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The γ -irradiation-induced chemical change from β -FeOOH to Fe_3O_4

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Abstract

The reactions of γ -irradiation on 5 nm β -FeOOH in the presence of isopropanol and water have been investigated. In the initial stage of the γ -irradiation, β -FeOOH turned into α -FeOOH. With the γ -irradiation continued, α -FeOOH was slowly reduced to Fe_3O_4 . After the γ -irradiation with a dose of 64.3 kGy, all the β -FeOOH and α -FeOOH disappeared and the product was a single phase of Fe_3O_4 , which had an average particle size of 54 nm. The process of this reaction is discussed. The γ -irradiation of β -FeOOH should be a new method of preparing magnetite. © 1999 Published by Elsevier Science Ltd. All rights reserved.

1. Introduction

Akaganeite (β -FeOOH) has been found as a major Fe-oxide component in soils and geothermal brines (Holm et al., 1983) and as a corrosion product of some steels or iron meteorites (Post and Buckwald, 1991). Both the natural and synthetic akaganeite typically occur as fine-grained masses with large specific surface area. As a kind of rich natural resources, the akaganeite has been expected to serve as the precursor of the iron oxide magnetic material. The procedure of preparing magnetite from β -FeOOH contains two steps: (1) Heated at 300°C for 2 h, β -FeOOH decomposed into α -Fe₂O₃; (2) then the α -Fe₂O₃ was reduced to Fe_3O_4 at 450°C in the stream of the mixture of H₂ and N₂ (Kishimoto et al., 1976).

The effect of γ -irradiation on the solid chemicals has been investigated intensively. In most cases, the γ -irra-

diated solid changed their properties, such as the crystalline size, the lattice parameter (Ramadan et al., 1989), the catalytic activity (Mucka, 1996), superconductivity (Leyva et al., 1995), etc. Mucka and Mizik, (1991) investigated the γ -irradiation effects on the physico-chemistry of ferric oxide. Also, Strukov et al. (1978) indicated that the γ -irradiation resulted in essential changes of the physical properties of the hydrogen bond ferroelectrics, triglycine sulphate (TGS) crystals. Based on these results, β -FeOOH may be affected by γ -irradiation. But to the best of our knowledge, the influence of the γ -irradiation on β -FeOOH has not been investigated till now. This paper reports on the phase transition and chemical reaction of the γ -irradiated β -FeOOH.

2. Experimental

The akaganeite was prepared by γ -irradiating the ferric hydroxide sol, which was prepared by dripping $\text{NH}_3 \cdot \text{H}_2\text{O}$ into the aqueous solution of FeCl_3 and keeping the concentration of Fe^{3+} and $\text{NH}_3 \cdot \text{H}_2\text{O}$ as

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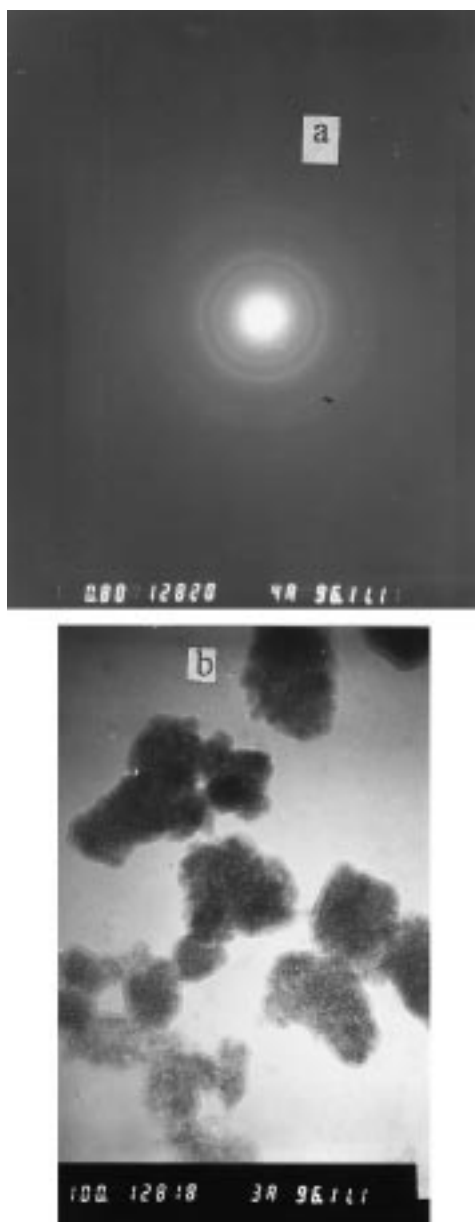


Fig. 1. TEM image of the β -FeOOH prepared by γ -irradiating the ferric hydroxide sol. (a) selected area diffraction pattern, (b) micrographs of the β -FeOOH.

