

## $Y_xFe_{2-x}O_3(x=0.82)$ 의 결정상 변환

김 정 기 · 김 영 진

한양대학교 자연과학대학 물리학과

### The Crystal-Phase Transition of $Y_xFe_{2-x}O_3(x=0.82)$

J. G. Kim and Y. J. Kim

Department of Physics, Hanyang University, Seoul, 133-791 Korea

**초 록**  $Y_xFe_{2-x}O_3(x=0.82)$ 의 결정상 변환을 상온에서의 X선 회절과 온도구간 80-541K에서의 Mossbauer 분광 방법에 의해서 연구하였다. X선 회절선은 시료가 orthorhombic 결정상과 garnet 결정상이 공존하고 있으며, 공존비는 실험오차 범위내에서 garnet 구조가 orthorhombic 구조보다 우세함을 보인다. 공존상중에서 garnet 구조의 자기상 변환온도는  $536 \pm 5$  K로 결정하였다. Debye 모형을 이용한 Mossbauer 스펙트럼의 recoil-free fraction 분석결과는 garnet 결정상내의 d자리나 a자리에 vacancy의 존재 가능성을 시사한다. 부가적으로 시료가 포함하는 각 결정상의 Debye 특성온도를 결정하였다.

**Abstract** The crystal phase transition of the sample of  $Y_xFe_{2-x}O_3(x=0.82)$  has been studied by the methods of X-ray diffraction at room temperature and Mossbauer spectroscopy within the temperature range of 80~541K. The X-ray diffraction pattern of the sample shows the coexistence of orthorhombic and dominant garnet crystal phase without any extra phases within the experimental error. The magnetic ordering temperature for the sample of the garnet phase is determined to be  $536 \pm 5$  K. The analysis of recoil-free fraction of the Mossbauer spectra using the Debye model indicates the possibility of existence of some vacancies in d- and/or a-site of the garnet crystal phase. The Debye temperatures for each phases of the sample were determined.

### 1. INTRODUCTION

The general chemical formula of yttrium-iron garnet (YIG) is  $Y_3Fe_5O_{12}$  or  $Y_xFe_{2-x}O_3(x=0.75)$ . The X-ray diffraction data show that YIG belongs to space group  $O_h^6-Ia3d$ . The unit cell contains 8 formula units  $\{Y_3\}[Fe_2](Fe_3)O_{12}$ , where  $\{\}$ ,  $[\ ]$ , and  $( )$  represent a dodecahedral c-, octahedral a-, tetrahedral d-site, respectively<sup>1,2)</sup>. The superexchange antiferromagnetic interaction between trivalent iron ion at d- and a-sites causes the garnet to be ferrimagnetism<sup>3,4)</sup>. The values of quadrupole interaction  $eqQ/2$  were determined to be  $(0.78 \pm 0.16)$  for the d-site (hereafter termed

the d subspectrum) and  $(0.94 \pm 0.18)$  mm/s for the a-site (hereafter termed the a spectrum) above Curie temperature(545 K)<sup>5)</sup>. Here  $eq$  and  $Q$  are the electric field gradient tensor in the direction of principal  $z$ -axis and the quadrupole moment of  $^{57}Fe$  nuclei, respectively. The orthoferrite  $YFeO_3(x=1.0)$  belongs to the space group  $D_{2h}^6-Pbnm$  which is a distorted perovskite. The crystallographic unit cell contains four equivalent iron ions. Each iron ion is coupled by superexchange to six iron neighbors intervening anion, resulting in high Néel temperature of 640 K<sup>6~8)</sup>. The purpose of this study is to carry out X-ray and Mossbauer measurement on the polycrystalline

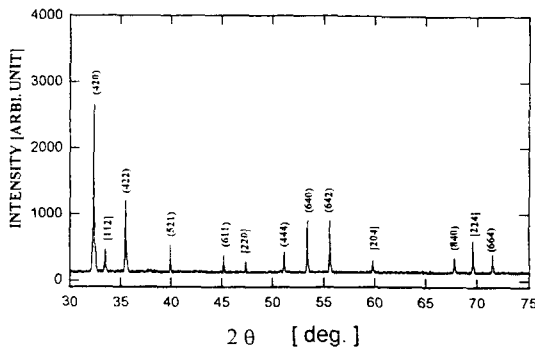


Fig. 1. X-ray diffraction pattern for the sample. ( ) garnet phase; [ ] orthorhombic phase

$Y_xFe_{2-x}O_3$  ( $x=0.82$ ) to examine the crystal phase transition from YIG to orthoferrite.

