

Charge Transformation of Cu-ions in $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ ($x = 0.1, 0.2$)

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Slowly cooled $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ ($x = 0.1, 0.2$) have been investigated over a temperature range from 82 to 700 K using the Mössbauer technique. X-ray diffraction shows that these have a single-phase cubic spinel structure of lattice parameters $a = 8.396$ and 8.398 \AA , respectively. Since Cu ions prefer B (octahedral) sites to A (tetrahedral) sites, the ionic distribution is $(\text{Fe})_A[\text{Fe}_{2-x}\text{Cu}_x]_B\text{O}_4$. Mössbauer spectra consisted of two sets of 6-line pattern from A site in ferric state and B site in ferrous-ferric state. Intensity ratio of B to A subspectra is 1.0 at 82 K and increases to 2.0 at 700 K with increasing temperature. After annealing the samples under vacuum at 450°C for a half hour, x-ray diffraction patterns have the peaks of magnetite- and hematite-phase. Lattice constants of magnetite-phase are 8.395 and 8.392 \AA smaller than 8.396 and 8.398 \AA before annealing, respectively. Mössbauer spectra reveal the conventional magnetite pattern with the additional hematite pattern. Intensity ratios of B to A subspectra for magnetite-phase become 1.9-2.0 over all temperature ranges and Cu ions are distributed over A and B sites randomly. Ratios of hematite to total intensity in Mössbauer spectra for $x = 0.1$ and $x = 0.2$ are 10 and 21%, respectively. These hematite ratios may be due to annealing under vacuum at 450°C , which transforms Cu^{2+} ionic states into Cu^{1+} . Verwey temperatures for $x = 0.1$ and $x = 0.2$ are $123 \pm 2 \text{ K}$ and $128 \pm 2 \text{ K}$.

Key words : Mössbauer, Verwey, magnetite, hematite, electron-hopping, substituted ferrite.

1. Introduction

Magnetite (Fe_3O_4) and other spinel ferrites, where iron is partially substituted for the transition-metal cations, have been extensively studied over the past 50 years. One of the most interesting phenomena encountered in these materials is the Verwey phase transition [1, 2], occurring near 121 K in stoichiometric Fe_3O_4 , and at lower temperature in nonstoichiometric and substituted compounds [2]. Fe_3O_4 is completely inverse spinel, and has the ionic distribution $(\text{Fe}^{3+})_A[\text{Fe}^{2+}\text{Fe}^{3+}]_B\text{O}_4$ below the Verwey transition temperature and $(\text{Fe}^{3+})_A[2\text{Fe}^{2.5+}]_B\text{O}_4$ with electron-hopping above the Verwey temperature, where A and B indicates tetrahedral and octahedral site in spinel structure, respectively. This is verified by measuring the area ratio of Mössbauer subspectra [3] corresponding to ^{57}Fe in A and B sites.

In this study, Mössbauer spectra of $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ ($x = 0.1, 0.2$) have been collected over a temperature range 82-700 K, before and after annealing under vacuum at 450°C .

Verwey transition was not observed before annealing. After annealing, $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ ($x = 0.1, 0.2$) have been separated into magnetite and hematite (Fe_2O_3) phase. In magnetite phase, Verwey transition and charge transformation of Cu^{2+} into Cu^{1+} have been observed.

2. Experimental

The samples $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ ($x = 0.1, 0.2$) were prepared by grinding together appropriate proportions of Fe_2O_3 , CuO , and Fe powders of 99.995%, 99.999%, and 99.995% purity, respectively, pressing the resulting mixtures into pellets at 6000 kg/cm^2 , firing in evacuated and sealed quartz ampoules at 1000°C for 4 days, and then cooled to room temperature at a rate of 30°C/h .

X-ray diffraction patterns of $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ ($x = 0.1, 0.2$) showed that the samples had a single-phase cubic spinel structure. The lattice constants at room temperature were found by using the Nelson-Riley function [4] and extrapolating to the backward diffraction ($\theta = 90^\circ$).

Mössbauer spectra were recorded using a conventional Mössbauer spectrometer of the electromechanical type with $10 \text{ mCi } ^{57}\text{Co}$ in a Rh matrix, which oscillated in a sinusoidal mode [5].

