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THERMAL ANALYSIS OF GOETHITE
Relevance to Australian indigenous art

R. L. Frost[*], *Z. Ding and H. D. Ruan*

Centre for Instrumental and Developmental Chemistry, Queensland University of Technology,
GPO Box 2434 Brisbane, Q 4001, Australia

Abstract

Differential scanning calorimetry shows two endotherms at 75 and 225°C for synthetic goethite. The latter endotherm is strongly asymmetric on the low temperature side. The endotherms were attributed to the loss of water and the dehydroxylation of the goethite. The temperature of the endotherms and the enthalpy of the phase change were found to be linear functions of the percentage of aluminium substitution into the goethite. High-resolution thermogravimetric analysis of goethite showed three mass loss steps, occurring at ~175, 196 and 263°C. The temperatures of these mass loss steps and the percentage of mass loss were also linearly related to the degree of Al substitution. The use of infrared emission spectroscopy confirmed the temperature of dehydroxylation. The observation of the low temperature dehydroxylation of goethite and its relation to ancient aboriginal cave art is discussed.

Keywords: dehydration, dehydroxylation, DSC, goethite, haematite, high-resolution TG

Introduction

Goethite was a commonly used colorant amongst indigenous tribes in prehistoric times [1]. The Australian aboriginals used goethite for face, body and cave paintings. The major deposit of goethite is in the Flinders ranges of South Australia and is not commonly found in other parts of Australia. One commonly accepted point of view is that minerals such as goethite, haematite and kaolinite may have been used for trade or as a monetary device. Most aboriginal cave paintings such as may be found at Chillagoe in North Queensland contain extensive ancient aboriginal paintings. Most of the paintings are now coloured red from haematite. Two basic questions arise: firstly were the paintings originally painted yellow/gold with goethite and the heat of the camp fires converted the goethite to haematite and secondly did the indigenous people of prehistory take goethite and place the mineral at or near a camp fire to convert the goethite to haematite. It is well known that goethite was used in mediaeval times as a colorant [2–4]. The question arises as to whether prehistoric tribes of Australia possessed the knowledge of the goethite haematite phase change if only as a change in colours of the mineral.

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[*] Author for correspondence: E-mail: r.frost@qut.edu.au

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Dehydroxylation of goethite to form haematite occurs due to natural and managed thermal transformation, and is a component of some manufacturing processes [5]. Since goethite and haematite are the most common forms of the crystalline iron oxides and the major impurities in bauxite, an understanding of the thermally topotactic transformation of goethite to haematite is of importance in the study of colorants of antiquity. The structure of goethite is based on the hexagonal close packing of oxygen atoms with 6-fold coordinated Fe atoms occupying octahedral position. The Fe atoms are arranged in double row to form what can be described as double chains of octahedra, which run the length of the *c*-axis. Within the double chains in the *b–c* plane all bonds are covalent with each octahedron sharing four of its edges with neighbouring octahedra. In contrast, bonding between double chains consists of relatively weak hydrogen bonding directed through apical oxygen irons directed along the *a*-axis [6]. In this case, stacking of double chains along the *a*-axis can be easily disrupted and this consequently induces structural defects, such as non-stoichiometric hydroxyl units incorporated into the goethite structure during crystal growth [5, 7–9].

When heated, goethite alters to haematite by the removal of hydroxyl sheets and some of the oxygen in strips parallel to the *c*-axis to form water. In this transformation the (100), (010) and (001) directions in goethite become the (001), (110) and (111) directions in the trigonal haematite cell [10]. The application of infrared spectroscopy is most useful, for determining the phase transformation of goethite to haematite. Haematite formed by dehydroxylation of goethite at low temperatures retains the residual of non-stoichiometric hydroxyl units from goethite and this feature is clearly shown in the hydroxyl-stretching region [11]. Recently a study of the mechanism of thermal transformation of goethite to haematite was reported [12, 13]. Other studies distinguished between bulk and surface properties in the dehydration-dehydroxylation of synthetic goethite [14] and the effect of mechanochemical activation of goethites [12, 13]. The objective of this research is to report the thermal transformation of Al-substituted goethites to haematite and compare the thermal transformations of the synthetic goethite with two naturally occurring goethites.

Experimental

Goethite minerals

Two naturally occurring goethites were obtained (a) from the ancient aboriginal source in the Flinders ranges in South Australia and from an aboriginal cave known as fern cave near Chillagoe in North Queensland. These minerals were checked for phase purity by X-ray diffraction.