0.01 M and 0.018 M, respectively. The pH value of the ferric hydroxide sol was 2.5. The γ -irradiation was carried out in the field of 70000 Ci ^{60}Co γ -ray source with a dose about 30 kGy till the precipitate occurred. The precipitate (β -FeOOH) was separated as soon as it occurred, and washed with distilled water, then dried at 40°C for several hours.

3 g akaganeite was added into 100 ml distilled water, then 20 ml isopropanol was poured into the sol-

ution as a OH-scavenger. This solution was γ -irradiated in the same field with different doses in the range from 0 to 64.3 kGy, stirring continuously. After the γ -irradiation, the precipitate was separated and dried at 40°C for several hours. X-ray powder diffraction (XRD) patterns were recorded at a scanning rate of $0.05^\circ \text{ s}^{-1}$ in the 2θ range from 10 to 70° using a Rigaku Dmax γ_{A} X-ray diffractometer with high-intensity Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$). TEM images were taken with a Hitachi model H-800 transmission electron microscope, using an accelerating voltage of 200 kV. Particle sizes were measured from the dark field TEM micrographs and also calculated from XRD patterns. A Mössbauer spectrometer (MS-500) with a ^{57}Co source in Rh matrix was used for the record of Mössbauer data at room temperature.

3. Results

Fig. 1 shows the TEM image and the selected area diffraction pattern of β -FeOOH (sample 1), which was prepared in the experimental. According to the electron diffraction pattern (Fig. 1a), the d -spaces corresponding to the ring are calculated from the formula $rd = L\lambda$, where r is the radius of each ring, d is the d -space to be calculated, and L and λ are the camera length and the electron wave length, respectively. The calculated d -spaces are well corresponding to the d -values of the standard β -FeOOH. The Mössbauer spectrum of sample 1 shows a doublet (Fig. 2). The isomer shift and quadrupole splitting are 0.39 and 0.65 mms^{-1} , respectively, which are in good agreement with that of β -FeOOH in the report (Terrell and Spijkerman, 1968). The XRD patterns (Fig. 3a) also show that all the diffraction peaks correspond well to the standard β -FeOOH. The Mössbauer spectrum combined with the XRD results indicated that the sample was a single phase of β -FeOOH. The particle size was calculated according to the Scherrer formula:

$$\beta = K\lambda/L \cos \theta \quad (1)$$

where λ is the wavelength, θ is the Bragg angle and K is the Scherrer constant (Langford and Wilson, 1978). The line broadening is obtained from the Warren and Biscoe equation (Wagner and Aqua, 1964):

$$\beta^2 = B^2 - b^2 \quad (2)$$

here B and b are the observed angular full width at half maximum for the sample under investigation and for standard sample, respectively. Calculated from XRD patterns (Fig. 3a), the average particle size found was 5 nm.

Fig. 3 shows the XRD patterns of the γ -irradiated β -

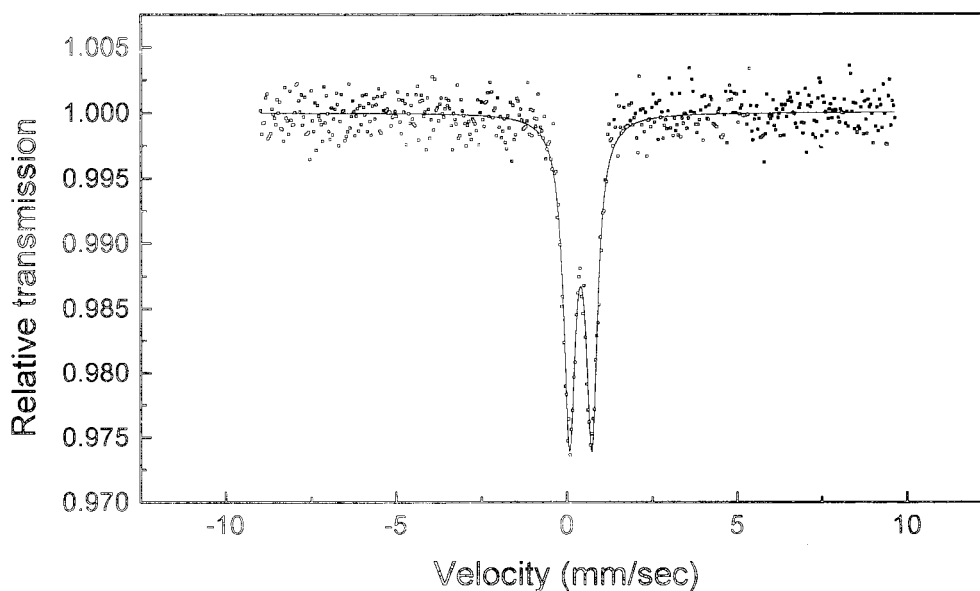


Fig. 2. Room temperature Mössbauer spectrum of sample 1.

