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ProScience 2 (2015) 26-30

ProScience

Conference Proceedings

1st International Conference on Applied Mineralogy & Advanced Materials - AMAM2015

Solid state transformation of iron-bearing hydrated sulfate to α-Fe_2O_3

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Abstract

Iron oxides are transition metal oxides of paramount importance for their technological applications. Their synthesis can be performed by a variety of methods, most of which are chemical methods. Hematite, α-Fe2O_3, can also be produced from iron sulfates by heating them sufficiently in air. In this work we have employed the thermal decomposition method to obtain hematite from the dehydration of fibroferrite, FeOH(SO_4)· 5H_2O, a secondary iron-bearing hydrous sulfate. The study was performed via Rietveld refinement based on *in-situ* synchrotron X-ray powder diffraction combined with thermogravimetric analysis and mass spectrometry. The integration of the data from these techniques allowed to study the structural changes of the initial compound, determining the stability fields and reaction paths and its high temperature products. Six main dehydration/transformation steps from fibroferrite have been identified in the heating temperature range 30-798 °C. In the last step of the heating process, above 760 °C, hematite is the final phase. The temperature behavior of the different phases was analyzed and the heating-induced structural changes are discussed.

Keywords: Fibroferrite; hematite; solid state transformations.

1. Introduction

Iron oxides are of great technological importance and find applications as catalysts, sorbents, pigments, flocculants, coatings, gas sensors, ion exchangers and for lubrication. Their synthesis can be performed by a variety of methods, most of which are chemically

ISSN: 2283-5954
Selection and peer-review under responsibility of AMAM2015 Scientific Committee
DOI:10.14644/amam.2015.005

based methods (Wu et al., 2006). Careful control of the preparation process of iron oxides is a challenging task to address the synthesis towards a particular application. In this work we have employed the thermal decomposition method to obtain hematite, α-Fe_2O_3 from the dehydration of fibroferrite, $FeOH(SO_4)\cdot 5H_2O$, an iron-bearing hydrous sulfate of secondary origin. The study was performed by employing Rietveld refinement based on *in-situ* synchrotron X-ray powder diffraction data in combination with thermal analysis and mass spectrometry.

The crystal structure of fibroferrite (Scordari, 1981) is based on $[Fe^{3+}(OH)_2(H_2O)_2O_2]$ octahedra linked via *cis*-octahedral vertices to form helical chains running parallel to the c axis (Fig. 1a). SO_4 groups share two oxygen corners with Fe^{3+}octahedra providing further intra-chain linkages. Adjacent chains link both by direct hydrogen bonding, and by a complex hydrogen-bonding network involving free water groups. The crystal structure of hematite (Fig. 1b), α-Fe_2O_3 (Blake et al., 1966), is isostructural with corundum, α-Al_2O_3.

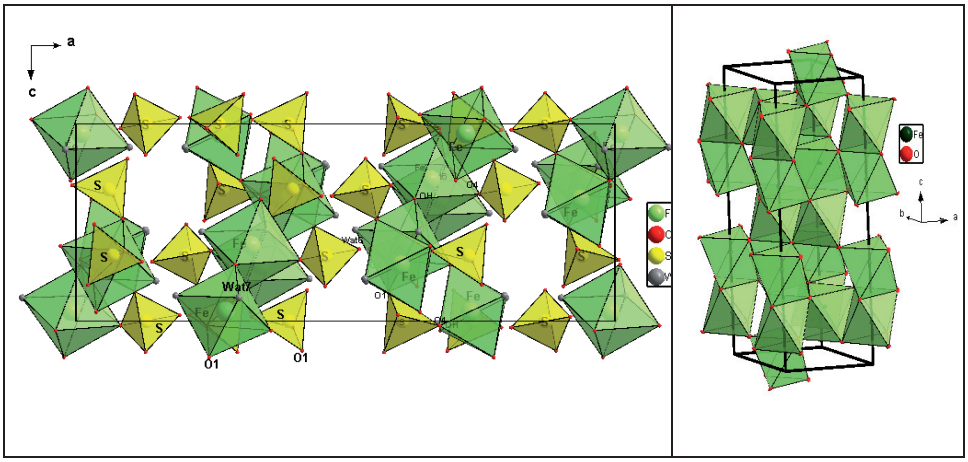

Fig. 1. Schematic representation of the structures of fibroferrite (a) and hematite (b). W stands for water.

