

Effects of Ga Substitution in $\text{LaFe}_{1-x}\text{Ga}_x\text{O}_3$ ($x = 0, 0.1, 0.3, 0.5, \text{ and } 0.7$)

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(Received 22 April 2002)

Crystallographic and magnetic properties of $\text{LaFe}_{1-x}\text{Ga}_x\text{O}_3$ ($x = 0, 0.1, 0.3, 0.5, \text{ and } 0.7$) were studied using XRD and Mössbauer spectroscopy. The crystal structures were found to be orthorhombic and the lattice parameters a , b , and c were found to decrease with increasing Ga substitution. Mössbauer spectra were obtained at various absorber temperatures ranging from 20 K to 750 K. The Mössbauer spectra were all sextets below T_N and were all singlets above T_N . Asymmetric broadening of the Mössbauer spectral lines at 20 K was explained by the multitude of possible environments for an iron nucleus. As the temperature increases to T_N , a systematic line broadening in Mössbauer spectra was observed and interpreted to originate from different temperature dependencies of the magnetic hyperfine fields at various iron sites.

Key words : Mössbauer, orthoferrite, magnetic dilution, $\text{LaFe}_{1-x}\text{Ga}_x\text{O}_3$

1. Introduction

Lanthanum orthoferrite (LaFeO_3) is considered as one of the most important transition metal mixed oxides due to its remarkable crystallographic, electric, and magnetic properties. Crystallographically, LaFeO_3 is an orthorhombically distorted perovskite. However, because of the large ionic radius of the lanthanum ion ($\sim 1.30 \text{ \AA}$), LaFeO_3 is crystallized in a pseudo-cubic structure. Electrically, LaFeO_3 is the charge-transfer type insulator which has 2 eV intrinsic charge gap resulting from a strong on-site Coulomb repulsion [1]. Magnetically, it is a G-type antiferromagnet [2, 3]. The simple structure mentioned above makes its exchange angle nearly 180° , giving rise to its Neel temperature as high as 750 K. LaFeO_3 also belongs to a group of magnetic oxides having the highest saturated hyperfine magnetic field value extrapolated to 0 K. These simple but durable properties of the compound make it a widely used parent-material for electromagnetic researches and technical applications [4].

The authors selected these materials because this high saturated hyperfine magnetic field at 0 K would guarantee

a better resolution in Mössbauer spectra throughout the extended temperature range. Furthermore, in spite of the simple structures of these compounds, few experimental reports were found elsewhere. In this paper will be given some results on the crystal structures and Mössbauer spectra of a series of Ga-substituted lanthanum orthoferrites, elucidating the features of magnetic dilution.

2. Experimental

The $\text{LaFe}_{1-x}\text{Ga}_x\text{O}_3$ compounds ($x = 0, 0.1, 0.3, 0.5, \text{ and } 0.7$) were prepared the conventional solid state sintering method starting with La_2O_3 , Fe_2O_3 , and Ga_2O_3 powders in appropriate proportions. A mixture of the compounds was ground and press-molded into a pellet, fired at 1100°C for 36 hours, and then slowly cooled down to room temperature at the rate of $10^\circ\text{C}/\text{hour}$. In order to obtain a homogeneous material, this process was repeated once again. X-ray diffraction (XRD) patterns of the samples were obtained with $\text{Cu K}\alpha$ radiation. The patterns at room temperature were taken at a slow scanning speed 0.5° advance in 2θ per min. to enhance the resolution. A Mössbauer spectrometer of conventional transmission type was used in the constant acceleration mode. ^{57}Co source in an Rh matrix with an activity of 50 mCi was used at room temperature.

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3. Results and Discussion

The X-ray diffraction patterns are shown in Figure 1. There are no remarkable changes in X-ray diffraction patterns with composition. An analysis of the patterns showed that the structure of the samples should be distorted orthorhombic. Using Bragg's diffraction equation, all the lattice parameters were fitted to calculate d -spacings by the following equation with the Miller indices h , k , and l known for orthorhombic unit cell.