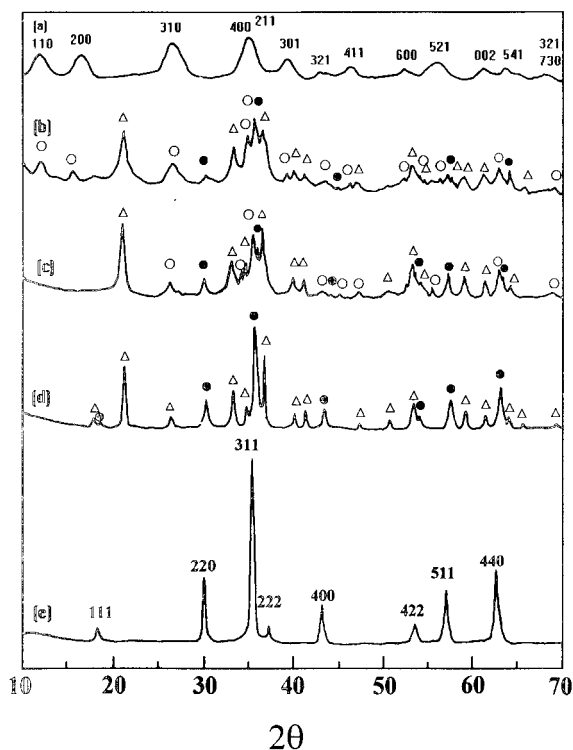


Fig. 3. XRD patterns of the product of γ -irradiated β -FeOOH with different doses: (a) non-irradiated (b) 4.2 kGy (c) 8.4 kGy (d) 21.0 kGy (e) 64.3 kGy; \circ , Δ and \bullet stand for β -FeOOH, α -FeOOH and Fe_3O_4 , respectively.

FeOOH with different doses. The correlation between the radiation doses and the component of the product is shown in Table 1. After γ -irradiation with a dose of 4.2 kGy, the sample mainly contained α -FeOOH, partially β -FeOOH and very little Fe_3O_4 . This indicates that the β -FeOOH turned into α -FeOOH partially. With the more doses of γ -irradiation on β -FeOOH, β -FeOOH turned into α -FeOOH further and the amount of Fe_3O_4 added (Fig. 3c). In Fig. 3d, all the peaks correspond to standard α -FeOOH or Fe_3O_4 , no peaks of β -FeOOH appeared and the amount of Fe_3O_4 increased to about the same level as α -FeOOH from the analysis of the intensity of the diffraction peaks. This indicates that β -FeOOH converted to α -FeOOH thoroughly. Sample 5 was γ -irradiated with a dose of 64.3 kGy. The diffraction patterns of sample 5 correspond to the single phase of the standard Fe_3O_4 . Table 2 shows the d -values of β -FeOOH, α -FeOOH and Fe_3O_4 corresponding to Fig. 3. Fe_3O_4 and γ - Fe_2O_3 are similar in crystal structure because they both belong to the spinel structure, which contains octahedral site (A) and tetrahedral site (B). In Fe_3O_4 , the A and B sites are occupied by $\text{Fe}^{2+}/\text{Fe}^{3+}$ and Fe^{3+} ions, respectively, while in γ - Fe_2O_3 both the A and B sites are occupied by Fe^{3+} and no Fe^{2+} exists in γ - Fe_2O_3 . The XRD patterns of Fe_3O_4 are similar to that of γ - Fe_2O_3 due to their similarity in crystal structure. To identify sample 5 further, Mössbauer spectrum was taken. The Mössbauer spectrum of sample 5 (shown in Fig. 4) can be divided into two sub-spectra, each sub-spectrum is sextet, which indicates the magnetic order arrangement of the iron atoms. It can be known (Daniels and Rosencwaig, 1969; Khalafalla and Morrish, 1972) that

Table 1
The correlation between the γ -irradiation doses on β -FeOOH and the component of the product