The goethite used in this study was synthesized from a ferrous salt. The Al goethites were synthesised from aluminium chloride ($AlCl_3 \cdot 6H_2O$) and ferrous chloride ($FeCl_2 \cdot 4H_2O$). The chemicals were mixed such that ($Al^{3+}/(Fe^{2+}+Al^{3+})$) mole percentages of 0, 10, 20 and 30% were obtained. Total cation concentrations were set at 0.1 M in a total volume of 4 litres. Sodium bicarbonate was used to buffer the system at pH of 7 during the oxidation process. The solution was oxidised by bubbling air at a rate of

25 cm^3 min^{-1} through a glass sinter. A solution of 0.2 M ammonium oxalate was used to extract the poorly crystalline compounds from the precipitates. The precipitate was washed several times with distilled water and finally by acetone before drying in an oven at 110°C. The chemical composition of the Al-substituted goethites was confirmed by atomic absorption spectroscopy. Phase composition was checked by X-ray diffraction. A detailed description of this synthetic goethite was published elsewhere [5].

Thermal analysis

Thermogravimetry (TG) was conducted on TA Instruments thermogravimetric analyser (TGA, Q500) equipped with evolved gas analysis (EGA) furnace, which was connected to a quadrupole mass spectrometer (Pfeiffer, QMS 200 Prisma) through a 1/8 inch, in diameter, transfer line. Nitrogen was used as the purging gas and the flow rate was controlled precisely at 80 mL min^{-1}. For each run, sample powders were loaded onto platinum sample pan and heated to 1000°C at high-resolution heating rate of 2°C min^{-1}, where the heating rate was dynamically and continuously modified in response to the changes in the rate of sample's mass loss, termed as controlled rate thermal analysis (CRTA).

Differential scanning calorimetry (DSC) was performed on a TA Instrument DSC Q10 analyser. Sample powders were loaded into sealed alumina pan and heated to 500°C at heating rate of 2°C min^{-1}. The empty alumina pan was used as reference and the heat flow between the sample and reference pans was recorded.

Infrared emission spectroscopy

FTIR emission spectroscopy was carried out on a Nicolet spectrometer equipped with a TGS detector, which was modified by replacing the IR source with an emission cell. A description of the cell and principles of the emission experiment have been published elsewhere [15–19]. Approximately 0.2 mg of the goethite mineral was spread as a thin layer (approximately 0.2 microns) on a 6 mm diameter platinum surface and held in an inert atmosphere within a nitrogen-purged cell during heating.

In the normal course of events, three sets of spectra are obtained firstly the black body radiation over the temperature range selected at the various temperatures, secondly the platinum plate radiation is obtained at the same temperatures and thirdly the spectra from the platinum plate covered with the sample. Normally only one set of black body and platinum radiation is required. The emittance spectrum (*E*) at a particular temperature was calculated by substraction of the single beam spectrum of the platinum backplate from that of the platinum+sample, and the result ratioed to the single beam spectrum of an approximate blackbody (graphite). The following equation was used to calculate the emission spectra.

$$E=-0.5\log\frac{Pt-S}{Pt-C} \tag{1}$$

This spectral manipulation is carried out after all the spectral data has been collected. The emission spectra were collected at intervals of 50°C over the range 200–750°C. The time between scans (while the temperature was raised to the next hold point) was approximately 100 s. It was considered that this was sufficient time for the heating block and the powdered sample to reach temperature equilibrium. The spectra were acquired by coaddition of 64 scans for the whole temperature range (approximate scanning time 45 s), with a nominal resolution of 4 cm^{-1}. Good quality spectra can be obtained providing the sample thickness is not too large. If too large a sample is used then the spectra become difficult to interpret because of the presence of combination and overtone bands. Spectral manipulation such as baseline adjustment, smoothing and normalisation was performed using the Grams® software package (Galactic Industries Corporation, Salem, NH, USA).

