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In situ FTIR study on the dehydration of natural goethite

P.S.R. Prasad[a,*], K. Shiva Prasad[a,d], V. Krishna Chaitanya[b], E.V.S.S.K. Babu[a], B. Sreedhar[c], S. Ramana Murthy[d]

[a]National Geophysical Research Institute, Hyderabad 500 007, India
[b]School of Physics, University of Hyderabad, Hyderabad 500 046, India
[c]Indian Institute of Chemical Technology, Hyderabad 500 007, India
[d]Department of Physics, Osmania University, Hyderabad 500 007, India

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Abstract

Fourier Transform Infrared (FTIR) spectroscopy, thermal analysis -Differential Scanning Calorimetry (DSC) and Thermo-Gravimetry (TG-DTG) were used to study the dehydration behavior of synthetic goethite and two naturally occurring goethite samples (Natural 1 and Natural 2) from Banded Iron Formation (BIF), at C.S. Halli, Chitradurg district, Karnataka, India. Goethites and its dehydration products were also identified by powder X-ray Diffraction (XRD) method. The dehydration temperatures were at 538, 567 and 578 K for synthetic, Natural 1 and 2 goethite, respectively. On approaching the dehydration temperature, infrared active modes of the hydroxyl groups have shown distinct variations. The peak position for the stretching mode around 3150 cm^{-1} was shifted upwards, while that for in-plane-deformation mode around 890 cm^{-1} was down shifted indicating weakening of strength of the hydrogen bonding. No intermediate phase, so called hydro-hematite, was observed in these studies. The total absorbance (area under the peak) of these modes have shown the Arrehenius type behavior in the temperature range 500–600 K, using which the activation energy for the dehydration process was estimated as 71, 103 and 85 kJ/mol for synthetic, Natural 1 and 2 goethites respectively.

Keywords: Goethite; Hematite; Dehydration; XRD; DSC; TG-DTG and FTIR

1. Introduction

Iron oxides play important roles as adsorbents controlling the mobility of trace contaminants, supplying plant nutrients, soil aggregation, soil classification and pedogenesis. Among iron oxy-hydroxides, goethite (α-FeOOH) is abundant constituent of terrestrial soils, sediments, oolitic iron ores and major weathering product of all rock types. It is predominant in younger sedimentary deposits, giving the rocks a yellow colour. On the other hand, hematite (α-Fe_2O_3) is abundant in ancient deposits imparting a red colour (Goss, 1987). Thermodynamically, goethite is the most stable of the iron oxides and is an end member of many transformations (Schwertmann and Cornell, 1991). However, both particle size and kinetic effects are important for the crystallization and stability of goethite and hematite (Goss, 1987; Langmuir, 1971, 1972; Gonzalze et al., 2000; Walter et al., 2001). According to Langmuir (1971, 1972), goethite with particle size less than 0.1 μm is thermodynamically more unstable than hematite. However, goethite is the commonest phase in younger deposits, as the reaction kinetics is slow. The hematite/goethite ratio in soils is thus an indicator of the carbon regime and climate (Tite and Linington, 1975). Pollack et al. (1970a,b) studied the kinetics of the dehydration reaction and suggested that chemical equilibrium in the goethite-hematite system determine the time average abundance of water vapor on Mars.

The dehydration transformation, which is topotatic has been subjected to number of investigations. It has been suggested that the thermally induced transformation can either be a direct transformation from goethite to hematite

* Corresponding author. Tel.: +91 40 23434700x2485; fax: +91 40 27171564.
E-mail address: psrprasad@ngri.res.in (P.S.R. Prasad).

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(Walter et al., 2001; Watari et al., 1979),

$$2\,\alpha(\mathrm{FeOOH}) \rightarrow \alpha(\mathrm{Fe_2O_3}) + \mathrm{H_2O},$$

or a transformation with the formation of an intermittent super structure phase so called proto-hematite or hydro hematite, before the final formation of hematite (Lima-de-Faria, 1963; Gualtieri and Venturelli, 1999; Ozdemir and Dunlop, 2000; Wolska (1981,1988); Wolska and Schwertmann (1989),

$$2\alpha(\mathrm{FeOOH}) \rightarrow 6/(6-x)\ \underset{\text{(super structure)}}{\alpha\mathrm{Fe}_{2-x/3}\,(\mathrm{OH})_x\mathrm{O}_{3-x}}$$

$$+\,(6-4x)/(6-x)\mathrm{H_2O} \rightarrow \alpha(\mathrm{Fe_2O_3}) + 3x/6 - x\mathrm{H_2O}.$$