Sample	Radiation dose (kGy)	Phase component	Size
1	0.0	β -FeOOH	5 nm
2	4.2	β -FeOOH + α -FeOOH + Fe ₃ O ₄ (a little)	–
3	8.4	β -FeOOH + α -FeOOH + Fe ₃ O ₄	–
4	21.0	α -FeOOH + Fe ₃ O ₄	–
5	64.3	Fe ₃ O ₄	–

the main differences of the Mössbauer parameters between Fe₃O₄ and γ -Fe₂O₃ are (1) the value of quadrupole in Fe₃O₄ is closer to zero than that of γ -Fe₂O₃; (2) the values of the hyperfine magnetic fields corresponding to A and B sites are different in Fe₃O₄, but almost the same in γ -Fe₂O₃, due to the existence of Fe²⁺ ions at the A sites in Fe₃O₄. Table 3 represents the values of the quadrupole and the hyperfine magnetic field of the typical Fe₃O₄ (Daniels and Rosencwaig, 1969), γ -Fe₂O₃ (Khalafalla and Morrish, 1972) and sample 5 in the present experiment. From Table 3 one can see that the Mössbauer parameters are in close agreement with that of Fe₃O₄. The Mössbauer spectrum combined with the result of XRD indicated that sample 5 was a single phase of Fe₃O₄. Fig. 5 shows the TEM image and selected diffraction patterns of sample 5. The d -spaces calculated from Fig. 5a are identical with the d values from XRD pat-

Table 2
the d -values of the β -FeOOH, α -FeOOH and Fe₃O₄ found in XRD (Fig. 3)

β -FeOOH		α -FeOOH		Fe ₃ O ₄	
hkl	d (Å)	hkl	d (Å)	hkl	d (Å)
110	7.43	110	4.21	111	6.869
200	5.24	120	3.384	220	2.975
310	3.36	130	2.691	311	2.534
211	2.546	021	2.586	222	2.4244
301	2.304	111	2.452	400	2.0959
411	1.948	121	2.253	422	1.7127
600	1.476	140	2.912	511	1.6135
521	1.64	221	1.718	440	1.4830
002	1.523	240	1.609		
541	1.446	151	1.561		
730	1.376	160	1.561		
712		002	1.509		
		061	1.454		

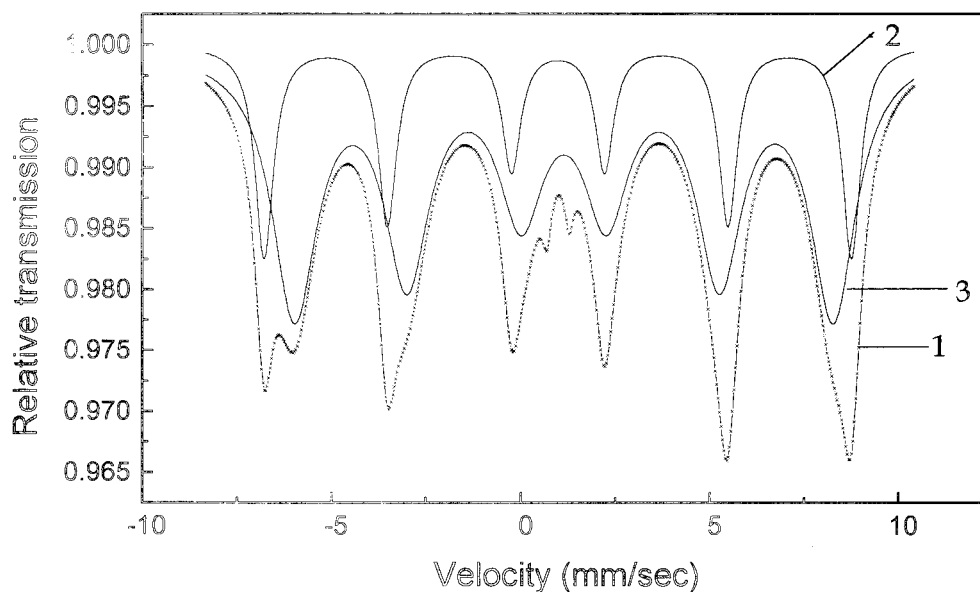


Fig. 4. Room temperature Mössbauer spectrum of sample 5; line 1 is the original spectrum, line 2 and 3 are the two sub-spectra, respectively.