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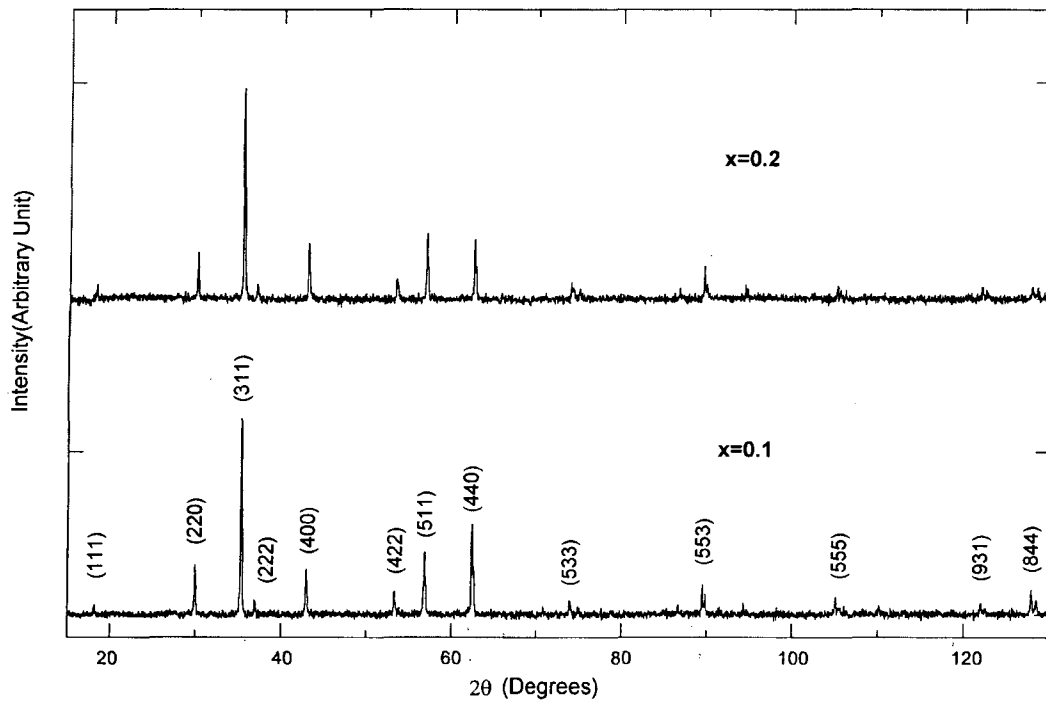


Fig. 1. X-ray diffraction patterns of $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ ($x = 0.1, 0.2$) at room temperature.