Results and discussion

Differential scanning calorimetry

The number of DSC studies of the goethite–haematite transition is scarce [12]. Figure 1 displays the DSC curves of the synthesised goethite and aluminium-substituted goethite. The results of the DSC are reported in Table 1. Two endotherms are observed and are complex. The 30% Al-substituted goethite displays a third endotherm. Clearly these endotherms shift to higher temperature with increasing Al substitution. The first

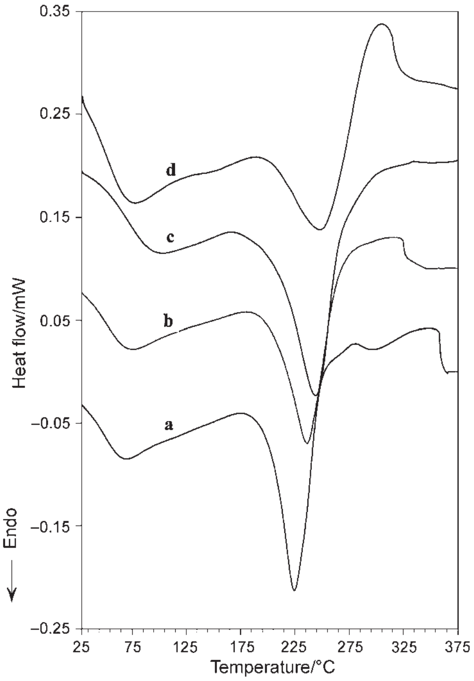

Fig. 1 DSC curves of Al-substituted goethites a – 0%; b – 10%; c – 20%; d – 30%

endotherm is observed at around 75°C and is associated with water loss as is shown from the mass spectrometric results of the evolved gases. Table 1 shows that there is a regular increase in the temperature of the endotherms and the % heat flow with increasing Al composition. This is illustrated in Figs 2 and 3. The amount of heat required for the first endotherm decreases with increase in %Al substitution and concurrently the quantity of heat required for the second endotherm increase with %Al substitution. The temperature of both the endotherms increases with %Al substitution.

Table 1 Results of the DSC of Al-substituted goethites a – 0%, b – 10%, c – 20%, d – 30%

Al-substituted goethites	0%	10%	20%	30%
	°C/%			
Heat flow step 1	71 55%	73 48%	99 42%	76 19%
Heat flow step 2				140 48%
Heat flow step 3	224 44%	236 52%	241 58%	245 32%
Heat flow step 4 (exothermic)				298 –14%

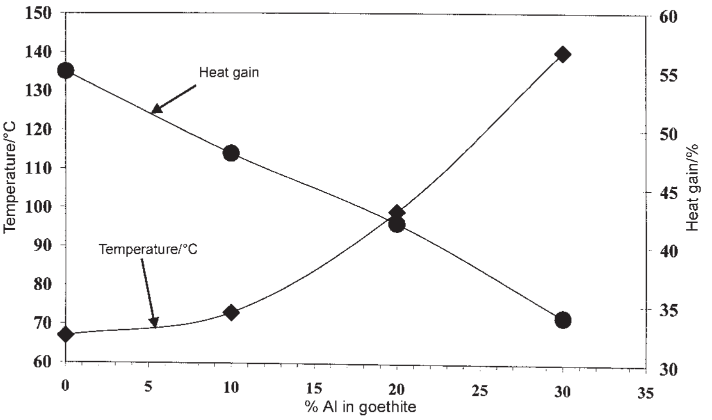

Fig. 2 Variation of the temperature of the first endotherm and the % heat gain as a function of the Al substitution

The first endotherm is observed at 71°C for synthetic goethite and the temperature increase to 99°C for 20% Al substitution. Two endotherms are associated with the 30% Al-substituted goethites. These are observed at 76 and 140°C. Such phase changes due to dehydration at these temperatures have not been previously reported. For the second endotherm, for pure synthetic goethite, the temperature of the phase change is 224°C and increases to 245°C for 30% Al-substituted goethite. The

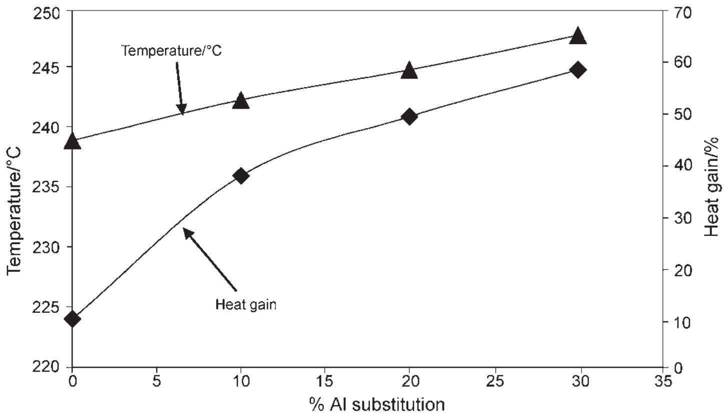

Fig. 3 Variation of the temperature of the first endotherm and the % heat gain as a function of the % Al substitution

endotherms become broader with increasing Al substitution. This endotherm is attributed to the goethite-haematite phase transition, which occurs at dehydroxylation.

