THE THERMAL CONVERSION OF LEPIDOCROCITE (γ-FeOOH) REVISITED

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Abstract

The thermal conversion of lepidocrocite (γ-FeOOH) into maghemite (γ-Fe$_2$O$_3$) and hematite (α-Fe$_2$O$_3$) has been studied by dynamic (DSC) and static heating experiments. Dynamic heating defines two main regions: conversion of lepidocrocite to maghemite (endothermal signal peaking at 255°C) and conversion of maghemite to hematite (exothermal signal peaking at 450°C). In addition, an exotherm following the lepidocrocite to maghemite endotherm is observed. The maghemite phase appears as porous aggregates of nanocrystals characterized by an extensive spin-canting. We suggest that the additional exotherm is associated with structural changes and a decreasing extent of spin-canting in the maghemite phase.

Keywords: hematite, lepidocrocite, maghemite, nanocrystals, thermal conversion

Introduction

Lepidocrocite (γ-FeOOH) occurs in a number of geochemical environments characterized by fairly rapid oxidation of Fe(II) ions [1, 2]. It is well-known that heating of lepidocrocite leads to the formation of maghemite and the special magnetic properties of this material has prompted a number of investigations for both geochemical and technical purposes [3–5]. It has likewise been recognized that heating to high temperatures ultimately yields hematite. Previous studies of the thermal conversion of lepidocrocite have indicated two stages in the process: an endothermal peak signifying the formation of maghemite (peaking around 250°C) followed by an exothermal peak due to formation of hematite (peaking around 500°C) [1]. Differential scanning calorimetry (DSC) of a number of synthetic lepidocrocite samples revealed an additional exothermal peak close to the maghemite formation temperature. This feature could be related to textural changes or recrystallization of the maghemite phase [6]. To further elucidate the nature of this thermal signal we have investigated a systematic series of samples prepared by static heating of lepidocrocite at various temperatures.

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Samples and experimental procedures

A synthetic lepidocrocite sample was prepared following a standard method [7]. By X-ray diffraction and spectroscopy the sample (henceforth referred to as the as-prepared sample) was found to consist of single-phase γ-FeOOH.

Dynamic heating experiments were conducted in a Polymer Laboratories PL-DSC instrument using a heating rate of 10 K min^{-1} and a nitrogen atmosphere. Samples of thermally decomposed lepidocrocite were prepared by heating 100 mg of the as-prepared sample isothermally at different temperatures between 100 and 800°C (100, 150, 175, 200, 225, 250, 275, 300, 325, 350, 400, 500, 600, 700 and 800°C). The heating was done in air for 24 h with a temperature accuracy of ±2 K. The samples were quenched to about 10°C. X-ray measurements were performed using a Siemens D 5000 diffractometer. The TEM work was carried out using a Philips EM 430 microscope operated at 300 kV. Infrared spectra were recorded on a Perkin Elmer FT-IR 2000 instrument. Mössbauer spectra were obtained using conventional Mössbauer spectrometers with a ^{57}Co source in rhodium. Low-temperature spectra were obtained utilizing a closed-cycle helium refrigerator (15–300 K) and a liquid-helium cryostat (5 K). External fields of up to 6 T were obtained by using a super-conducting magnet system.

Results and discussion

Figure 1 shows the DSC curve of the as-prepared lepidocrocite. The diagram exhibits four distinct features: 1. A relatively weak endothermal signal below 100°C due to desorption of water from the grain surfaces (will not be discussed further here). 2. A strong endothermal peak centered at 255°C. The peak has its extrapolated onset at 220 and it is completed at 270°C. 3. A broad, asymmetric exothermal signal ranging

