JOURNAL OF SOLID STATE CHEMISTRY 36, 1–8 (1981)

Magnetic and Electrical Properties in the Defect Perovskite System $La_{1-x}Na_xFeO_{3-\delta}$

HIROSHI YAMAMURA, HAJIME HANEDA, SHIN-ICHI SHIRASAKI

National Institute for Research in Inorganic Materials, 1-1, Namiki, Sakura-Mura, Niihari-Gun, Ibaraki, Japan

AND KOU TAKADA

Faculty of Engineering, Chiba University, Yayoi-Cho, Chiba, Japan

Received November 6, 1979; in revised form March 17, 1980

Magnetic and electrical properties were studied for the defect perovskite system $La_{1-x}Na_xFeO_{3-\delta}$. X-Ray diffraction showed that the materials with a composition range $x = 0.0$–0.25 were monophasic perovskite-like compounds with orthorhombic symmetry. The present ferrite solid solution showed a parasitic-ferromagnetic property, accompanying the antiferromagnetism. Values of both ferromagnetic moment and magnetic susceptibility increased with increase in Na content. Furthermore, the magnetization was strongly affected by oxygen partial pressure. These experimental facts seem to have a close relation with the oxygen vacancies. Electrical conductivity measurements suggested the presence of mixed valencies of Fe^{3+} and Fe^{4+} on a basis of the compositional dependence of the conductivity and its activation energy.

Introduction

Perovskite-type compounds are very important because of their application to electroceramic devices. However, their electric and magnetic properties are very sensitive to the presence of impurities and lattice defects.

The space group of $LaFeO_3$ has been determined as $Pbnm(D_{2h}^{16})$ by Geller and Wood (*1*). This structure is a distorted perovskite with four equivalent iron ions per unit cell. Neutron diffraction has indicated that each Fe^{3+} ion is surrounded by six Fe^{3+} neighbors whose spins are alternately antiparallel (G-type structure) (*2*). $LaFeO_3$ shows a parasitic ferromagnetism, which was first reported by Forestier and Güiot-Guillain (*3*).

In perovskite-type structures containing iron such as $La_{1-x}Sr_xFeO_{3-\delta}$ (*4*) and $SrFeO_{3-\delta}$ (*5*), it is often seen that the iron ion is in the state of mixed valencies of Fe^{3+} and Fe^{4+}, accompanied by oxygen nonstoichiometry. However, information on their defect structures is not extensive. Recently, Grenier *et al.* (*6*) have investigated the defect structure intermediate between the brownmillerite and the perovskite type in the system $CaTiO_3$–$Ca_2Fe_2O_5$.

The present study concerns the oxygen defect-perovskite system $La_{1-x}Na_xFeO_{3-\delta}$, in which La^{3+} is replaced by Na^+ in order to control the oxygen content. The present authors have already reported the Mössbauer spectra for this system (*7*). In addition, some interesting magnetic behavior was observed, which is expected to be

0022-4596/81/010001-08$02.00/0

applicable to electroceramic devices. It seems to originate from the presence of the oxygen vacancy and the mixed valencies of Fe^{3+} and Fe^{4+}.

Experimental Procedures

Intimate mixtures of the constituent reagents, Fe_2O_3, La_2O_3, and Na_2CO_3 in the desired ratio were prefired at 1000°C in air. After the prefired powder sample was pressed into a disk, it was fired at 1200°C in air and then air quenched. Firing time was changed from 20 to 5 hr as the Na content of the sample increased because of its good sinterability and of the control of Na vaporization. La_2O_3 was heat-treated at about 1000°C before weighing due to its hygroscopic property.

In order to check the amount of Na vaporization, a chemical determination of Na content was made using a flame photometry method. In this series, it is presumed that the materials have not only oxygen vacancies, but also the mixed valencies of Fe such as Fe^{3+} and Fe^{4+} due to the deficiency of cation charge. Since it is well known that Fe^{4+} does not occur by firing *in vacuo* (*8*), we tried to estimate Fe^{4+} content by the measurement of weight gain, when the sample was again heat-treated in air after its heat treatment at 800°C *in vacuo* ($\sim 2 \times 10^{-5}$ mm Hg).