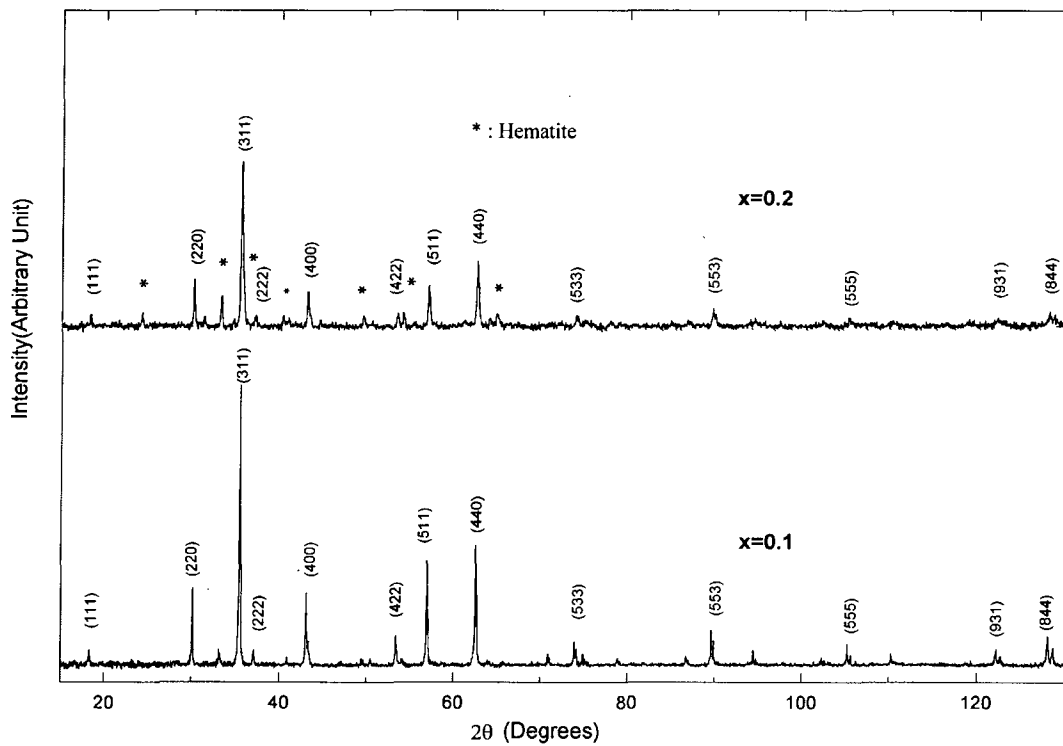


Fig. 2. X-ray diffraction patterns of $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ ($x = 0.1, 0.2$) at room temperature annealed under vacuum at $450\text{ }^\circ\text{C}$.

3. Results and Discussion

Figure 1 and 2 show XRD patterns of $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$

($x = 0.1, 0.2$) at room temperature before and after annealing under vacuum at $450\text{ }^\circ\text{C}$ for a half hour, respectively. Before annealing, Lattice constants for $x = 0.1$ and 0.2 are 8.396 and 8.398 \AA , respectively. Lattice constants for

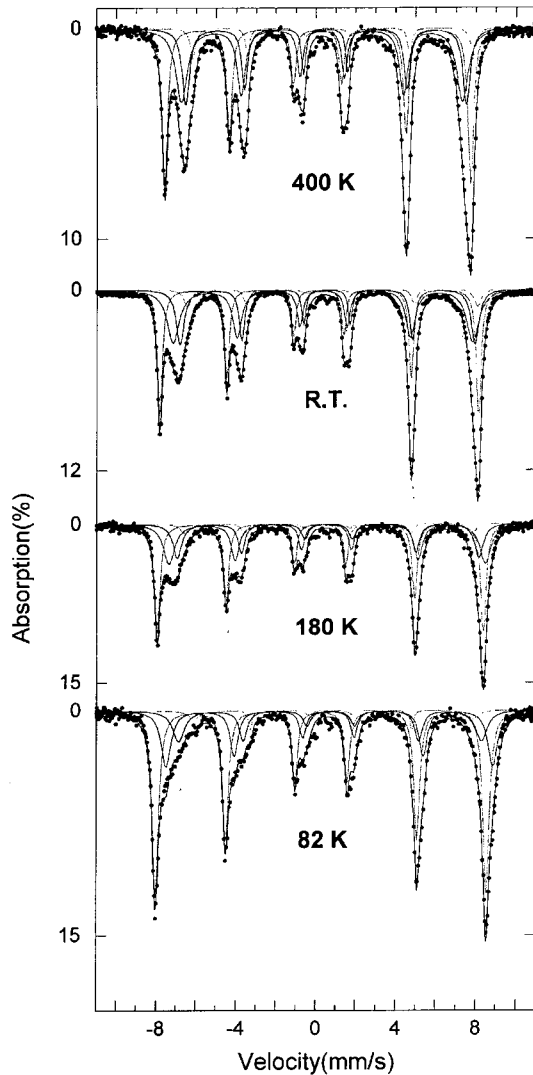


Fig. 3. Mössbauer spectra of $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ ($x=0.2$) at various temperatures.

magnetite phase of annealed $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ ($x=0.1, 0.2$) are 8.395 and 8.392 Å, respectively, which are smaller than those before annealing. These are interpreted by that the decreasing of ionic radius [6] in charge transformation $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ are larger than the increasing of $\text{Cu}^{2+} \rightarrow \text{Cu}^{1+}$ during the annealing under vacuum at 450 °C. Before annealing, the reason that lattice parameter for $x=0.2$ is larger than that for $x=0.1$ is not explainable at present.