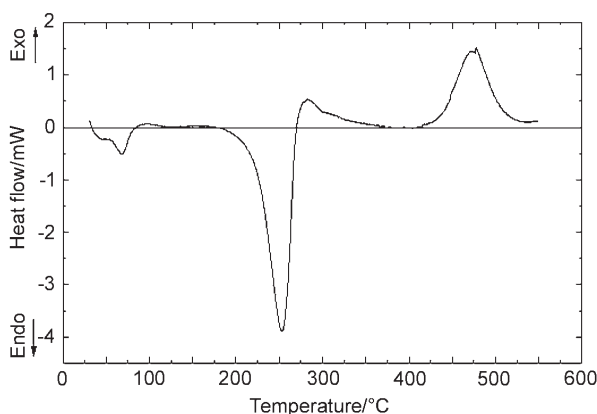**Fig. 1** DSC curve of the γ-FeOOH sample obtained with a heating rate of 10 K min^{-1} in N$_2$ atmosphere. Positive values of the heat flow correspond to exothermic reactions while negative values correspond to endothermic reactions
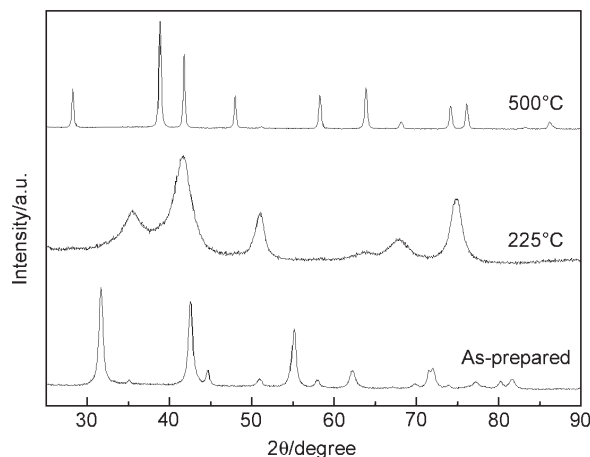
Fig. 2 X-ray diagrams of the as-prepared lepidocrocite (the bottom curve) and of two lepidocrocite samples heated for 24 h at 225 and 500°C, respectively

from 270 to about 350 with peak maximum at 283°C. 4. A strong exothermal response peaking at 475, with extrapolated onset at 435 and completion at 510°C. The strong endothermal signal at 255°C marks the dehydroxylation of the lepidocrocite structure leading to the formation of maghemite. The broad exothermal signal around 475°C is associated with the transformation of maghemite into hematite. For the temperature range between the dehydration endotherm and the γ to α conversion exotherm no phase transformations are expected. By interrupting the DSC experiment at different temperatures it has previously been found that the exotherm is not due to a partial conversion of maghemite into hematite [6]. Rather, it seems to be related to structural changes of the newly formed maghemite.

The statically heated lepidocrocite samples were analyzed by means of X-ray diffraction. Figure 2 shows the diffraction diagrams obtained for the as-prepared sample and the samples heated at 225 and 500°C, respectively. The diagrams demonstrate the two major steps of the conversion of lepidocrocite. For the as-prepared sample a distinct γ-FeOOH pattern is observed. For the sample heated at 225°C no features related to the presence of γ-FeOOH can be observed and the new pattern corresponds to that of maghemite. There are no indications of features related to hematite. Thus, at 225°C the static heat-treatment has lead to formation of single-phase maghemite. The 500°C sample shows a characteristic hematite pattern demonstrating that the γ–α transformation has been completed. The peak widths of the XRD patterns were used for estimating the mean crystal dimensions of the three phases (strain and other effects that could influence the peak widths were ignored in this analysis). For the as-prepared sample the value of the mean crystal diameter (MCD) depends strongly on the reflection direction. For the [120] peak and the [031] peak a value of 24 nm is obtained. For the [111] peak the MCD is about 60 nm. The apparent shape anisotropy is in good agreement with the TEM work showing that the γ-FeOOH parti-