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (1)$$

Their lattice parameters are listed in Table 1. LaFeO_3 has an orthorhombic symmetry with the lattice parameters $a = 5.564 \text{ \AA}$, $b = 5.553 \text{ \AA}$, and $c = 7.858 \text{ \AA}$, respectively. These values are very close to the already known lattice parameters $a = 5.556 \text{ \AA}$, $b = 5.565 \text{ \AA}$, and $c = 7.862 \text{ \AA}$ [5]. As shown in the table, successive substitution of iron ions by gallium ions in LaFeO_3 decreases the lattice parameters of the compounds. The resulting decrease in lattice parameters could be attributed to the difference between the ionic radii of the iron and gallium ions. The known ionic radii in octahedral coordination for high spin Fe^{3+} is 0.785 \AA and for Ga^{3+} is 0.760 \AA [6].

Figures 2 and 3 illustrate Mössbauer spectra taken at absorber temperature of 20 K and 290 K, respectively.

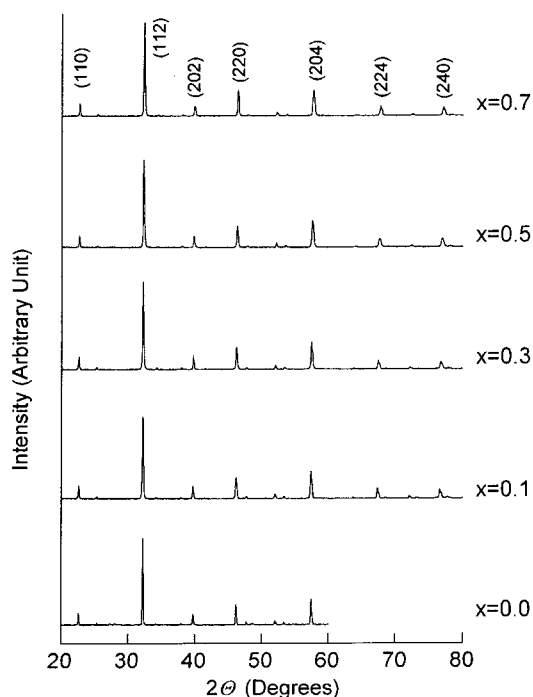


Fig. 1. XRD patterns of $\text{LaFe}_{1-x}\text{Ga}_x\text{O}_3$.

Table 1. Lattice parameters of $\text{LaFe}_{1-x}\text{Ga}_x\text{O}_3$.

x	a (Å)	b (Å)	c (Å)
0.0	5.564	5.553	7.858
0.1	5.559	5.554	7.856
0.3	5.556	5.548	7.853
0.5	5.549	5.534	7.841
0.7	5.533	5.530	7.799

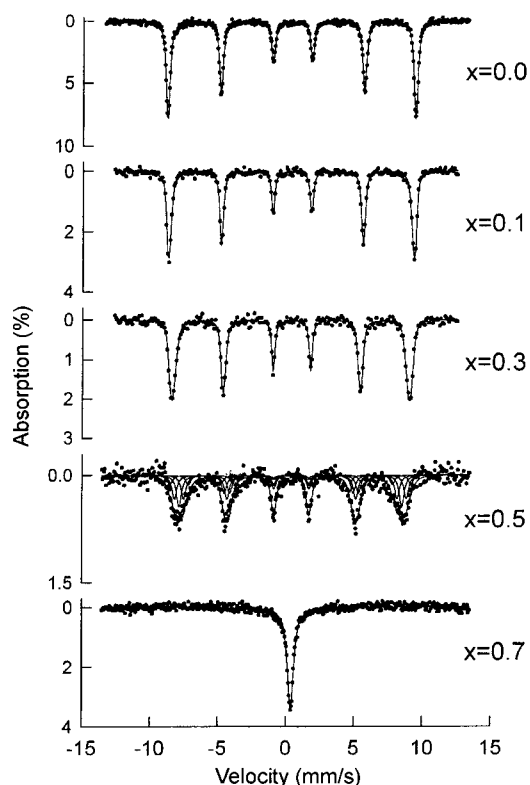


Fig. 2. Mössbauer spectra for $\text{LaFe}_{1-x}\text{Ga}_x\text{O}_3$ at 20 K.