Thermogravimetric and derivative thermogravimetric analysis

The TG and DTG curves for goethite and Al-substituted goethites are shown in Fig. 4. Included are the TG and DTG analyses of two naturally occurring goethite samples associated with the production of ancient aboriginal art. The results of the component analyses of the DTG curves are provided in Table 2. Included in Table 2 for comparison are the mass changes as determined by mass spectrometry. A steady mass loss of adsorbed water is observed over the ambient to 150°C temperature range, as is indicated by the TG curve. The principal mass loss occurs over the 196 to 224°C temperature range, depending on the amount of Al substitution. A second mass loss is observed at slightly lower temperatures. A third mass loss is observed in the 263 to 282°C temperature range. The theoretical mass loss for the conversion of goethite to haematite according to the equation:

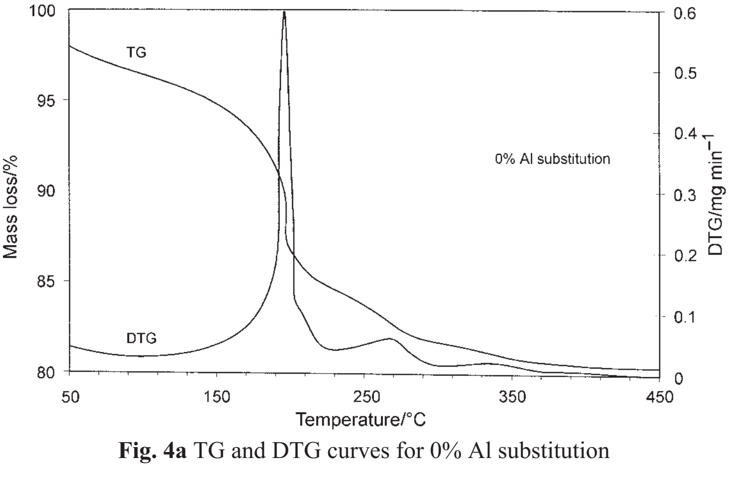

Fig. 4a TG and DTG curves for 0% Al substitution

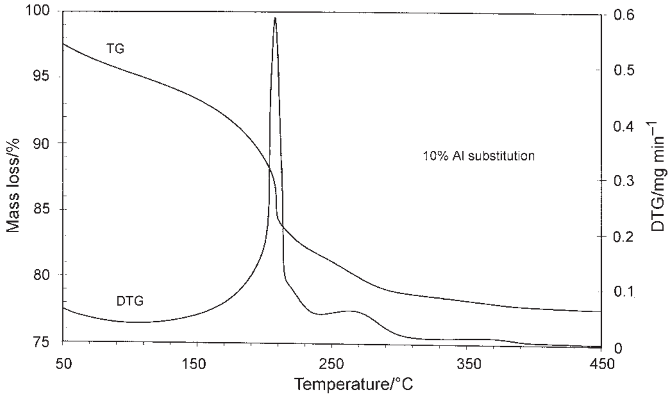

Fig. 4b TG and DTG curves for 10% Al substitution

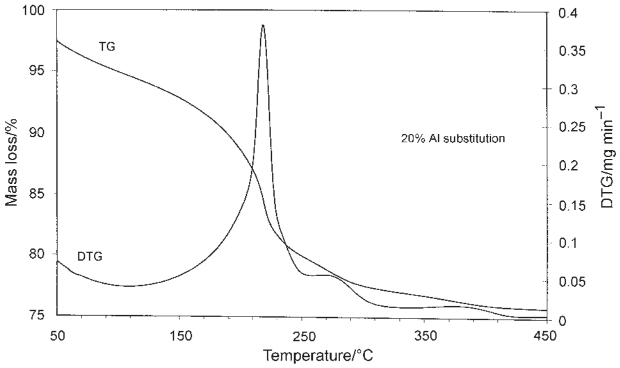

Fig. 4c TG and DTG curves for 20% Al substitution

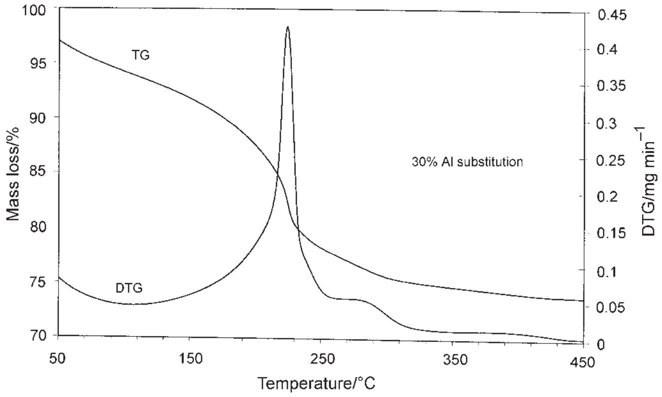

Fig. 4d TG and DTG curves for 30% Al substitution

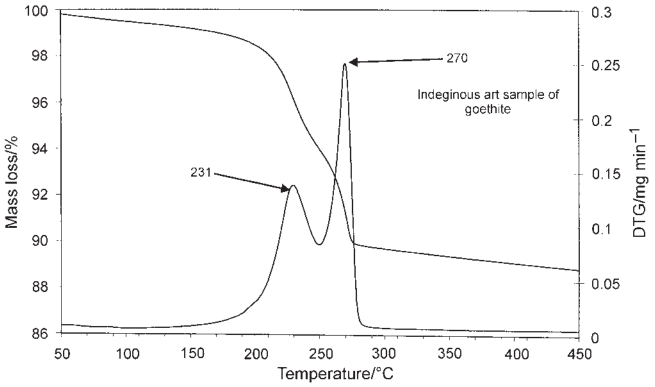

Fig. 4e TG and DTG curves for a sample of goethite used in indigenous art

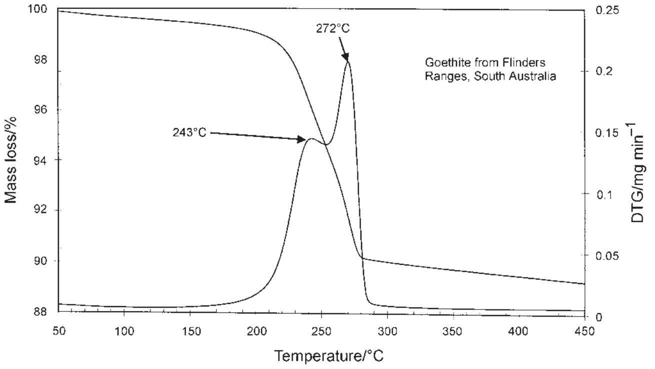

Fig. 4f TG and DTG curves for a sample of goethite used in indigenous art from the Fliders Ranges, South Australia

$$2FeO(OH)\rightarrow Fe_2O_3+H_2O$$

should be precisely 10.1%.