cles are lath-shaped and elongated in the crystallographic c-direction (Fig. 3a). For the heated samples the MCD of the γ-FeOOH phase is only slightly decreasing, indicating that the characteristics of the remaining γ-FeOOH remains unchanged. As seen in Fig. 2, the maghemite phase gives rise to a very broad-lined XRD pattern. In the diffraction diagram of the sample heated at 150°C the peaks for maghemite could barely be seen. However, by subtracting the signal of the as-prepared sample a distinct γ-Fe$_2$O$_3$ pattern was obtained. From this pattern the crystallite sizes was estimated to be 3 nm for the [220] peak and the [311] peak and 8 nm for the [400] peak. This suggests that the crystallites are somewhat anisotropic in shape. The γ-Fe$_2$O$_3$ peaks become more intense and sharper with increasing temperature. In the 150–300°C temperature range the MCD values obtained for the [200] and the [311] reflections increased from 3 to 8 nm. For the [400] peak the MCD value increased from 8 to 16 nm in the same temperature range. Hence, the shape anisotropy is conserved as the crystallites grow. The first weak features associated with the presence of hematite were observed for the sample heated at 250°C. For the 300°C sample a distinct α-Fe$_2$O$_3$ pattern superimposes the broad-lined γ-Fe$_2$O$_3$ pattern. Compared to the maghemite phase the hematite phase gives rise to relatively sharp peaks even at the lowest temperatures. For the 325°C sample a MCD of about 50 nm is obtained. At higher heating temperatures the grain size increases rapidly as the thermal treatment leads to sintering.

Figure 3 shows TEM pictures of the as-prepared lepidocrocite and three of the heat-treated samples. The as-prepared sample consists of lath-shaped grains (Fig. 3a). The typical dimensions for the particles are ~5×25×100 nm. Heating at moderate temperatures (100–300°C) does not cause significant changes of the overall morphology, although there is a tendency for the particle edges to become more rounded. Considering the crystallite sizes obtained from the XRD measurements it appears that
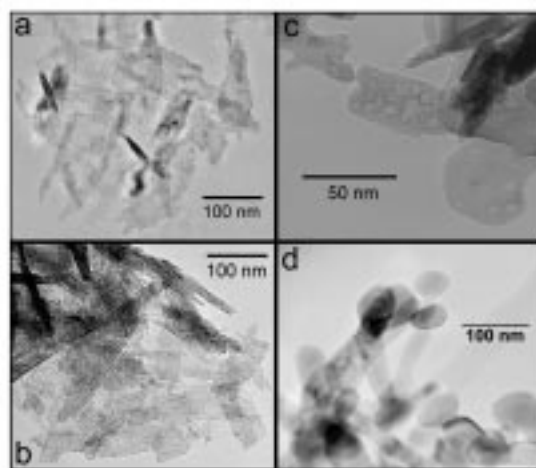

Fig. 3 Transmission electron micrographs. a – the as-prepared γ-FeOOH,
b – the 225°C sample, c – the 325°C sample, d – the 500°C sample

maghemite has formed via multiple nucleation sites within the precursory γ-FeOOH grains. The sample heated between 100 and 400°C exhibit highly irregular grain surfaces, which appear to be covered by small holes or pores (Figs 3b and c). The pores occur as disk-like features with a diameter of 1–5 nm. Formation of micro-pores following dehydroxylation have previously been reported for goethite (α-FeOOH) [8] and lepidocrocite [6, 9]. The pores are produced as the crystal lattice contracts in order to fill the vacancies formed by the dehydration. In high concentrations they may occur as slits and in lower concentration as disk-shaped features. In the present study pores have mainly been seen as disks. Figure 3d shows a particle produced by heating at 500°C. The pores that were formed during the dehydroxylation no longer appear and the grains have become rounded. Comparing with the XRD results we find that the grain size coincides with the value obtained from the XRD peak widths. This indicates that the nucleation processes leading from γ-FeOOH to γ-Fe$_2$O$_3$ and from γ-Fe$_2$O$_3$ to α-Fe$_2$O$_3$ differs significantly: Maghemite is formed as nanocrystals via multiple nucleation sites within the original lepidocrocite grains, whereas hematite is formed via a small number of nucleation sites immediately leading to relatively large crystals.