The Mössbauer spectra were all sextets below T_N . The Mössbauer spectra of LaFeO_3 displayed a sharp six-line pattern through the extended temperature range up to as high as $0.9T_N$. The spectrum for $x = 0.1$ was also sharp at 20 K. On the other hand, the spectra for $x = 0.3$ and $x = 0.5$ broadened increasingly with increasing Ga concentration. This asymmetric broadening of the Mössbauer spectral lines may result from the multitude of possible environments for an iron nucleus. In this structure, each Fe ion has 6 nearest neighbor transition-metal sites. Accordingly, there are 7 possible configurations of magnetic environments by various occupancies of Fe and Ga ions. The Mössbauer absorption line width also increased with increasing temperature, as shown for $x = 0.3$ in Figure 4. These systematic line-broadening effects were interpreted to originate from different temperature dependencies of the magnetic hyperfine fields at various iron

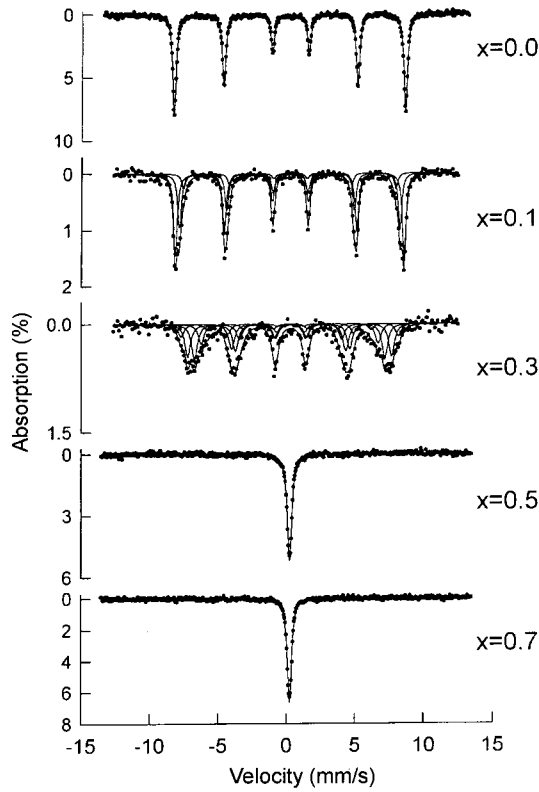


Fig. 3. Mössbauer spectra for $\text{LaFe}_{1-x}\text{Ga}_x\text{O}_3$ at 290 K.

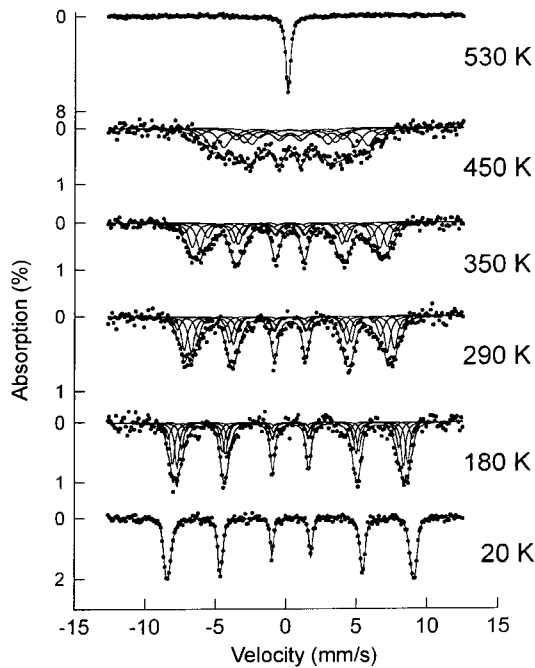


Fig. 4. Mössbauer spectra for $\text{LaFe}_{0.7}\text{Ga}_{0.3}\text{O}_3$ at various absorber temperatures.

sites. The same explanation was given to the analysis of Mössbauer spectra for spinel system $\text{CuFe}_{2-x}\text{Cr}_x\text{O}_4$ [7].