Magnetic susceptibility and magnetization were measured using the Faraday-type magnetic balance (Shimazu Co.). The present ferrite system shows a parasitic ferromagnetic property, accompanying the antiferromagnetism. Therefore, both the magnetic susceptibility (χ_g) and the spontaneous magnetization (σ_0) were separately estimated from the magnetic field dependence, according to the equation, $\sigma_g = \sigma_0 + \chi_g H$, where σ_g and H represent total magnetization and magnetic field, respectively. Paramagnetic Mohr's salt and $Co[Hg(SCN)_4]$, the susceptibilities of which are 32.6×10^{-6} and 16.4×10^{-6} emu/g at 20°C, respectively, were used as standard materials. Electrical conductivities were measured from room temperature to 400°C in air. Four-probe and two-probe methods were used appropriately for the specimens with the composition $x = 0.0$, 0.05, and 0.15 in the system $La_{1-x}Na_xFeO_{3-\delta}$.

The Mössbauer spectra at room temperature were taken using a commercial spectrometer (Elscient Co.) working in a constant acceleration mode and ^{57}Co dispersed in a Pd matrix as a source. The velocity in millimeters per second was calibrated relative to metallic iron foil.

Experimental Results

X-Ray diffraction showed that the materials with compositional range $x = 0.0$–0.25 were monophasic perovskite-like compounds with orthorhombic symmetry within the limits of detection of the X-ray method. When Na content is over $x = 0.25$, the α-$NaFeO_2$ phase appeared along with the perovskite-type phase. Figure 1 shows the compositional change in the lattice constant, which is approximated to the cubic perovskite structure. The lattice constant

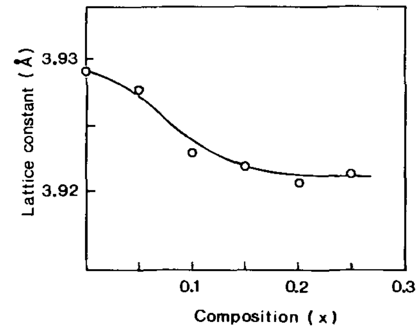

FIG. 1. Compositional change in the lattice constant in the system $La_{1-x}Na_xFeO_{3-\delta}$.

decreased steeply at first, and gradually later as Na content increased.

The result of the chemical analysis showed that no loss of sodium was detected for the sample with $x = 0.05$ and 0.10, and that Na vaporization was around 10 wt% for the samples with the higher Na content.

The amount of Fe^{4+}, which was estimated from the weight change, was 0.8 wt% of the total Fe content for the sample with $x = 0.05$, and increased gradually with increase in Na content in the samples. The chemical composition of this system can, therefore, be determined as a basis of the equation, $La_{1-x}Na_yFe^{3+}_{1-z}Fe^{4+}_zO_{3-(3x-y-z)/2}$, where x, y, and z are initial La content, Na content observed, and Fe^{4+} content estimated, respectively. The results are summarized in Table I.

The relation between magnetization and magnetic field, and the temperature dependence of the magnetization were investigated over the composition range, x = 0.0–0.25. The parasitic ferromagnetic component varied with Na content, measuring atmosphere, and cooling in the magnetic field after heat treatment above the Néel temperature.

Typical magnetic data in the present solid-solution system are summarized in Table II. Values of both χ_g and σ_0 increased with increase in Na content, and decreased at $x = 0.25$.