## 2. EXPERIMENT

The sample was synthesized by the usual ceramic method.  $Fe_2O_3$  and  $Y_2O_3$  with the purity of over 99.995% in powder form were used as the starting materials. A mixture of the proper proportions of the materials was ground, pressed into a pellet at  $6,000 \text{ kg/cm}^2$ , and sealed in and evacuated quartz tube. The sealed mixture was heated at  $700^\circ\text{C}$  for 12h,  $900^\circ\text{C}$  for a day, and  $1,050^\circ\text{C}$  for two days, and then cooled down to room temperature at the rate of  $15^\circ\text{C/h}$ . In order to obtain a homogeneous material the product was reground, pressed into a pellet, and refired at  $1,050^\circ\text{C}$  for two days in an evacuated and sealed quartz ampoule. X-ray diffraction pattern of the sample at room temperature was obtained using a Japanese-made Rigaku diffractometer with  $\text{Cu}_{K\alpha}$  radiation. The Mössbauer spectra were measured at various absorber temperatures from liquid nitrogen temperature to  $550 \text{ K}$  using an Austin constant acceleration spectrometer with laser calibration. To produce a uniform thickness over the area of the Mössbauer absorber, the sample was mixed with boron nitride powder and clamped between two thin boron nitride plates. The absorber thickness was approximately  $0.12 \text{ mg/cm}^2$  of  $^{57}\text{Fe}$ .

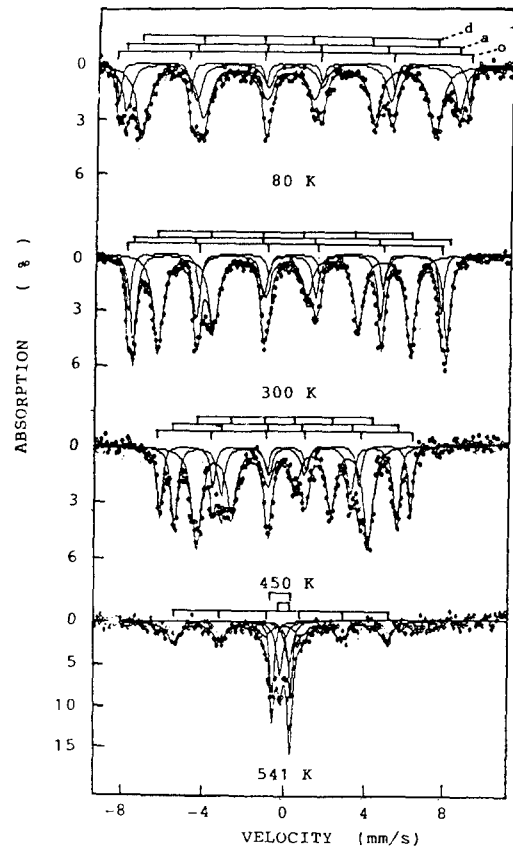


Fig. 2. Mössbauer spectra for the sample. d d-site; a a-site; o orthorhombic phase