The mass loss step for the 0% Al-substituted goethite is 10.13% which agrees well with the theoretical value. As the Al-substitutes for the Fe in the goethite according to the formula: $Fe_xAl_{(1-x)}O(OH)$, the mass loss increases. For example for the 10% Al-substituted goethite, the theoretical mass loss is 10.5%. The measured result according to the TG pattern measured between 150 and 245°C is 11.9%.The variation of the temperatre of the mass loss steps and the % heat flow as a function of the %Al substitution is illustrated in Figs 5a and b. The temperature of the mass loss steps increases regularly with the increase in %Al substitution. Such an effect is in harmony with the results of the changes in the temperature of the endotherms as observed through DSC measurements. The mass loss for mass loss steps 2 and 3 decreases with increasing Al substitution. The mass loss for step 1 increases with increasing Al substitution. Such an observation suggests that this step is associated with the Al in the goethite and that the two mass loss steps 2 and 3 are associated with the Fe in the goethite.

The mineral goethite was of extreme importance to the indigenous ancient peoples of Australia. Figures 4e and f display the TG/DTG curves for two goethites

Table 2 Results of the mass losses of the DTG and MS for Al-substituted goethites

Percentage of Al-substitution	0%		10%		20%		30%	
°C/%	DTG	MS	DTG	MS	DTG	MS	DTG	MS
Step 1	175 18.2	173 32.7	200 56.0	190 56.8	203 47.4	184 30	207 49.3	190 37
Step 2	196 61.7	194 31.5	208 31.8	204 38.8	219 43	215 68.7	224 44.3	221 61.6
Step 3	263 20.0	269 7.3	267 10.8	275 4.3	275 7.4	287 1.3	282 6.3	293 1.0