Fig. 3 shows some of the Mössbauer spectra for $x=0.2$, which are identical with those for $x=0.1$. From the well-known fact [7] that Cu ions prefer the B-sites to the A-sites, the cationic distribution of $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ becomes $(\text{Fe})_A[\text{Cu}_x\text{Fe}_{2-x}]_B\text{O}_4$. We have fitted the spectra in Fig. 3 to a model based on a random distribution of Fe and Cu ions on the B sites. The hyperfine fields for locally different B sites are assumed to obey the relationship $H_n = H_0(1 - n\Delta H)$.

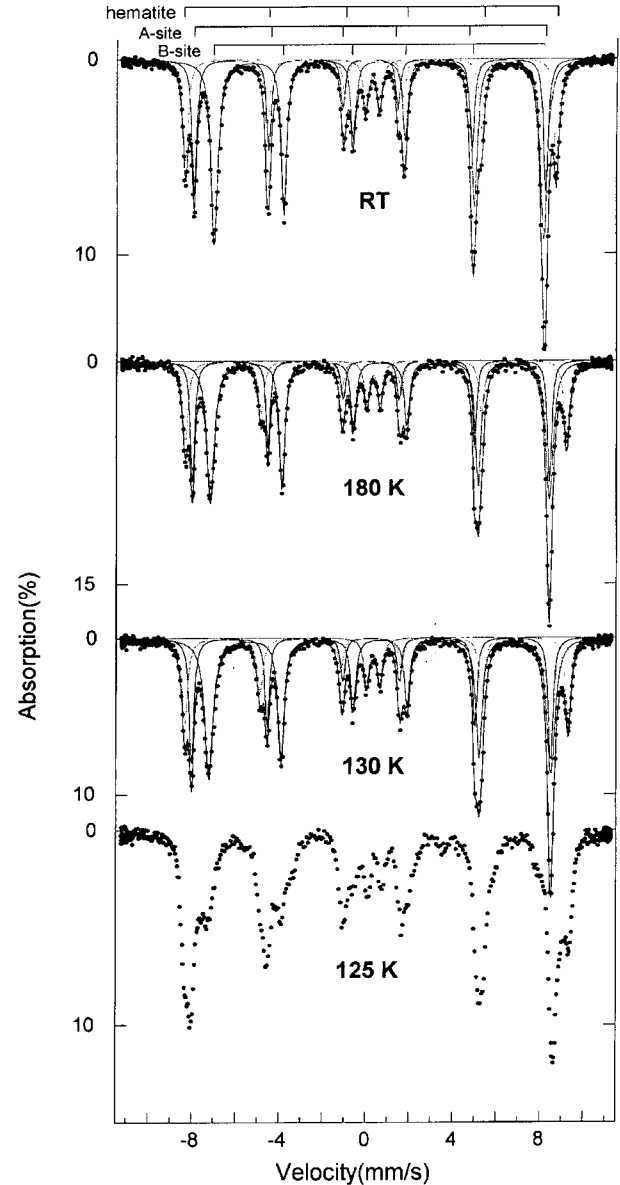
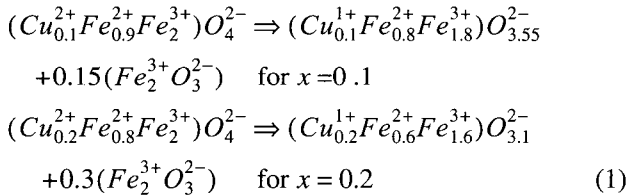


Fig. 4. Mössbauer spectra of $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ ($x=0.2$) annealed under vacuum at 450 °C at various temperatures.

n is the number of Cu ions among the next nearest neighbor B sites of the B-site Fe ion that has a hyperfine field H_n . H_0 is the hyperfine field at a B-site Fe ion that has no Cu ions among next nearest neighbor B sites. ΔH is the fractional decrease in the hyperfine field as a result of replacing one B-site Fe by Cu. The relative intensity of the different B subspectra is given by $P(n, x) = {}_6C_n x^n (1-x)^{6-n}$ with $x=0.1$ and 0.2 . The constraints of the B subspectrum are the equal linewidths and $I_j = I_{7-j}$ of intensity with $I_1 : I_2 : I_3 = 3 : 2 : 1$, and those of the A subspectrum are $I_j = I_{7-j}$ and $\Gamma_j = \Gamma_{7-j}$ ($j=1,2,3$) of the linewidths. Intensity ratio of B to A subspectra is 1.0 at 82 K and increases to 2.0 at 700 K with

increasing temperature. These results mean that Verwey transition does not exist in $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ ($x = 0.1, 0.2$), or Verwey transition temperature varies depending on different concentrations of Cu ions in each grain of $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$.

