Synthesis, Structure, and Properties of $LaSr_3Fe_{3-x}Ga_xO_{10-\delta}$: An Intermediate Fe^{3+} Spin State

B. Shankar and H. Steinfink

Department of Chemical Engineering and Materials Science and Engineering Program, The University of Texas at Austin, Austin, Texas 78712

The solid solubility of Ga in this solid solution extends to $x = 2$. A phase change occurs near the composition $x = 1$ from tetragonal to orthorhombic. A Rietveld X-ray powder diffraction structure determination of $LaSr_3FeGa_2O_9$ indicates that Fe occupies the central octahedral interstice in the triple octahedral layer. Oxygen vacancies are present in the equatorial positions of the central octahedron and in the bridging oxygen positions. The phase change is driven by the increase of the c/a ratio of the tetragonal phase. The phases are antiferromagnets with Néel temperatures of 45 K for the tetragonal phases that go to zero for the orthorhombic phase. The effective magnetic moment for the tetragonal phase is 6 μ_B for high spin Fe^{3+}. An intermediate spin state of 4 μ_B is observed for the orthorhombic phase indicative of three unpaired electrons. © 1996 Academic Press, Inc.

INTRODUCTION

As part of an investigation of Ruddlesden–Popper phases with the generic formula $A_{n+1}B_nO_{3n+1}$, $n = 3$, the crystal structure and physical properties of phases $(LaSr_3)(Fe_{3-x}M_x)O_{10-\delta}$, $M = $ Al and Cu, were investigated. The crystal structure, magnetic properties and Mössbauer spectra have been reported (1, 2). The elements Al and Cu had limited solubility ranges in their ability to replace Fe in the octahedral sites of the structure. It was noted that Al preferentially substituted in the middle of the octahedral interstice of the triple octahedral layer. Also, most of the oxygen ion vacancies occurred in the equatorial layer of the central octahedron. We continued the investigation of the effect of substitution on the crystal chemistry and on the physical properties using Ga with the expectation that the extent of solubility should be greater than for Al. A more extensive substitution of a nonmagnetic ion should considerably alter the magnetic properties. We report here the synthesis and properties of the phases $LaSr_3Fe_{3-x}Ga_xO_{10-\delta}$ and the crystal structure of $LaSr_3FeGa_2O_9$.

EXPERIMENTAL

Sample Preparation

Samples with compositions $LaSr_3Fe_{3-x}Ga_xO_{10-\delta}$ were prepared by solid state reactions of stoichiometric amounts of $SrCO_3$, La_2O_3, Fe_2O_3, and Ga_2O_3. Powders were mixed and heated in air at temperatures between 1200 and 1400°C for 24 h. The compounds with $x = 0.2, 0.4, 0.6$, and 0.8 can be obtained between 1300 and 1350°C, but the compound $x = 1$ can be synthesized only between 1400 and 1420°C. Near 1450°C and above the compounds decompose to form cubic perovskites. However, the compositions $x = 1.5$ and 2.0 form at lower temperatures, between 1200 and 1250°C. Single phase material could not be obtained for compositions with $x > 2$. All reaction products were black.

X-Ray Powder Diffraction

The diffraction patterns were obtained with $CuK\alpha$ radiation and a diffractometer equipped with a diffracted beam graphite monochromator. The powder diffraction patterns for the samples $x = 0.2$ to 0.8 could be indexed with a tetragonal cell, space group $I4/mmm$. The crystal structure for compositions $x > 1.0$ to 2.0 is orthorhombic, space group $Fmmm$. The lattice parameters refined by least squares of the powder data are listed in Table 1.

Thermogravimetric Analysis

The analyses were carried out with a Perkin–Elmer TGA-7 system. The curves for $x = 0.2, 0.4, 0.6, 1$, and 2 show that oxygen is reversibly lost on heating and reintercalated upon cooling for all samples except for $x = 2$. Initial weight loss begins at about 130°C and reaches a maximum loss at about 210°C; thereafter oxygen is gradually absorbed until a maximum gain is reached at 350°C after which it is lost continuously until 900°C. Cooling in air causes oxygen resorption. As the Ga content increases from $x = 0.2$, decreasing amounts of oxygen are lost upon heating to 900°C. At $x = 0.2$ the loss is 1.2% while at $x = $

TABLE 1

Lattice Parameters for LaSr$_3$Fe$_{3-x}$Ga$_x$O$_{10-\delta}$

x	a	b	c
0.2	3.858(2)	^{a}	28.11(1)
0.4	3.866(2)	^{a}	28.20(1)
0.6	3.871(2)	^{a}	28.37(2)
0.8	3.865(3)	^{a}	28.57(3)
1.0	5.46(1)	5.51(2)	28.88(4)
1.1	5.440(3)	5.517(3)	29.013(9)
1.5	5.444(3)	5.52(2)	29.048(9)
1.7	5.459(4)	5.499(9)	29.12(2)
2.0^b	5.4219(4)	5.4914(2)	29.1869(10)

^{a} Tetragonal.
^{b} Lattice parameters from Rietveld refinement.