TABLE I

CHEMICAL FORMULAS IN THE SYSTEM $La_{1-x}Na_xFeO_{3-\delta}$

Composition (x)	Chemical formula
0.0	$LaFeO_3$
0.05	$(La_{0.95}Na_{0.049})Fe^{3+}_{0.992}Fe^{4+}_{0.008}O_{2.954}$
0.10	$(La_{0.10}Na_{0.098})Fe^{3+}_{0.988}Fe^{4+}_{0.012}O_{2.905}$
0.15	$(La_{0.85}Na_{0.135}\square_{0.015})Fe^{3+}_{0.987}Fe^{4+}_{0.013}O_{2.847}$
0.20	$(La_{0.80}Na_{0.179}\square_{0.021})Fe^{3+}_{0.984}Fe^{4+}_{0.016}O_{2.798}$
0.25	$(La_{0.75}Na_{0.220}\square_{0.028})Fe^{3+}_{0.963}Fe^{4+}_{0.983}Fe^{4+}_{0.017}O_{2.744}$

TABLE II

MAGNETIC DATA IN THE SYSTEM $La_{1-x}Na_xFeO_{3-\delta}$

Composition (x)	$\chi_g \times 10^{6\,a}$ (emu/g)	$\chi_g \times 10^{6\,b}$ (emu/g)	σ_0^a (emu/g)	σ_0^b (emu/g)	T_N (°C)
0.0	8.7	8.7	0.018	0.018	461
0.05	16.0	13.3	0.830	0.587	425
0.10	33.7	30.9	2.12	1.79	415
0.15	47.7	50.0	2.76	2.40	410
0.20	60.0	62.7	3.89	3.53	400
0.25	31.1	39.3	2.27	1.95	407

[a] In air.
[b] In vacuum.

Temperature dependence of the total magnetization is shown typically in Fig. 2 for the sample with $x = 0.25$. The thermomagnetization curves showed a thermal hysteresis, i.e., different behavior in heating and cooling measurements. The magnetization at room temperature before heating was smaller than that after cooling in the magnetic field. In order to investigate the origin, the magnetization was measured as a function of magnetic field, as shown in Fig. 3. After cooling in the magnetic field, the magnetic parameters for the sample with $x = 0.25$ were $\chi_g = 31.1 \times 10^{-6}$ emu/g

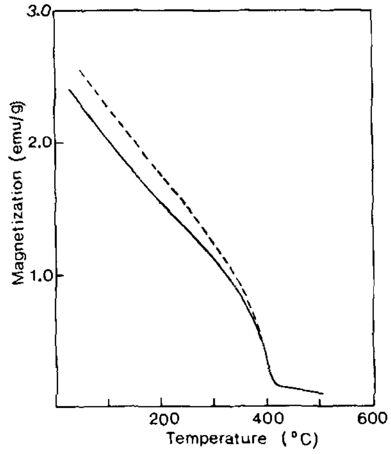

FIG. 2. Temperature dependence of the magnetization for the sample with $x = 0.25$ at $H = 11.5$ kOe.

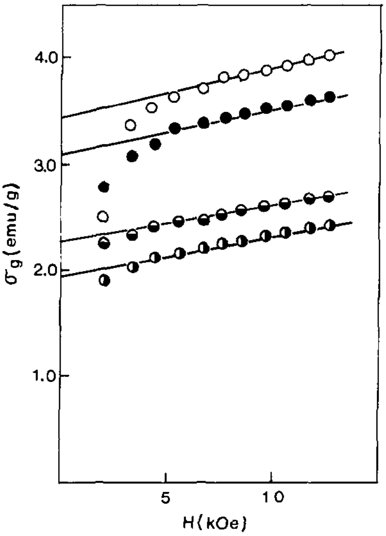

FIG. 3. Magnetization curve at room temperature for the sample with $x = 0.25$ under the various conditions; in air (○), *in vacuo* (◒), *in vacuo* after cooling in magnetic field (○), and again in air after being left for a day after the introduction of air (●).

and $\sigma_0 = 2.27$ emu/g, whereas the magnetic susceptibility remained constant. The ratio of the σ_g value before heating to that after cooling in magnetic field *in vacuo* was 3.67 for $LaFeO_3$ at room temperature and decreased with increasing Na content, i.e., 1.33, 1.20, 1.14, 1.07, and 1.10 for the samples with $x = 0.05, 0.10, 0.15, 0.20$, and 0.25, respectively.