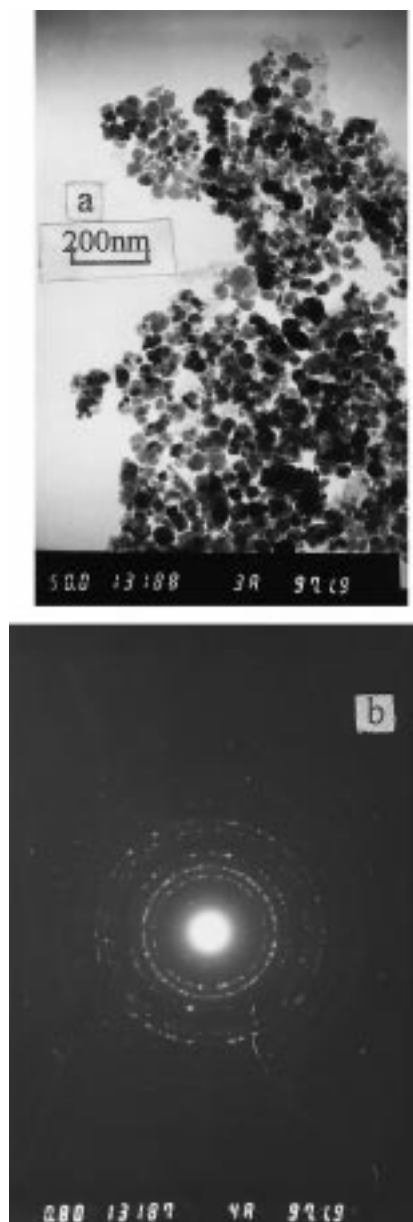


Fig. 5. TEM image of the Fe_3O_4 prepared by the γ -irradiated β -FeOOH with a dose of 64.3 kGy (a) selected area diffraction pattern, (b) micrographs of Fe_3O_4 .

terns (Fig. 3e). As shown in Fig. 5b, the Fe_3O_4 are granular particles with the average size of 54 nm.

4. Discussion

β -FeOOH is a substeady compound and can decompose easily into α - Fe_2O_3 when heated at about 300°C (Kishimoto et al., 1976). The result from the present

Table 3

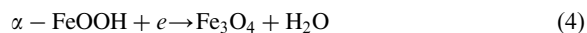
Mössbauer parameters of the typical Fe_3O_4 , γ - Fe_2O_3 and sample 5 in the present experiment

Sample	Position	Quardupole splitting (mms^{-1})	Hyperfine magnetic field (KOe)
Fe_3O_4	A	0.01 ± 0.04	497 ± 2
	B	0.04 ± 0.04	462 ± 2
γ - Fe_2O_3	A	0.59	497.2
	B	0.72	497.3
Sample 5	A	-0.002	483.7
	B	0.011	443.4

experiment indicates that β -FeOOH is also sensitive to γ -irradiation. In the initial stage of γ -irradiation, β -FeOOH changed into α -FeOOH at room temperature. This change can be expressed as:



Combining this result and another fact that the precipitate separated out from the γ -irradiated ferric hydroxide sol was β -FeOOH instead of α -FeOOH (details in the experimental section of this paper), we think that β -FeOOH is relatively steady in dynamics while α -FeOOH in thermodynamics. The unstable factors in β -FeOOH should exist in two aspects: firstly, β -FeOOH belongs to the monoclinic symmetry, which is lower than that of α -FeOOH (orthorhombic symmetry), secondly, the effect of the crystalline size. The very little size of β -FeOOH particles used in the experimental (average particle size is no more than 5 nm) has a very large surface area and high surface energy (Cavicchi et al., 1984). The large number of the surface particles are very active and easily take place reactions (Ball and Garwin, 1992). The authors also think that the phase transition from β -FeOOH to α -FeOOH was a topological equivalence, because the two compounds have the same chemical component but different atomic arrangement in the crystalline lattice. The γ -ray provides the essential energy for this phase transition. Fe_3O_4 as the only final product was obtained by the γ -irradiation-induced reduction of the α -FeOOH. This reaction may be explained analogously the γ -irradiation chemistry of aqueous solution (Allen, 1971):



The water in the system provided the H radicals which play an important role in the course of reduction, and the isopropanol act as a OH-scavenger which should prevent α -FeOOH from being reduced into Fe_3O_4 . Compared with other method of preparing magnetite,

the γ -irradiation-induced reduction of β -FeOOH carried on at room temperature and the product can be easily controlled. The authors think that the other analogs such as α -FeOOH, γ -FeOOH etc., which has a similar component to β -FeOOH should be reduced to the same product by γ -irradiation. The γ -irradiation of ferric oxides may be a useful method of preparing magnetite.

5. Conclusion

1. The nanocrystalline of β -FeOOH changed into the α -FeOOH in the initial stage of γ -irradiation. This phase transition belongs to topological equivalence.
2. With the γ -irradiation continued, the α -FeOOH decomposed into Fe_3O_4 .

The change from β -FeOOH to α -FeOOH can take place more easily than from α -FeOOH to Fe_3O_4 due to the non-stability of β -FeOOH. This experimental provide a new synthetic method of magnetite or other analogs.

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