## 3. RESULTS AND DISCUSSION

As shown in Fig. 1 the X-ray diffraction pattern of the sample shows the coexistence of orthorhombic and dominant garnet crystal phase without any extra phases within the experimental error. The lattice constant of the  $a_0$  of garnet phase for the sample was determined to be  $12.367 \text{ \AA}$ . The lattice constant of garnet phase can be compared with the value of  $12.376 \text{ \AA}$ <sup>11</sup>. Fig. 2 shows some of the Mössbauer spectra for the sample. The spectra of the sample are fitted to a mixed-electric quadrupole plus magnetic hyperfine pattern without considering two a-site lines due to two possible angles between the principal axis of the electric field gradient and the magnetic field<sup>53</sup>. The widths that are assumed to be the same in

respective subspectra and overall absorption areas of the spectra are independently varied as free parameters. However, within the subspectra the following constraints for the areas of spectrum are imposed:

$$b_i A_{i,o} = A_{i,o}, A_i = A_{i,d} \quad (1)$$

where  $b_i$  is the best-fit parameter and  $t = a$  or  $d$ ;  $o$  is termed the spectrum for orthorhombic phase; and  $i$  goes from 1 to 3. The magnetic hyperfine fields of orthorhombic phase, a-, and d-site are found to be  $482 \pm 5$ ,  $483 \pm 5$ , and  $389 \pm 5 \text{ kOe}$  at room temperature, respectively. The magnetic ordering temperature for the sample of the garnet phase is determined to be  $536 \pm 5 \text{ K}$ . The magnetic hyperfine fields and the ordering temperature are comparable to other measured values<sup>8,9)</sup>. The spectrum of the sample at  $541 \text{ K}$  shows the co-existence of the orthorhombic<sup>9)</sup> and garnet crystal phase, which is in good agreement with the result of X-ray diffraction. The values of the quadrupole splitting  $eqQ/2$  at  $541 \text{ K}$  are  $0.45 \pm 0.05$  and  $0.91 \pm 0.05 \text{ mm/s}$  for the a- and d-site, respectively. They can be compared with  $0.500$  and  $0.934 \text{ mm/s}$  for YIG<sup>9)</sup>. Fig.3(a) and (b) show the temperature dependence of the absorption area ratio of d to a subspectra and the orthorhombic phase to garnet phase,

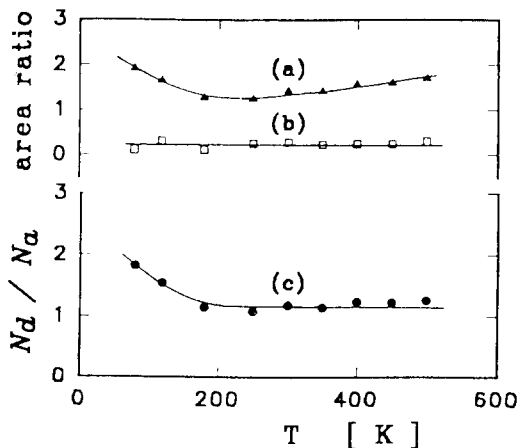


Fig. 3. Temperature dependence of the absorption area ratio of d to a-site(a), orthorhombic phase to garnet phase(b), and  $N_d/N_{d0}$ (c).

respectively. It is noteworthy in Fig.3(a) that the area ratio has a minimum at around  $200 \text{ K}$ . On the other hand the ratios of orthorhombic phase to garnet phase keep a nearly constant values (Fig.3(b)). The Debye model gives the following expression for the recoil-free fraction<sup>10)</sup>

$$f = \exp\left\{-\frac{3E_R}{2k_B\Theta}\left[1 + \frac{4T^2}{\Theta^2} \int_0^{\Theta/T} \frac{xdx}{e^x-1}\right]\right\} \quad (2)$$

where  $E_R$  is the recoil energy of  $^{57}\text{Fe}$  for the  $14.4\text{-keV}$  gamma ray.  $\Theta$  and  $k_B$  represent the Debye temperature and Boltzmann constant, respectively. The recoil-free fraction  $f$  can be written as Eq.(3) for the temperature ranges of  $T > 0.5\Theta$ .