The Néel temperature of $LaFeO_3$ was 461°C which agreed with the reported values, 460°C (*9*) and 465°C (*10*). However, the Néel temperature of the present solid solution decreased with Na content and reached about 400°C at $x = 0.25$ (Table 2).

It was found that the σ_g values of these materials were very sensitive to the experimental atmosphere. Thus, the magnetization at room temperature was traced as a function of time, after the atmosphere in a closed vessel was degassed to about 10^{-3} mm Hg. Figure 4 shows the relation between $\sigma_g(t)/\sigma_g(0)$ and t, where $\sigma_g(0)$ and $\sigma_g(t)$ represent the room-temperature values of the total magnetization before degassing and at a given time *in vacuo* after degassing, respectively. It can be seen that the $\sigma_g(t)/\sigma_g(0)$ value sharply decreased in early stages and then saturated over an extended time. The $\sigma_g(t)/\sigma_g(0)$ value at saturation decreased with increase in Na content, up to $x = 0.25$, i.e., the solubility limit of Na. At the composition $x = 0.30$, the change in the σ_g value was almost insensitive to atmosphere. Care was taken to see that the reduced value of σ_g was almost recovered in the measurement after the introduction of air. However, no recovery in the reduced magnetization was obtained by introduction of inert gases such as N_2 and He. The variation of σ_g, therefore, should be associated with oxygen partial pressure only. In addition to the magnetization curve for the sample with $x = 0.25$ cooled in the magnetic field, Fig. 3 also shows the magnetization curves at room temperature under three different conditions: (a) in atmospheric pressure, (b) *in vacuo* (about 10^{-3} mm Hg), and (c) again in atmospheric pressure after being left for a day after introduction of air into the vessel for the same sample. The χ_g values remained constant, irrespective of the measuring atmosphere, whereas the σ_0 values were influenced considerably by the surrounding atmosphere. The change in σ_g

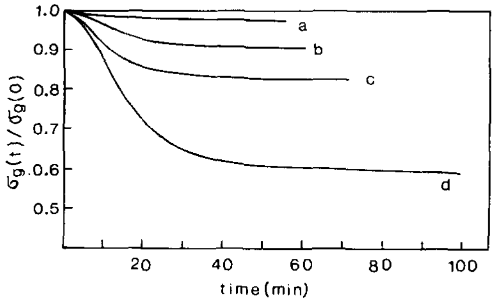

FIG. 4. Change in the $\sigma_g(t)/\sigma_g(0)$ value as a function of time at room temperature for the system $La_{1-x}Na_xFeO_{3-\delta}$: (a) $x = 0.10$, (b) $x = 0.15$, (c) $x = 0.20$, and (d) $x = 0.25$.

may, therefore, be interpreted in terms of the change in σ_0. On the other hand, the magnetization of the sample heat-treated at 800°C *in vacuo* was not influenced by the surrounding atmosphere at room temperature. This fact suggests that the change in magnetization with surrounding atmosphere has a close relation not only with oxygen vacancies, but also with mixed valencies such as Fe^{3+} and Fe^{4+}.

The Mössbauer spectrum of $LaFeO_3$ (x = 0.0) in Fig. 5a consists of a six-line pattern characteristic of an antiferromagnetic material. The values of the isomer shift (I.S.) and the internal magnetic field (H_i) were +0.403 mm/sec and 526 kOe, respectively, which agreed well with previously reported values for octahedrally surrounded Fe^{3+} in lanthanum orthoferrite (*8*).