The infrared active OH vibrations of the lepidocrocite are very distinct features of the spectrum at 748, 1022 and 1163 cm^{-1} (Fig. 4). The conversion of lepidocrocite to maghemite in the temperature interval 100 to 200°C is causing a general weakening of the intensities of these bands. After heating to 200°C the structure of lepidocrocite is essentially lost and the absorption bands due to maghemite dominate the composite spectrum. From the position of the absorption bands it appears that the characteristics of the last-converted lepidocrocite is similar to those of the as-prepared sample and that the local structure of the maghemite is constant within this temperature range. We have not observed direct evidence for excessive hydroxyl groups
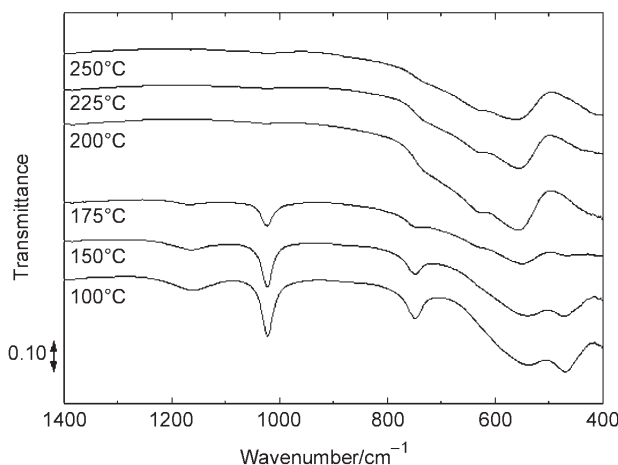

Fig. 4 Mid-IR spectra of lepidocrocite samples heated at different temperatures as labelled

in the maghemite from the IR spectra, as e.g. described for the goethite to hematite conversion [10]. However, it is likely that the characteristic formation of small crystals and porous aggregates described for the lepidocrocite to maghemite conversion facilitates removal of hydroxyls. At higher temperatures the characteristics of hematite appear (not shown) and exhibit a typical crystal size dependence indicating thermally induced growth [11].
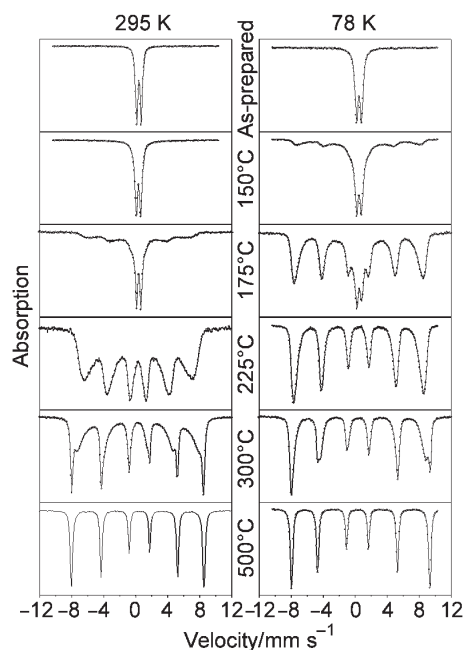

Fig. 5 Mössbauer spectra of the as-prepared and heat-treated lepidocrocite (see the labels). The spectra in the left column were recorded at room temperature, while the spectra in the right column were recorded at 78 K