TABLE 2

Positional and Isotropic Displacement Parameters for LaSr$_3$FeGa$_2$O$_9$

Atom^a	Occupancy	Site	x	y	z	$B(\mathring{A}^2)$
($\frac{1}{4}$La, $\frac{3}{4}$Sr)1	1	8i	0	0	0.57716(1)	0.25(6)
($\frac{1}{4}$La, $\frac{3}{4}$Sr)2	1	8i	0	0	0.70177(1)	0.63(6)
Fe	1	4a	0	0	0	0.9(2)
Ga	1	8i	0	0	0.14523(1)	0.7(1)
O1	1	16j	$\frac{1}{4}$	$\frac{1}{4}$	0.1372(5)	1.74
O2	0.760(3)	8i	0	0	0.0709(6)	1.74
O3	1	8i	0	0	0.2150(3)	1.74
O4	0.628(3)	8e	$\frac{1}{4}$	$\frac{1}{4}$	0	1.74
R_P	13.17					
R_{WP}	17.26					
S	3.94					
D-WD	0.37					

^{a} The atom designations are the same as in Ref. (1).

1 it is 0.3%. No appreciable weight loss is observed for the sample $x = 2.0$. As the Ga^{3+} content increases, the ability to charge compensate by the remaining Fe^{4+} decreases, and the oxygen stoichiometry approaches 9. To confirm this, an iodometric analysis was carried out on a sample of composition $x = 2$. A charge balance calculation yielded an oxygen stoichiometry of 9.03.

Previous work had shown that the c axis is a sensitive function of the oxygen stoichiometry (1). Similar behavior occurs in the Ga substituted phases, Fig. 1, but the changes in the c axis reflect both the increasing Ga and the decreasing oxygen content. The transformation of the orthorhombic structure makes these compounds isostructural with La$_4$Ni$_3$O$_{10}$ (3). The substitution of Ga causes the tetragonal cell to rotate 45° so that the orthorhombic cell is $a_{ortho} = \sqrt{2}\, a_{tet}$. This transformation was detected in the diffraction pattern of the samples with x very close to 1 and coincides with the change in slope of the curve in Fig. 1.
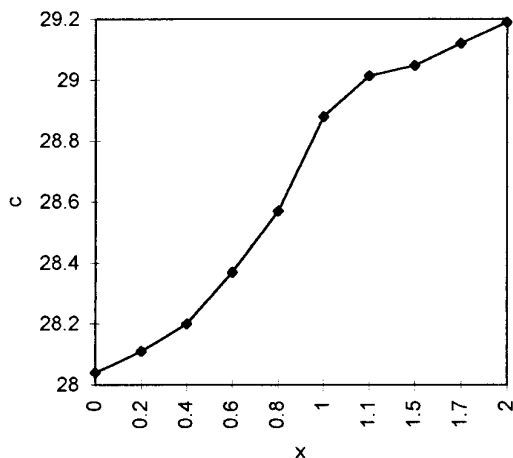
Rietveld Refinement LaSr$_3$FeGa$_2$O$_9$

A total of 5941 reflections were collected covering the 2θ range from 10° to 120° in steps of 0.02° 2θ and 4 s count rate using diffracted beam monochromatized CuKα radiation. The starting parameters were those of LaSr$_3$Fe$_3$O$_{10-\delta}$ after transformation to the orthorhombic space group *Fmmm* (1). The PC version of program DBWS-9006 was used (4). The refinement converged to the parameters shown in Table 2. Since X-ray data Rietveld refinement for oxygen parameters in a heavy atom structure are subject to uncertainties the choice of a model was heavily influenced by the results of the refinement by powder neutron diffraction and single crystal diffraction of the tetragonal phases (1). The oxygen content from the refinement of this data set is 8.78 compared with 9 from the iodometric analysis, lending support to the oxygen vacancy assignments. Figure 2 shows a portion of the refinement profile for LaSr$_3$FeGa$_2$O$_9$. Bond lengths and angles of interest from these coordinates are listed in Table 3.