Table 2. Probability $P(x, N)$ of an Fe ion having N nearest-neighbor Fe ions in the $\text{LaFe}_{1-x}\text{Ga}_x\text{O}_3$

N	$P(x, N)$			
	0.1	0.3	0.5	0.7
0	0.000	0.001	0.016	0.118
1	0.000	0.010	0.094	0.303
2	0.001	0.060	0.234	0.324
3	0.015	0.185	0.313	0.185
4	0.098	0.324	0.234	0.060
5	0.354	0.303	0.094	0.010
6	0.531	0.118	0.016	0.001

The relative absorption area for the subspectra should be proportional to the population of ^{57}Fe ions with different environments in the lattice. Since the substitution of iron ion by gallium ion is a random process, the probability of finding an iron ion with both $6-N$ nearest gallium ions and N nearest iron ions in the first coordination sphere $P(x, N)$ ($N = 0$ to 6) is given by the following binomial distribution function.

$$P(x, N) = \binom{6}{N} (1-x)^N x^{6-N} \quad (2)$$

The probabilities calculated with different N values for each composition x are listed in Table 2.

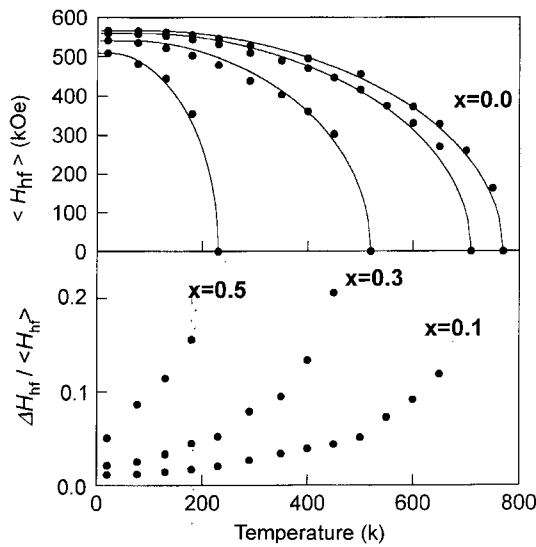
The magnetic hyperfine field at Fe with n Ga^{3+} neighbors may be written as $H_0 - n\Delta H$. H_0 values at 20 K were all about 566 kOe and were nearly constant with respect to Ga concentration. This indicates that the ionic state of iron is a tri-valent state. On the other hand, ΔH were obtained to be 8, 11, and 20 kOe for $x = 0.1$, $x = 0.3$, and $x = 0.5$, respectively at 20 K. The three results showed non-linear increase with increasing Ga concentration. The compound for $x = 0.7$ showed no magnetic order even at 20 K.

Magnetic transition temperatures were determined from the shapes of the spectra. The Mössbauer spectra were all singlets above T_N with their line width 0.34, 0.37, 0.39, 0.40, and 0.37 mm/s for $x = 0, 0.1, 0.3, 0.5,$ and 0.7 , respectively. Corresponding Neel temperatures were 750, 710, 530, 210, and below 20 K, respectively (Table 3). It is interesting to note that both $\text{LaFe}_{1-x}\text{Mn}_x\text{O}_3$ and $\text{LaFe}_{1-x}\text{Co}_x\text{O}_3$ which have the same crystal structure as the present compounds, revealed quadrupolar doublet just above T_N [8]. This could be explained by the multi-valence-nature of manganese and cobalt ions.

Figure 5(a) shows temperature dependencies of averaged hyperfine magnetic fields of the samples. It can be seen fairly good agreements between the theoretical spin

Table 3. Several typical Mössbauer parameters of $\text{LaFe}_{1-x}\text{Ga}_x\text{O}_3$ in some selected temperatures.

x	H_{hf} (kOe)			E_Q (mm/s)			δ (mm/s)			T_N (K)
	20 K	77 K	290 K	20 K	77 K	290 K	20 K	77 K	290 K	
0.0	567	566	528	-0.04	-0.04	-0.04	0.37	0.36	0.26	750
0.1	560	558	510	-0.03	-0.03	-0.03	0.37	0.36	0.26	710
0.3	542	536	439	-0.04	-0.03	-0.04	0.36	0.37	0.28	530
0.5	509	482	0	-0.04	-0.03	0	0.37	0.37	0.25	210
0.7	0	0	0	0	0	0	0.36	0.36	0.25	<20

**Fig. 5.** Temperature dependencies of (a) hyperfine magnetic fields and (b) their fractional spreads for $\text{LaFe}_{1-x}\text{Ga}_x\text{O}_3$.