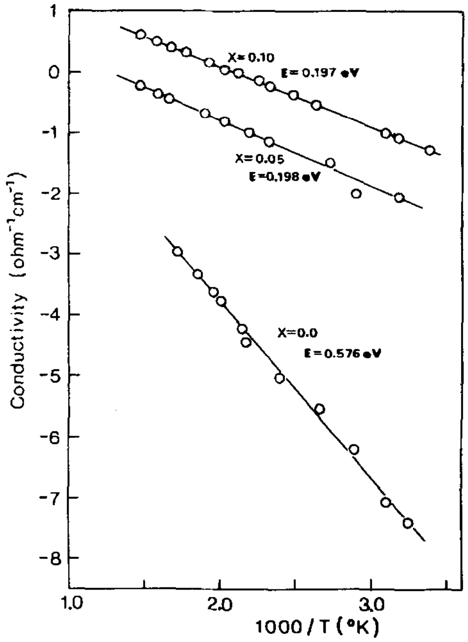

FIG. 6. Electrical conductivity as a function of temperature in the system $La_{1-x}Na_xFeO_{3-\delta}$.

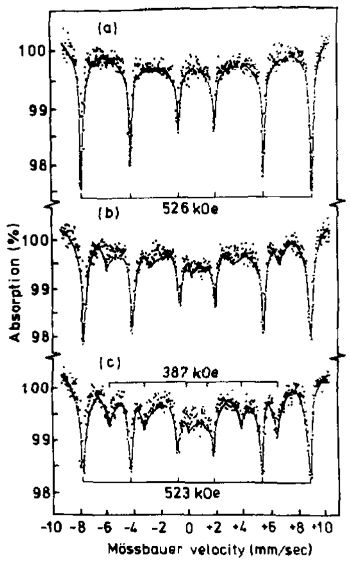

FIG. 5. Mössbauer spectra at room temperature in the system $La_{1-x}Na_xFeO_{3-\delta}$: (a) x = 0.0, (b) x = 0.15, and (c) x = 0.25.

In the materials with $x \geq 0.15$, a new six-line pattern appeared in addition to that of the octahedral Fe^{3+}; the intensity of the new peak increased as x increased (Figs. 6b and c). The values of I.S., H_i, and quadrupole splitting (ΔE_Q) of the new pattern were +0.193 mm/sec, 387 kOe, and 0.010 mm/sec, respectively. The respective Mössbauer parameters of the two six-line patterns remained almost constant regardless of the composition. The absorption lines of the octahedrally surrounded Fe^{3+} became broad with increase in Na content; the linewidth for the material with x = 0.25, for example, was two times larger than that for $LaFeO_3$.

The Mössbauer parameters for the new six-line pattern agreed with those for tetrahedrally surrounded Fe^{3+} in $Ca_2Fe_2O_5$ with a brownmillerite-type structure, which has two crystallographically nonequivalent Fe^{3+} sites, i.e., octahedral and tetrahedral sites (*11*). It was also noted that the peak intensity ratio of the octahedral site to the tetrahedral site in the new six-line group, for example, was 2.8 in the material with x = 0.25. This value clearly agreed with the existent ratio (0.75/0.25 = 3.0) of the respective sites calculated by assuming that each oxygen vacancy introduced into the material reduces the coordination number of one Fe site from 6 to 4. It may, therefore, be concluded that the new peak corresponds to Fe^{3+} in tetrahedral sites.

Figure 6 shows the electrical conductivity as a function of temperature. The conductivity (σ_c) of $LaFeO_3$ was 2.8×10^{-8} ohm^{-1} cm^{-1} at room temperature and its activation energy was 0.58 eV. The σ_c value increased with increase in Na content, while the activation energy lowered to 0.20 eV for the samples containing Na, remaining constant irrespective of Na content. The high conductivity and the low activation energy of the samples containing Na support the presence of mixed valencies of iron ion. In studies of conductivity measurement, it is well known that the activation energy for conductivity of spinel-type ferrites and garnets is around 0.5 eV and that their conductivity at room temperature is 10^{-8}–10^{-10} ohm^{-1} cm^{-1} and increases considerably with incorporation of impurities or lattice defects due to the occurrence of the mixed valencies of Fe^{2+} and Fe^{3+} (*12*).