Magnetic Susceptibility

Data were obtained with a Quantum Design Co 5000 DC SQUID magnetometer between room temperature and 10 K in an applied field of 1 kG. Diamagnetic corrections were applied. The materials are antiferromagnets with the parameters shown in Table 4. The straight line sections of the $1/\chi$ vs T graphs extends from about 100 to 300 K and were used in the calculations of effective moments.

DISCUSSION

The crystal structure of this series of solid solutions consists of a triple layer of corner sharing octahedra separated
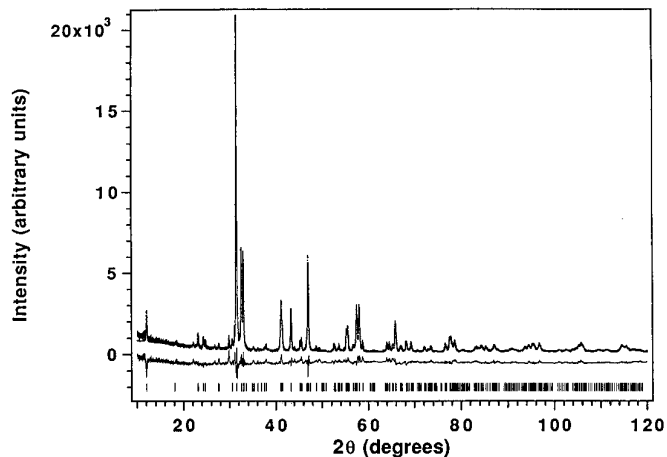

FIG. 1. Variation of c axis with Ga composition, x.

FIG. 2. X-ray Rietveld refinement profile for $LaSr_3FeGa_2O_9$. Points are the raw data and the solid line is the calculated profile. Tick marks below the difference curve show the allowed reflections.

TABLE 4
Magnetic Parameters
for $LaSr_3Fe_{3-x}Ga_xO_{10-\delta}$

x	T_N (K)	μ_{eff} (μ_B)	θ (K)
0.4	45	6.1	−72
0.8	45	6.0	−42
1.0	<15	3.9	−41
2.0		4.0	−48

by (La,Sr)–O layers in the well-known arrangement for Ruddlesden–Popper phases, Fig. 3. The octahedral interstices are occupied by Fe and Ga. The central octahedron of the triple octahedral layer of the orthorhombic structure of $LaSr_3FeGa_2O_9$ has tetragonal symmetry and is elongated along the c axis. The Fe ion was assigned to this interstice not only on the basis of the space group requirement but the assignment was also based on the results of the Rietveld refinements. The assumption of complete random distribution of Fe and Ga over the cation sites led to acceptable R values. When the displacement parameters for these two atoms were refined to their final values and then held constant, the occupancy refinements indicated a smaller electron density in the central octahedron interstice than for the occupant of the outer octahedron. Thus, Fe

was placed into position $4a$ of $Fmmm$ and refinements converged to the values shown in Table 2. The refinement process initially permitted the oxygen displacement parameters to vary with the occupancies fixed at unity. The values for O2 and O4 became large while the values for O1 and O3 were reasonable and were eventually adopted as fixed values for all oxygen atoms. In the final least squares refinement all parameters were fixed except for the oxygen occupancies. The values for O1 and O3 converged to 1 and were fixed at that value; the occupancies for O2 and O4 converged to the values shown in Table 2. The oxygen vacancies found for this compound occur in the same crystallographic positions as previously determined (1).

The outer octahedron maintains the fourfold symmetry but the apical bond lengths differ by 0.13 Å. The longer bond length of 2.170(15) is to the bridging O2. It is noteworthy that the apical bond lengths are almost equal in $LaSr_3Fe_3O_{9.88}$, the nearly stoichiometric compound, but become unequal in the same manner as the oxygen deficiency increases and with Al substitution (1). The Ga ion is 0.23 Å out of the plane of the four O1 ions. The movement away from the center of the equatorial plane is most likely due to the oxygen vacancies in the O2 site, reducing the shielding between the two cations. The (La,Sr) coordi-

TABLE 3
Bond Lengths (Å) and Angles (deg) from Rietveld Refinement of $LaSr_3FeGa_2O_9$