5/2 Brillouin curves and the data points. The spread ΔH_{hf} of hyperfine magnetic field is defined by

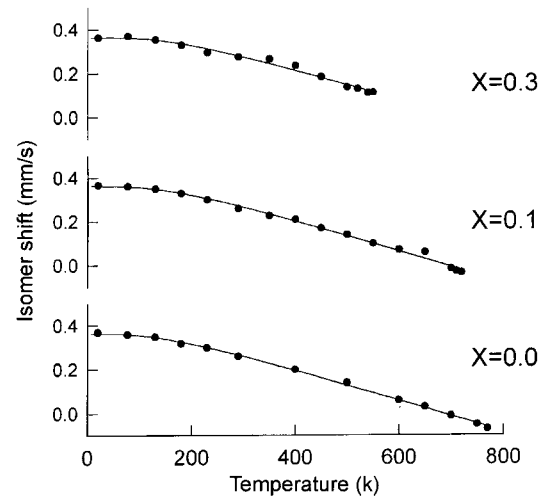
$$\Delta H_{hf} = (\langle H_{hf}^2 \rangle - \langle H_{hf} \rangle^2)^{1/2} \quad (3)$$

Their values relative to the averaged values $\langle H_{hf} \rangle$ as a function of T/T_N are represented in Figure 5(b). It can be noted in the figure that hyperfine magnetic field values spread widely and non-linearly as the temperature increased to T_N .

Quadrupole splitting values were in the range of -0.03~ -0.04 mm/s within experimental errors for all the samples in the whole temperature range examined. This meant the electronic environmental symmetry was not so much altered by the Ga substitution.

Figure 6 shows the temperature variations of isomer shift for $x = 0, 0.1, \text{ and } 0.3$. Using a Debye model, variation of isomer shift with absorber temperature can be expressed as [9]

$$\delta(T) = a + dT - \frac{9k_B\Theta_D}{16Mc} \left[1 + 8 \left(\frac{T}{\Theta_D} \right)^4 \int_0^{\Theta_D/T} \frac{x^3}{e^x - 1} dx \right] \quad (4)$$

**Fig. 6.** Temperature dependencies of isomer shift for $\text{LaFe}_{1-x}\text{Ga}_x\text{O}_3$.

where k_B is Boltzmann's constant, Θ_D is the Debye temperature, and M is the atomic mass of the Mössbauer nucleus. The parameters a , d , and Θ_D can be obtained by a least-square fit of the experimental data. Solid curves represented the best fits with $\Theta_D = 610, 620, \text{ and } 614$ K for $x = 0, 0.1, \text{ and } 0.3$, respectively. Eibschutz *et al.* insisted that the Debye temperature for LaFeO_3 was about 800 K as deduced from temperature variation of Mössbauer absorption area [5]. The difference in values between the former and present paper seemed to stem from using different calculation methodology. From the values of isomer shifts listed in Table 3, it was apparent that the charge state of iron ion was tri-valent. It was also clear that s-electron density at the Fe nucleus was not affected by the Ga substitution.

4. Conclusions

Crystallographic and magnetic properties of $\text{LaFe}_{1-x}\text{Ga}_x\text{O}_3$ ($x = 0, 0.1, 0.3, 0.5, \text{ and } 0.7$) were investigated by using XRD and Mössbauer spectroscopy. Special focus was concentrated on the variations of Mössbauer parameters during Ga substitution. The crystal structures were found

to be orthorhombic. The lattice parameters decreased with increasing Ga substitution. The Mössbauer spectra were all binomially distributed sextets below T_N , while they were all singlets above T_N . Two different origins of line-broadening effects were detected. First, the asymmetric broadening of the Mössbauer spectral lines with Ga substitution at 20 K were explained by the multitude of possible environments for an iron nucleus. Second, as the temperature increased to T_N for a given x , a systematic line broadening in Mössbauer spectra was observed and interpreted to originate from different temperature dependencies of the magnetic hyperfine fields at various iron sites.

Acknowledgement

This work was supported by Grant No. R05-2001-000-00128-0 from the Basic Research Program of the Korea Science & Engineering Foundation.

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