Discussion

It was found that La^{3+} ($r = 1.06$ Å) could be replaced by Na^+ ($r = 1.062$ Å) in the orthoferrite structure up to $x = 0.25$. The substitution of Na^+ in place of La^{3+} will result in cation-charge deficiency. This charge deficiency may be compensated in three ways, i.e., (a) change in the valence state from Fe^{3+} to Fe^{4+}, (b) occurrence of oxygen vacancies, and (c) a state intermediate to (a) and (b). The system $(La,Sr)FeO_3$ prepared under high oxygen pressure corresponds to case (a). On the other hand, the same solid-solution system prepared *in vacuo* corresponds to case (b). $SrFeO_{3-\delta}$ prepared by firing in air has both oxygen vacancy and mixed valencies of Fe^{3+} and Fe^{4+} (case (c)). It was found in the present solid-solution system that the cation-charge deficiency due to the substitution of Na^+ in place of La^{3+} could be compensated mostly by oxygen vacancies and partly by the mixed valencies of Fe^{3+} and Fe^{4+} (Table I). The assumption of the presence of Fe^{4+} may be reasonable considering the following experimental facts: (a) the electrical conductivity of the ferrites containing Na was abnormally high, compared to that of pure $LaFeO_3$, and (b) the reversible weight change was observed by changing oxygen partial pressure. However, Mössbauer spectroscopy did not detect Fe^{4+}, supposedly because the Mössbauer effect cannot always detect separately the mixed valencies due to the rapid electronic exchange between them (*4*). Furthermore, in the present system, Fe^{4+} content was very low. Therefore, Fe^{4+} could not be detected by the Mössbauer effect, even if the rapid electronic exchange did not happen.

Although the ionic radius of La^{3+} is nearly equal to that of Na^+, the lattice constant decreased with increase in Na content. The decrease in the lattice constant may be ascribed to the occurrence of small amounts of Fe^{4+}, the ionic radius of which is smaller than that of Fe^{3+} (*5*). In addition, it has been reported that a contraction of the unit cell volume of lead titanate took place as a result of the introduction of Pb and/or oxygen vacancies into the crystal (*13*). The decrease in the lattice constant will be reasonable for the present system which contains both Fe^{4+} and oxygen vacancies.

In the compositional change in the values of χ_g and σ_0, both magnetic parameters increased with Na content. An increase in the magnetic susceptibility of antiferromagnetic material may be due to a disordering of antiparallel spin arrangement, i.e., the oxygen vacancies disturb antiparallel spin ordering in Fe^{3+}–O–Fe^{3+} linkage in G-type spin arrangement (*2*). According to the results of the Mössbauer spectra, on the other hand, the oxygen vacancies changed the oxygen coordination number of iron from 6 to 4. The increase in ferromagnetic moment can be understood by the lowering of symmetry around Fe^{3+} coordinated with oxygen, because the occurrence of parasitic ferromagnetism is a result of the disturbing effect of the crystal field on the much stronger exchange field and has a close relation with the symmetry around the magnetic ion (*15*). Similar magnetic behavior has been observed in poorly crystallized lanthanum orthoferrite, which was prepared by heat treatment of coprecipitated hydroxides of iron and lanthanum ions (*16*). An effect of the presence of small amounts of Fe^{4+} can be negligible in this series because the superexchange interaction between Fe^{3+} and Fe^{4+} is fairly weak (*5*). Although an origin of the decrease in χ_g and σ_0 at the composition $x = 0.25$ is not obvious, it may be that the structural perturbation was added because of the presence of too many oxygen vacancies.