$$f = \exp\left[-\frac{6E_R T}{k_B \Theta^2}\right] \quad (3)$$

Because the absorption area is proportion to  $f$ , the  $\ln(\text{area})$ -versus- $T$  curve should be straight line for  $T > 0.5\Theta$ ; hence  $\Theta$  can be determined from the slop of the straight line. Fig. 4 shows the least-squares fits to the data points for the sample of d-(a), a-site(b), and the orthorhombic phase(c), respectively. From this the Debye temperatures are determined to be  $327 \pm 10, 269 \pm 10$ , and  $407 \pm 10 \text{ K}$  for d-, a-site, and the orthorhombic phase of the sample, respectively. Sawatzky *et al.*<sup>1,2)</sup> obtained Mossbauer spectra of YIG in the temperature range  $300\text{-}800 \text{ K}$  and found that the Debye temperatures for d- and a-site were  $\Theta_d = 406 \pm 15 \text{ K}$  and  $\Theta_a = 366 \pm 15 \text{ K}$ , respectively. Our results are less than those. And the tempera-

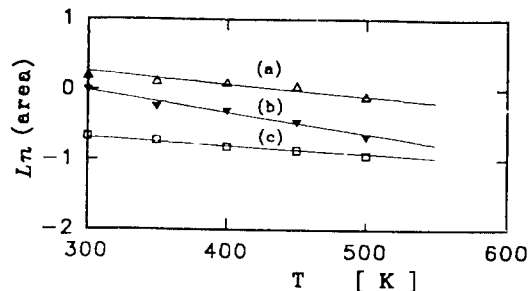


Fig. 4. Natural logarithm of the absorption area of d (a), a subspectra(b), and orthorhombic phase(c) of the sample.

ture of the orthorhombic phase is much lower than  $800 \pm 50 K$  of  $YFeO_3$ <sup>9)</sup>. The absorption area ratio of d- to a-subspectra is

$$\frac{I_d}{I_a} = \frac{N_d f_d}{N_a f_a} \quad (4)$$

where  $f_d$ ,  $f_a$ ,  $N_d$ , and  $N_a$  represent the recoil-free fractions and the number of  $^{57}Fe$  for d- and a-site, respectively. The recoil-free fractions of d- and a-site can be calculated from Eq.(3) using the Debye temperature for each site. Fig.3(c) shows the ratio of  $N_d/N_a$  for the sample. As seen in Fig.3(c) the ratio decrease as increasing temperature up to about 200 K and then keeps an average value of 1.21. This value is less than that of 1.5 for YIG<sup>12)</sup> and indicates the possibility of existence of some vacancies in d- and/or a-site.

The authors would like to acknowledge the financial supports of the Korea Science and Engineering Foundation.

#### REFERENCES

1. S. Geller and M.A. Gilleo, J. Phys. Chem. Solids 3, 30(1957).
2. J.W. Nielsen and E.F. Dearborn, J. Phys. Chem. Solids 5, 202(1958).
3. F. Bertaut and F. Forrat, Compt. Rend. 242, 382(1956).
4. M.A. Gilleo and S. Geller, Phys. Rev.110, 73(1958).
5. C. Alff and G.K. Wertheim, Phys. Rev.122, 1414(1961).
6. S. Geller and E.A. Wood, Acta Cryst.9, 536(1956).
7. S. Geller, J. Chem. Phys.24, 1236(1956).
8. M. Eibschütz, S. Shtrikman, and D. Treves, Phys. Rev. 156, 562(1967).
9. V.N. Belogurov and V.A. Bilinkin, Phys. Stat. Sol.(a)63, 45(1981).
10. R.L. Mössbauer and W.H. Wiedermann, Z. Phys.159, 33(1960).; B. Kaufman and H. J. Lipkin, Ann. Phys. (N.Y.)18, 294 (1962).
11. A.J.F. Boyle, D.St.P. Bunbury, C. Edwards, and H.E. Hall, in the Mössbauer Effect, edited by D. Pines (W. A. Benjamin, Inc., N.Y., 1963).
12. G.A. Sawatzky, F. Van Der Woude, and A.H. Morrish, Phys. Rev.183, 383(1969).