Fig. 4 shows the Mössbauer spectra at various temperatures for $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ ($x = 0.2$) annealed under vacuum at 450 °C. At 125 K, spectrum is similar to that of pure magnetite measured by other researcher [8] below Verwey temperature. Spectrum above Verwey temperature consists of three sextets and one quadrupole doublet, that is, the A- and B-site subspectrum of magnetite phase and hematite phase, and the quadrupole doublet due to Ishikawas paramagnetic cluster [9] near zero velocity. We determined Verwey temperature as 123 ± 2 K for $x = 0.1$ and 128 ± 2 K for $x = 0.2$. Increasing Verwey temperature with increasing substitution x in $\text{Me}_x\text{Fe}_{3-x}\text{O}_4$ (Me = transition metal) is the exact opposite to current research results [2]. Intensity ratios of B to A subspectra for magnetite-phase become 1.9-2.0 over all temperature ranges and Cu ions are distributed over A and B sites randomly. Ratios of hematite to total intensity in Mössbauer spectra for $x = 0.1$ and $x = 0.2$ are 10 and 21%, respectively. These hematite ratios may be determined by electroneutrality as annealing under vacuum at 450 °C transforms Cu^{2+} ionic states into Cu^{1+} , namely,



The calculated ratios of the Fe atoms in hematite to total Fe atoms are

$$\begin{aligned} \frac{0.15 \times 2}{0.8 + 1.8 + 0.15 \times 2} &= 10.3\% \quad \text{for } x = 0.1 \\ \text{and } \frac{0.3 \times 2}{0.6 + 1.6 + 0.3 \times 2} &= 21.4\% \quad \text{for } x = 0.2 \end{aligned} \quad (2)$$

As shown in Fig. 2, reliability of hematite phase existence is not clear in XRD patterns. The analysis of hematite phase in Mössbauer spectra gives the temperature dependence of magnetic hyperfine field and electric quadrupole shift illustrated in Fig. 5. Particularly, a sudden change of electric quadrupole shift near 280 K indicates characteristic of hematite and corresponds to Morin transition [10].

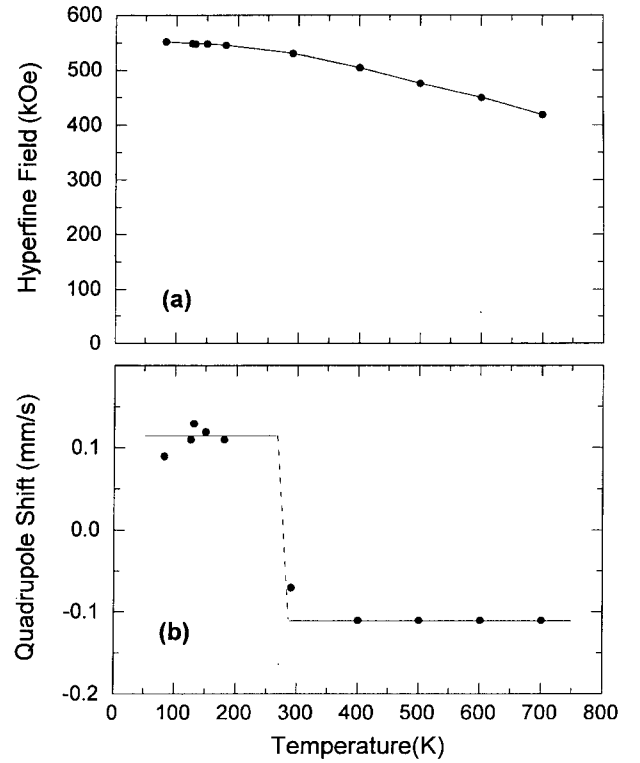


Fig. 5. Temperature dependence of (a) magnetic hyperfine fields and (b) electric quadrupole shifts of hematite phase for $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ ($x = 0.2$) annealed under vacuum at 450 °C.

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