Thermal hysteresis was observed (Fig. 2). It is well known as "thermoresidual magnetization" (magnetization remaining in the samples after cooling from the Néel temperature in a magnetic field). It originates from very high coercive force. Belov *et al.* (*17*) reported that the magnetic domain of $LaFeO_3$ with a particle size of 1000 Å did not rotate under a magnetic field over 20 kOe. In the present study, therefore, the thermoresidual magnetization observed may be due to the presence of very fine particles below 1000 Å. In fact, secondary electron microscopic observation revealed that particles below 1000 Å were dispersed among the relatively large particles with average particle size of several micrometers. The average particle size increased with Na content. The decrease in the ratio of the σ_g value before heating to that after cooling in a magnetic field may be interpreted by the increase in the average particle size, that is, by the decrease in the number of particles smaller than 1000 Å.

The ferromagnetic moments of the present perovskite solid solution containing oxygen vacancies were changed with measuring atmosphere. According to the experimental fact that the change in magnetization is strongly dependent upon the oxygen partial pressure, it may be reasonable that the oxygen goes into and out of the defect-perovskite lattice, depending on the oxygen partial pressure and temperature. This phenomenon can be understood by considering the oxidation/reduction reaction between Fe^{3+} and Fe^{4+}.

It may be emphasized that oxygen diffuses in out of the perovskite lattice at room temperature. Furthermore, the experimental fact that the magnetization is affected by oxygen partial pressure may be applicable to electroceramic devices.

Acknowledgment

The authors are indebted to Mrs. Kobayashi who performed the chemical analysis of sodium.

References

1. S. Geller and F. E. Wood, *Acta Crystallogr.* **9**, 563 (1956).
2. W. C. Koehler and E. D. Wollan, *J. Phys. Chem. Solids* **2**, 100 (1957).
3. H. Forestier and G. Guiot-Guillain, *C.R. Acad. Sci. (Paris)* **230**, 1844 (1957).
4. U. Shimony and J. B. MacChesney, "The Mössbauer Effect," Symposia of the Faraday Society, No. 1, p. 40 (1968).
5. J. B. MacChesney, R. C. Sherwood, and J. F. Potter, *J. Chem. Phys.* **43**, 1907 (1965).
6. Jean-Claude Grenier, Gerard Schiffmacher, Paul Caro, Michel Pouchard, and Paul Hagenmuller, *J. Solid State Chem.* **20**, 365 (1977); *Mat. Res. Bull.* **11**, 1219 (1976).
7. Hiroshi Yamamura, Shin-ichi Shirasaki, Koichiro Takahashi, and Kazuyuki Kakegawa, *J. Amer. Ceram. Soc.* **59**, 533 (1976).
8. Hiroshi Yamamura and Ryoiti Kiriyama, *Bull. Chem. Soc. Japan* **45**, 2702 (1972).

9. D. Treves, *J. Appl. Phys.* **36**, 1033 (1965).
10. M. A. Gilleo, *Phys. Rev.* **109**, 777 (1958).
11. Whitefield, *Aust. J. Chem.* **20**, 859 (1967).
12. K. J. Standley, "Oxide Magnetic Materials," p. 133, Clarendon Press, Oxford (1972).
13. S. Shirasaki, K. Takahashi, and K. Manabe, *Bull. Chem. Soc. Japan* **44**, 3189 (1971).
14. Saburo Mori, *J. Amer. Ceram. Soc.* **49**, 600 (1966).
15. I. E. Dzialoshinsky, *Sov. Phys. JETP* **6**, 1259 (1958); *Sov. Phys. JETP* **6**, 1120 (1958).
16. Hiroshi Yamamura, Shin-ichi Shirasaki, Hirotoshi Oshima and Kazuyuki Kakegawa, *J. Solid State Chem.* **18**, 329 (1976).
17. K. P. Belov, V. I. Iveronova, M. A. Zaitseva, A. M. Kadomtseva, A. A. Katanel'son, and K. Yatskul'yak, *Sov. Phys. Solid State* **6**, 80 (1964).