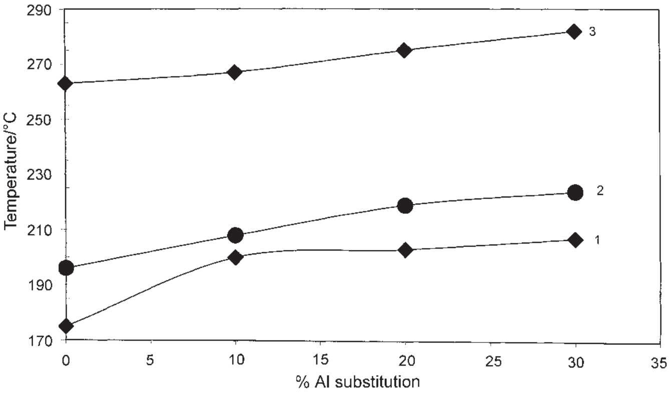

Fig. 5a Variation of the temperature of the differential mass loss as a function of %Al substitution. The numbers represent the mass loss step

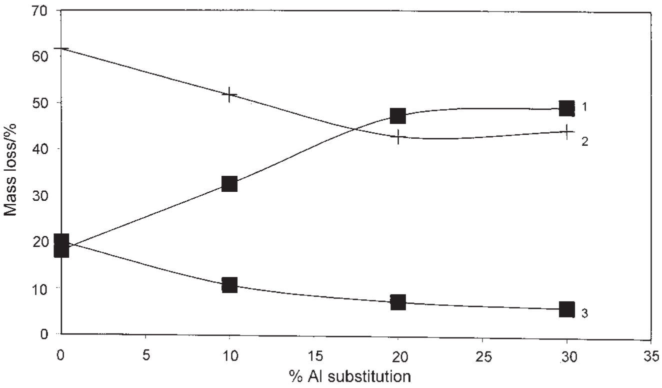

Fig. 5b Variation of the % differential mass loss as a function of %Al substitution. The numbers represent the mass loss step

firstly from Fern Cave, near Chillagoe and secondly from a deposit used by the aboriginal peoples over a long period of time. The major mass loss step occurs around the 250°C temperature mark. Two steps in the DTG curves are observed at 231 and 270°C for the goethite found in the base of Fern Cave. For the Flinders ranges sample two DTG steps at 243 and 272°C are observed. The mass loss for both goethites is precisely 10.1%. One proposition is that goethite was used as a monetary mechanism and was exchanged for goods. Thus goethite from South Australia was in all likelihood transported across the country. Goethite has been found in locations where no goethite has been known to exist.

Infrared emission spectroscopy

In order to assess the molecular changes of the goethite structure as a function of temperature and with % aluminium substitution, the complimentary technique of infrared emission spectroscopy has been used. This technique allows for the infrared spectrum of the goethite *in situ* at the elevated temperatures to be obtained. Figures 6 and 7 display the infrared spectra at 25°C intervals starting at 100°C for the hydroxyl stretching and hydroxyl deformation regions respectively. A number of spectral features are present. Two major emission bands are present centred upon 3184 and 3429 cm^{-1}. These two bands are assigned to the hydroxyl stretching bands of goethite. Bands of low intensity are observed 2908 cm^{-1} and are attributed to impurities of ammonium adsorbed upon the surface of the goethite and result from the synthesis of the goethite.

The IES spectra clearly show that the hydroxyl stretching bands are lost over the 175 to 275°C temperature range. For the 0% Al-substituted goethite, the OH stretch-

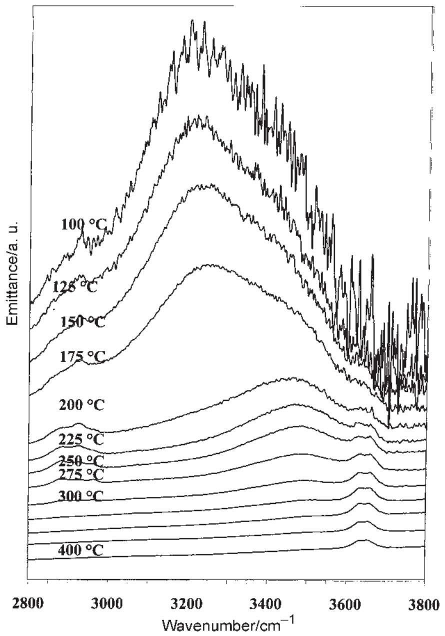

Fig. 6a Infrared emission spectra of the hydroxyl-stretching region of synthetic goethite