All the products of the static heating were investigated by Mössbauer spectroscopy at 295 and 78 K and selected spectra are shown in Fig. 5. The spectra of the as-prepared sample display a broad paramagnetic doublet. At room temperature the isomer shift is 0.37 mm s^{-1} and the quadrupole splitting is 0.55 mm s^{-1} as expected for γ-FeOOH [12]. The Neél temperature of the as-prepared lepidocrocite was determined to 54 K. The paramagnetic doublets dominate the spectra of the sample heated at 150°C and are still clearly resolved in the spectra of the sample heated to 175°C. In addition to the doublet, a magnetically ordered sextet is detected in the spectrum measured at 78 K following heating at 150°C. After heating at 175°C the relative content of this sextet increases and part of it remains in the spectrum measured at 295 K. The sample produced after heating at 225°C displays spectra completely dominated by magnetically ordered components. At 78 K the lines of the spectrum are fairly sharp and a distinct asymmetry may be detected. The sextet has zero quadrupole splitting,
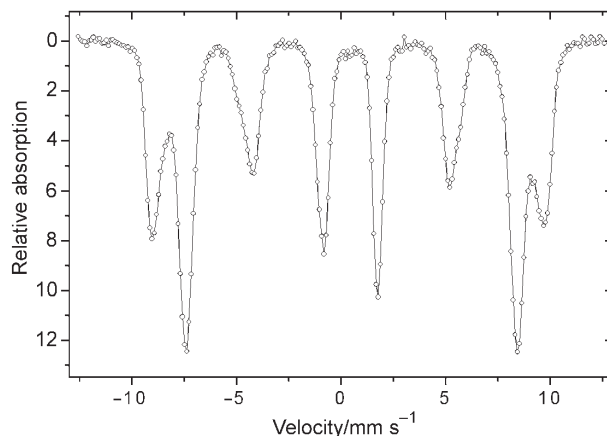
Fig. 6 Mössbauer spectrum of the lepidocrocite sample heated at 225°C. The spectrum was obtained at 5 K and with an applied magnetic field of 6 T directed parallel to the γ-ray direction

an isomer shift of 0.45 mm s^{-1} and a hyperfine field of 50.3 T. This is in good agreement with the standard parameters of small-grained maghemite and in good agreement with the phase identification from XRD and IR. The presence of two slightly different sites in maghemite is the major reason for the asymmetry. At 295 K the spectrum is strongly broadened and in fact a reasonable description can only be achieved by use of a hyperfine field distribution model. This behavior can be explained by mutually strong magnetic exchange interactions between the crystals within the aggregates. The occurrence of much reduced magnetic hyperfine fields is characteristic for such superferro-magnetically ordered systems [13]. The changes occurring in the spectral component due to maghemite, as a function of heating temperature, can accordingly be explained by assuming both increasing concentrations of maghemite within the lepidocrocite host and an increase in the interaction strength. In this dilute state the behavior of the maghemite will be like classically simple non-interacting crystals exhibiting superparamagnetic relaxation. This behavior can be overcome by simply decreasing the temperature of the system. Maghemite has a ferrimagnetic spin structure and therefore its properties can be explored further investigating its response to an external magnetic field. At high external fields a splitting of the two subspectra of the ferrimagnetic structure may be achieved. In Fig. 6 the spectrum obtained at 5 K of the sample heated at 225°C is shown. The spectrum was measured with an external magnetic field of 6 T parallel to the γ-ray propagation direction. Ideally the lines 2 and 5 of the two subspectra would vanish under such conditions. From the spectra it is seen that considerable intensity remain in this lines, indicating extensive spin canting in the structure [14]. The fraction of canted spin is about 50% and decreases with increasing heating temperature (from about 54% at 175°C to about 47% at 250°C). The high extent of spin-canting could be associated with the porosity of the maghemite aggregates giving rise to a large fraction of surface-near

spins that may be subject to canting due to the absence of neighboring spins. The spin-canting may, however, also occur within the interior of the maghemite crystals. For heating temperatures above 300°C a sharp-lined sextet with hyperfine values of $\Delta E_Q = -0.11$ mm s^{-1}, $\delta = 0.25$ mm s^{-1} and $B_{hf} = 51.3$ T are observed and for heating temperatures above 400°C this component completely dominates the spectra. The hyperfine field increases slightly (to 51.7 T) with increasing temperature. These observed hyperfine parameters correspond to those reported for pure hematite [1]. The increasing hyperfine field is properly related to the thermally induced growth, which leads to more bulk-like properties.

Conclusions

The thermal conversion of lepidocrocite into maghemite and hematite occur via two markedly different pathways. In the former one a relative high concentration of nuclei leads to the formation of aggregates of nanocrystalline, strongly magnetically interacting maghemite crystals. At temperatures just above the formation temperature the maghemite is characterized by the presence of extensive spin canting. The spin canting decreases and the excess energy contributes to the exothermal signal.

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