature* (London) **395**, 677 (1998).
- ²J. M. D. Coey, M. Viret, and S. von Molnar, *Adv. Phys.* **48**, 167 (1999).
- ³M. T. Anderson, K. B. Greenwood, G. A. Taylor, and K. R. Poeppelmeier, *Prog. Solid State Chem.* **22**, 197 (1993).
- ⁴A. W. Sleight and J. F. Weiher, *J. Phys. Chem. Solids* **33**, 679 (1972).
- ⁵A. W. Sleight, J. Longo, and R. Ward, *Inorg. Chem.* **1**, 245 (1962).
- ⁶M. Abe, T. Nakagawa, and S. Nomura, *J. Phys. Soc. Jpn.* **35**, 1360 (1973).
- ⁷K.-I. Kobayashi, T. Kimura, Y. Tomioka, H. Sawada, K. Terakura, and Y. Tokura, *Phys. Rev. B* **59**, 11159 (1999).
- ⁸W. Westerborg, O. Lang, C. Felser, W. Tremel, M. Waldeck, F. Renz, P. Gütlich, C. Ritter, and G. Jakob, *cond-mat/0004275*.
- ⁹J. Gopalakrishnan, A. Chattopadhyay, S. B. Ogale, T. Venkatesan, R. L. Greene, A. J. Millis, K. Ramesha, B. Hannoyer, and G. Maset, *Phys. Rev. B* **62**, 9598 (2000).
- ¹⁰L. Pinsard-Gaudart, R. Suryanarayanan, A. Revcolevschi, J. Rodriguez-Carvajal, J.-M. Greneche, P. A. I. Smith, R. M. Thomas, R. P. Borges, and J. M. D. Coey, *J. Appl. Phys.* **87**, 7118 (2000).
- ¹¹A. S. Ogale, S. B. Ogale, R. Ramesh, and T. Venkatesan, *Appl. Phys. Lett.* **75**, 537 (1999).
- ¹²H. Q. Yin, J. S. Zhou, R. I. Dass, J. P. Zhou, J. T. McDevitt, and J. B. Goodenough, *J. Appl. Phys.* **87**, 6761 (2000).
- ¹³J. M. Greneche, M. Venkatesan, R. Suryanarayanan, and J. M. D. Coey, *Phys. Rev. B* **63**, 174403 (2001).
- ¹⁴H. Kawanaka, I. Hase, S. Toyama, and Y. Nishihara, *J. Phys. Soc. Jpn.* **68**, 2890 (1999).