There has been no general agreement on the mechanism of thermal transformation in goethite. In recent times, this solid state transformation has been subjected to experimental investigations. Gualtieri and Venturelli (1999) have studied this transformation by in situ synchrotron X-ray powder diffraction using pure, synthetic stoichiometric goethite with 1 μm long needle-shaped crystals. They reported that the dehydration of goethite started at 200 °C and concluded at about 270 °C; and the resultant phase is with non-stoichiometric composition called proto-hematite. This was eventually converted to hematite at around 800 °C. Ozdemir and Dunlop (2000), also reported an intermediate phase particularly in partially dehydrated goethite in the temperature range 238–402 °C. Wolska (1981,1988); Wolska and Schwertmann (1989) also reported the formation of a hydrohematite [$\mathrm{Fe_{1.83}(OH)_{0.5}O_{2.5}}$] phase during the thermal dehydration of goethite in the range 180–250 °C, and this phase finally transforms into the hematite in the temperature range 800–1050 °C. On the other hand, mechano-chemical and thermal studies of the transformation by Gonzalez et al. (2000) using TEM and XRD reported a direct transformation of goethite to hematite. They also have reported conversion of goethite (original particle size 400–700 nm) to a hematite phase, when the average particle size was decreased to 19–25 nm, from goethite by mechanical grinding. Goss (1987) studied the kinetics of goethite to hematite transformation and suggested a direct transformation. Katoh et al. (2001); Walter et al. (2001) also reported a direct transformation to hematite, at approximately 220 °C. Ruan et al. (2001, 2002a,b) have studied the dehydration behavior of synthetic goethites and those from Australian bauxite using FTIR spectroscopy. Recently Frost et al. (2003) reported two-step phase changes during dehydration in naturally occurring and synthetic goethite samples using thermal analysis. Naturally occurring goethites are rarely stoichiometric and usually contain number of isovalent or heterovalent cations, like Ni^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, Cr^{2+}, Ga^{2+}, V^{3+}, Mn^{3+}, Co^{3+}, Si^{3+}, Pb^{4+}, Ge^{4+}, Si^{4+}, and Ti^{4+}. These cations can partially replace the Fe^{3+} without a change in crystal structure (Huynh et al., 2002). It was reported that the dehydration temperature of Cu-substituted goethites decreases to 221 °C, while that of pure goethite is 238 °C (Huynh et al., 2002). On the other hand, the effect of Al and Cr was opposite and the dehydration temperatures increase (Ruan et al., 2002a).

Most of the above studies were on well-synthesized goethite and to the best of our knowledge the dehydration mechanism was not studied on natural samples. In this we report in situ Fourier Transform Infrared (FTIR) spectroscopic results of dehydration mechanism on two naturally occurring goethite samples from Banded Iron Formation (BIF), C.S. Halli, Chitradurg district, Karnataka, India, and the mechanism is compared with a synthetic sample. The main objective of this study is to get the FTIR signatures of hydro- (proto-) hematite, often observed in the literature as an intermediate product during the dehydration (Gualtieri and Venturelli, 1999; Wolska, 1989; Ruan et al., 2001).

2. Materials and methods

2.1. Sample description

Natural samples were extracted from a Banded Iron-Formation (BIF) occurring at C.S. Halli, Chitradurg district, Karnataka, India. This formation is the youngest among the several BIF bands in the Chitradurg schist belt, Ingaldahl copper mine. We have chosen samples within two patches spatially separated by about 4–5 mm, one dark brown in colour, another brown-yellow in colour, and in the latter has a width of about 3–4 mm. The material within the brown-yellow portion (Natural 1) could easily be removed by a sharp edge. Whereas, the material from dark brown portion (Natural 2) is more difficult to scratch. The sample contains bands of chert with hydrous alteration towards the formation of goethite. The goethites are of needle type and are embedded in chert.

The synthetic sample was prepared using the method of Schwertmann and Cornell (1991). A precipitate was formed by mixing 5 ml of 1 M ferric nitrate solution to 45 ml of 1 M KOH. This suspension of hydrous ferric oxide was then aged for one week at ambient conditions, and the formation of goethite was intermittently checked by FTIR spectra. The suspension was washed thoroughly with distilled water to remove residual KOH and nitrates before using it for dehydration studies. The residue was filtered and dried. IR and XRD confirmed the formation of mono-phase goethite.

2.2. X-ray diffraction

The X-ray diffraction patterns obtained were recorded using Phillips PW-1830 powder diffractometer with Ni-filter, θ–2θ scan. The radiation used was Cu Kα radiation. The 2θ scan was from 10–80°. The rate at which the sample rotates was 3 degrees/min.