Bond lengths

Fe–O2	2.069(15) × 2	($\frac{1}{4}$La, $\frac{3}{4}$Sr)1–O1	2.606(10) × 4	O1–O1	2.7110(2) × 2
O4	1.92920(8) × 4	–O2	2.7520(10) × 2	O1	2.7457(1) × 2
Ga–O1	1.9434(18) × 4	–O2	2.7168(10) × 2	O2	2.73(1) × 4
O2	2.170(15)	–O4	2.965(2) × 4	O3	2.298 × 4
O3	2.037(9)	($\frac{1}{4}$La, $\frac{3}{4}$Sr)2–O1	2.697(10) × 4	O2–O4	2.83(1) × 4
		–O3	2.7731(13) × 2	O3–O3	3.42(1) × 2
		–O3	2.7381(13) × 2	O3	3.39(1) × 2
		–O3	2.428(9)	O4–O4	2.7110(2) × 2
				O4	2.7457(1) × 2

Bond angles

O1–Ga–O1	166.2(6)
O1–Ga–O1	88.44(7)
O1–Ga–O1	89.90(8)
O1–Ga–O2	83.1(4)
O1–Ga–O3	96.9(4)

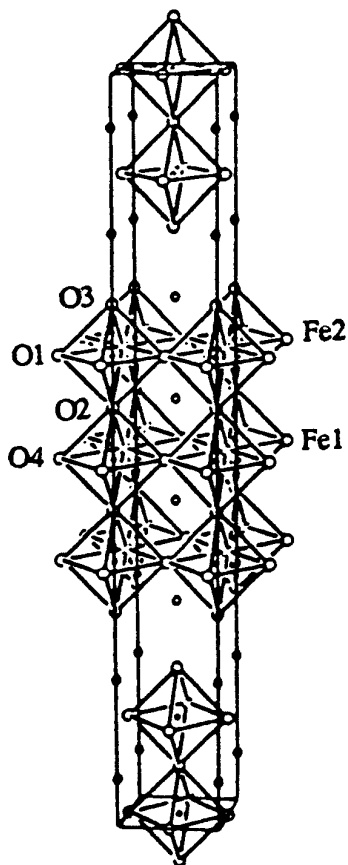**FIG. 3.** The crystal structure of the tetragonal unit cell for LaSr$_3$Fe$_{3-x}$Ga$_x$O$_{10-\delta}$. Open circles connected by bonds are oxygen; solid circles within the octahedra are Fe/Ga; nonbonded open circles are La/Sr. The oxygen levels are labeled (1).

the *c* vs *x* curve at that composition, Fig. 1. The phase change is driven by the increasing *c/a* ratio. The *c* axis increases nearly 1 Å between *x* = 0 and 1.1. The structure becomes unstable and changes to the orthorhombic configuration. Further Ga substitution results in a smaller rate of increase of *c/a*. On the other hand, the compound LaSr$_3$Fe$_3$O$_{10-\delta}$ does not exhibit this phase transformation. Its *c* axis expands about 0.5 Å for $0.8 \geq \delta \geq 0.1$ and the structure becomes less stable with increasing oxygen vacancies. When $\delta = 0.8$ the compound changes to a perovskite in less than 10 min at room temperature.

The compounds are antiferromagnets and insulators. The Weiss constant and the other magnetic parameters shown in Table 4 display distinct changes at the phase transformation. The Neél temperature for the tetragonal phase is 45 K but goes to zero for the orthorhombic phase because of the increasing Ga concentration. Most notable is the change in μ_{eff}. For the tetragonal structure the value is consistent with the presence of high spin Fe^{3+}, while for the orthorhombic structure it indicates an intermediate spin state. The oxygen vacancies of the Fe coordination octahedron distort it and raise the energy levels of the spin-up *d* electron manifold to where they overlap the spin-down levels. The highest energy spin-up electron transfers into a lower lying, empty, spin-down state giving rise to three unpaired Fe spins and a μ_{eff} of 4 μ_{B}.

ACKNOWLEDGMENT

REFERENCES

1. J. Y. Lee, J. S. Swinnea, H. Steinfink, W. M. Reiff, S. Pei, and J. D. Jorgensen, *J. Solid State Chem.* **103,** 1 (1993).
2. W. M. Reiff and H. Steinfink, *Z. Anorg. Allg. Chem.* **616,** 172 (1992).
3. C. Brisi, M. Vallino, and F. Abbattista, *J. Less-Common Met.* **79,** 218 (1981).
4. A. Sakthivel and R. A. Young, "User's Guide to Programs DBWS-9006 and DBWS-9006PC." Georgia Institute of Technology, 1993.

nation polyhedra are similar to those previously determined (1) except for the orthorhombic distortion of the bond lengths to O2 and O3.

The powder X-ray diffraction patterns indicated that the phase change from tetragonal to orthorhombic occurred at approximately *x* = 0.9. There is an inflection point in