2. Materials & methods

Thermogravimetric analyses (TGA) and differential thermal analysis (DTA) curve. were performed using a Seiko SSC 5200 thermal analyzer equipped with a TG/DTA 320U module. For mass spectromety data an ESS, GeneSis Quadstar 422 was employed

X-ray powder diffraction (XRPD) profiles were collected at the GILDA Beamline in the range 30-789 °C employing an Image Plate detector that translated as the temperature increased.

Specifically, 61 diffractograms were acquired, one every 13 °C. After the phase identification step, the phase fraction analysis was carried out using the Rietveld method.

3. Results and discussion

The TGA-DTA patterns (Fig. 2) show six main dehydration/transformation steps in the heating temperature range. Above 760 °C, hematite is the final phase. The DTA curve

shows six main endothermic peaks (arrows in Fig. 2) . The relevant weight losses are quantified using the combined TG curve. The total loss observable in the whole range corresponded to 68%.

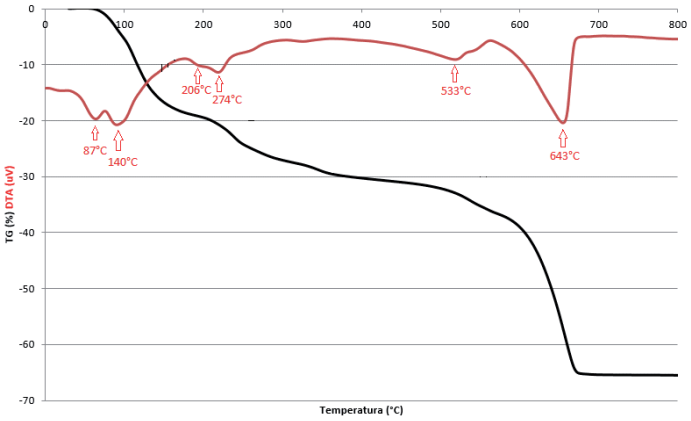

Fig. 2. Experimental trend of TG (black curve) and DTA (red curve).

Mass spectrometry (Fig. 3) permits to observe that the weight losses, related to the endothermic reactions up to 500 °C are due to dehydration. At 600 °C the last weight loss is associated to desulphurization.

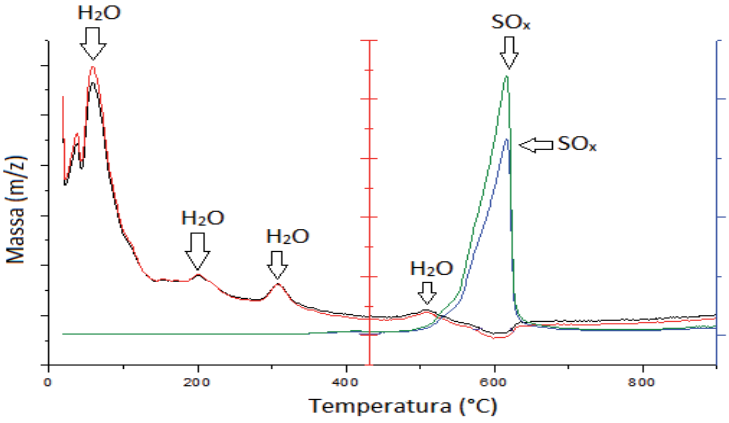

Fig. 3. Mass spectra of the investigated sample.

Combining the results obtained from the phases identification using *in situ* high temperature XRPD and the thermal analysis, it was found that the complete thermal decomposition of fibroferrite occurs in six steps, that schematically summarized as follows:

Starting phase at RT: $Fe(OH)(SO_4)\cdot 5H_2O$ fibroferrite

1st step (68-94 °C):
$Fe(OH)SO_4 \bullet 5H_2O \rightarrow Fe(OH)SO_4 \bullet 4H_2O + H_2O$
(see Fig. 4 below)