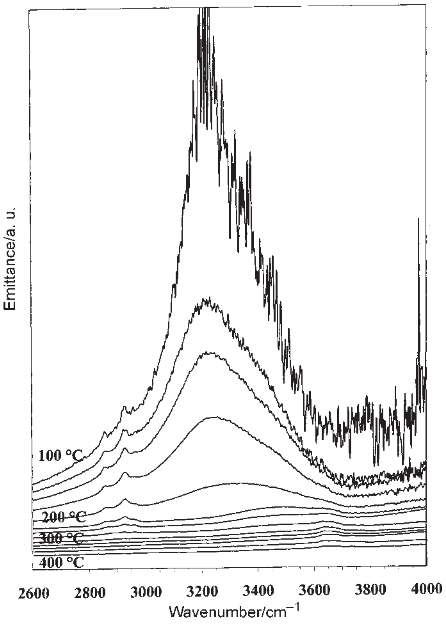

Fig. 6b Infrared emission spectra of the hydroxyl stretching region of 10% Al-substituted synthetic goethite

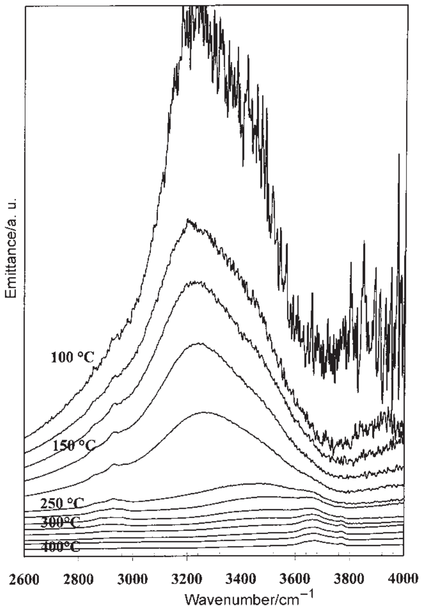

Fig. 6c Infrared emission spectra of the hydroxyl stretching region of 20% Al-substituted synthetic goethite

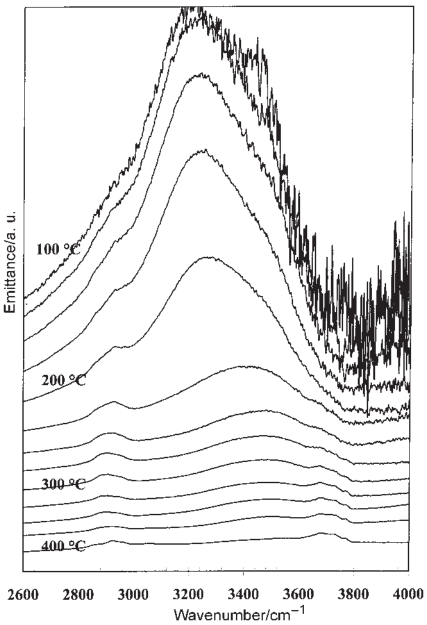

Fig. 6d Infrared emission spectra of the hydroxyl stretching region of 30% Al-substituted synthetic goethite

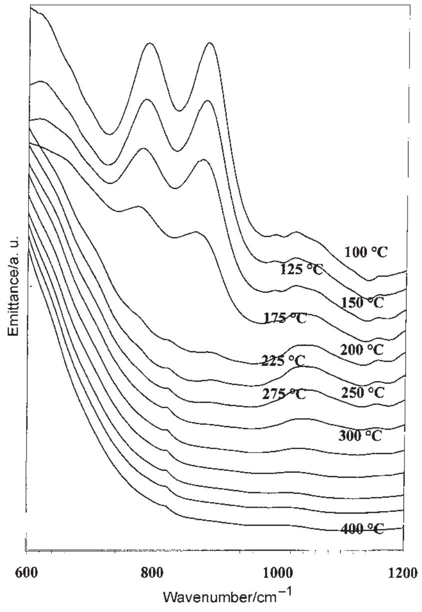

Fig. 7a Infrared emission spectra of the hydroxyl deformation region of synthetic goethite

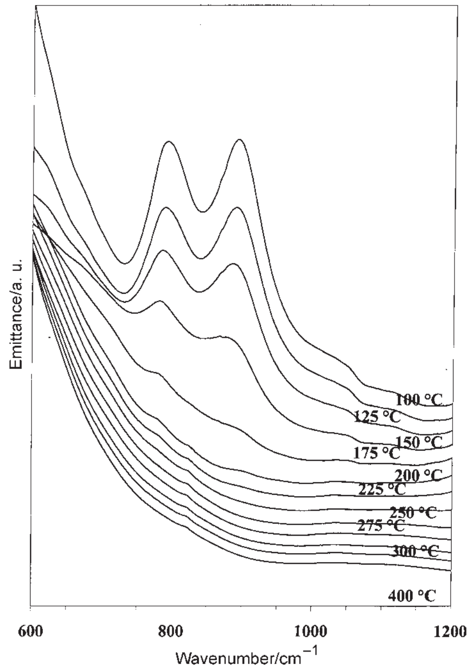

Fig. 7b Infrared emission spectra of the hydroxyl deformation region of 10% Al-substituted synthetic goethite

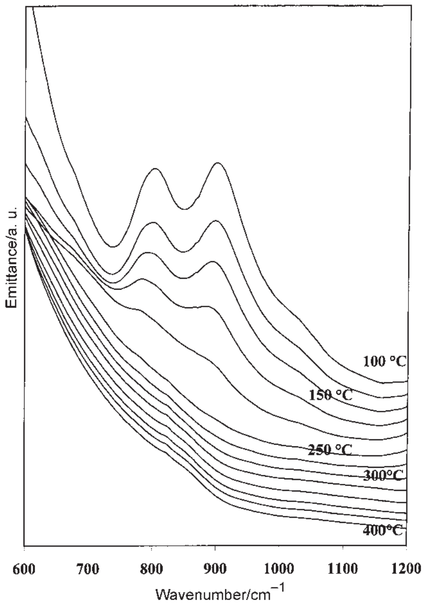

Fig. 7c Infrared emission spectra of the hydroxyl deformation region of 20% Al-substituted synthetic goethite

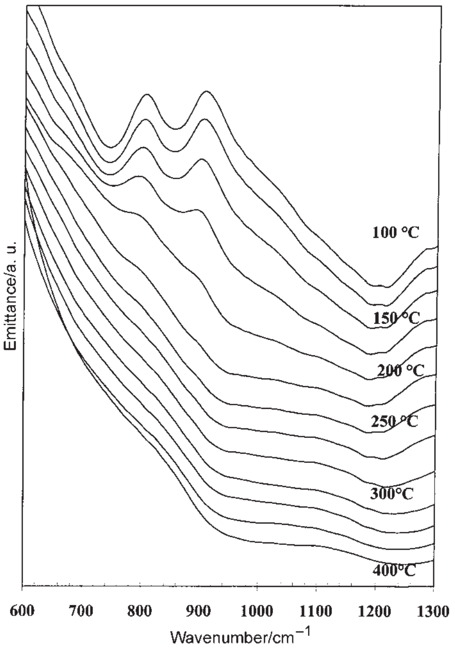

Fig. 7d Infrared emission spectra of the hydroxyl deformation region of 30% Al-substituted synthetic goethite

ing band observed at 3184 cm^{-1} appears to be lost and the band at 3429 cm^{-1} shifts to higher wavenumbers with temperature increase. This band shows zero intensity at 325°C. The observation of the loss of hydroxyls in two steps is in harmony with the DTG curves, where two steps in the DTG curves were observed. Figure 7 shows the hydroxyl deformation modes and in harmony with the observation of two hydroxyl-stretching modes, two hydroxyl deformation modes are observed. The intensity of these bands is lost by 225°C.

Conclusions

There are a two-phase changes observed using DSC for the synthetic and Al-substituted goethites. These occur at ~75°C and in the 224 to 245°C temperature range. The temperatures of these endotherms and the enthalpy of the phase change is a linear function of the %Al substitution. The first endotherm occurs without any mass change and is attributed to a structural rearrangement at the molecular level. The temperature of the mass loss steps and the % mass loss were also found to be linear functions of the %Al substitution. DTGA shows the presence of three definable mass loss steps (a) in the 175 to 207°C temperature range (b) in the 196 to 224°C temperature range and (c) in the 263 to 282°C temperature range. These temperatures are in excellent correspondence with the results of the mass spectrometry of the evolved water vapour from the dehydroxylation of the goethite.

This work has shown that the thermal transformation of goethite occurs over a wide temperature range. Such temperatures are readily achievable through camp fires of the indigenous Australian aboriginals such as might occur in their caves. Whilst no proof exists that the aboriginals painted their primitive drawings with goethite, such an event is highly likely. It is probable that the goethite was then transformed to haematite through very low heating.

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