2nd step (107-132 °C):
$Fe(OH)SO_4 \bullet 4H_2O \rightarrow Fe(OH)SO_4 \bullet 3H_2O + H_2O$
$Fe(OH)SO_4 \bullet 4H_2O \rightarrow Fe(OH)SO_4 \bullet 2H_2O$ (butlerite) $+ 2H_2O$

3rd step (145-196 °C)
$Fe(OH)SO_4 \bullet 3H_2O \rightarrow Fe(OH)SO_4 \bullet 2H_2O + H_2O$
$Fe(OH)SO_4 \bullet 2H_2O$ (butlerite) → amorphization

4th step (260-311 °C):
$Fe(OH)SO_4 \bullet 2H_2O \rightarrow FeOHSO_4 + 2H_2O$

5th step (427-606 °C):
$5Fe(OH)SO_4 \rightarrow Fe_2(SO_4)_3 + Fe_2O(SO_4)_2 + Fe + 3/2O_2 + 5/2H_2O$

6th step (631-683 °C):
$Fe_2O(SO_4)_2 \rightarrow Fe_2O_3 + 2SO_2 + O_2$
$Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_2 + 3/2O_2$
(see Fig. 5 below)

Final reaction (T >760 °C): α-Fe_2O_3

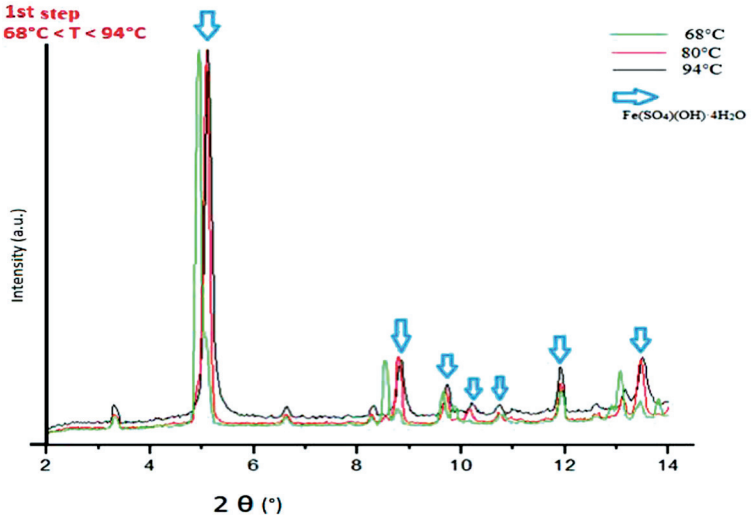

Fig. 4. XRPD patterns illustrating the first step of the fibroferrite temperature behavior.

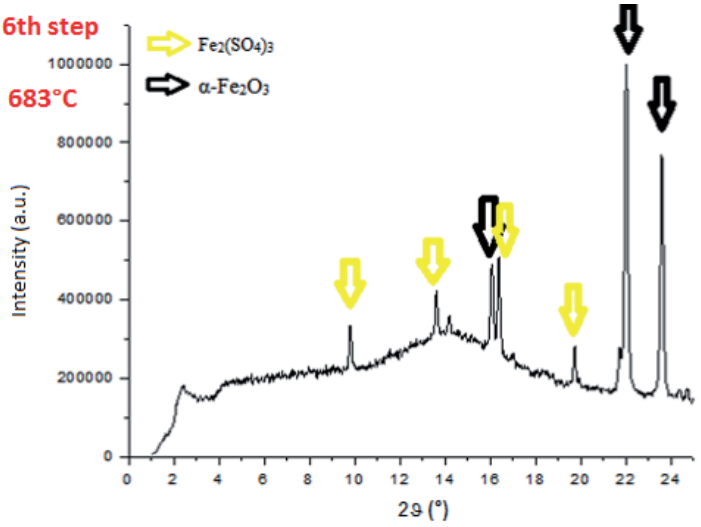

Fig. 5. XRPD pattern illustrating the sixth step of the fibroferrite temperature behavior.

4. Conclusions

With the method of high temperature in situ XRPD with synchrotron radiation combined with profile analysis, the dehydration/transformation of fibroferrite to hematite, α-Fe_2O_3 was found out to occur in 6 steps. Hematite occurs in XRPD patterns in the 631-683 °C temperature interval coexisting with $Fe_2(SO_4)_3$, but remains the only crystal phase at T > 760 °C.

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