STUDIES ON HYDROGEN FERRITE PHASE IN γ-Fe$_2$O$_3$ SYNTHESISED FROM FERROUS FUMARATE HALF HYDRATE PRECURSOR

A. Venkataraman

Department of Chemistry, Gulbarga University, Gulbarga-585 106, Karnataka, India

Abstract

Thermal techniques viz., TG/DTA/DSC methods have been employed in understanding the formation and decomposition of hydrogen ferrite phase (H–F) as a metastable intermediate in the conversion of γ-Fe$_2$O$_3 \cdot x$H$_2$O, to α-Fe$_2$O$_3$. Magnetic hysteresis measurements carried out at liquid N$_2$ and at room temperature for the vacancy ordered γ-Fe$_2$O$_3$ and its H–F phase also supplement these studies.

Introduction

γ-Fe$_2$O$_3$ continues to play a leading role as an important magnetic tape recording material and also is one of the important ferrite material used as a heterogeneous catalyst [1]. Newer methods for synthesis of this material with ultra fine grains having requisite magnetic properties is an on going process [2–5]. Our earlier reports [1, 6, 7] have shown the existence of an intermediate phase viz., the hydrogen ferrite phase (H–F) having the structural formulae Fe$_8^{3+}$[Fe$_{12}^{3+}$[H$^+$]$_4$]O$_{32}$, in the conversion of γ-Fe$_2$O$_3 \cdot x$H$_2$O to vacancy ordered γ-Fe$_2$O$_3$. This communication reports the utility of employing thermal analysis to study the formation and decomposition of H–F phase, of the γ-Fe$_2$O$_3 \cdot x$H$_2$O, where xH$_2$O is some amount of water molecules, synthesised from ferrous fumarate half hydrate precursor. The thermal analysis study includes TG/DTA/DSC techniques under static air and dynamic nitrogen atmospheres. The magnetic hysteresis measurements are made for H–F and γ-Fe$_2$O$_3$ samples at liquid N$_2$ temperature and are compared with values obtained at room temperature. To understand the molecular structure, infrared spectra were also taken for these samples. The progress of formation and decomposition is represented by the following equation:

$$\gamma\text{-Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O} \rightarrow \text{H--F} \rightarrow \gamma\text{-Fe}_2\text{O}_3 \rightarrow \alpha\text{-Fe}_2\text{O}_3 \qquad (1)$$

Experimental

The measurement of magnetic hysteresis parameters employing Hysteresis Loop Tracer (HLT) is reported earlier [8].

The TG/DTA measurements were carried out employing Stanton-Redcroft simultaneous Thermal Analyser, 781 series, U.K. The sample mass taken was 2.5 mg and the heating rate used was 20 deg·min^{-1} under static air and nitrogen atmospheres.

TG/DSC measurements were carried out using DUPONT 910, Thermal Analyser, under the dynamic nitrogen atmosphere with heating rate 10 deg·min^{-1} and N$_2$ flow rate of 25 ml·min^{-1}.

γ-Fe$_2$O$_3 \cdot x$H$_2$O, was synthesised by thermal decomposition of ferrous fumarate half hydrate under a controlled atmosphere of dynamic air containing water vapour [2].

Results and discussion

Figure 1, shows the TG/DTA traces under static air atmosphere and Fig. 2 is the DSC trace under dynamic nitrogen atmosphere for γ-Fe$_2$O$_3 \cdot x$H$_2$O samples.

In Fig. 1, the TG trace remains constant up to 80°C which then shows a weight loss of 1.5% to 140°C. The TG trace now shows an increase in weight (0.15%) and then remains constant up to 310°C. At this temperature (310°C) there is again an increase in weight (0.15%) up to 422°C and thereafter the sample remains stable up to 722°C. In DTA trace a very broad endotherm from 50 to 525°C with a peak at 330°C was observed.

The first weight loss occurring on the TG trace from 80 to 140°C would be due to loss of absorbed water. On further rise in temperature the increase in weight may indicate the absorbed water being lost is partial and it is believed that at some critical temperature well below 140°C, γ-Fe$_2$O$_3$ sample starts acting as a catalyst splitting water into hydrogen and oxygen, the oxygen escaping out into the environment and the hydrogen starts entering into the lattice thereby showing an increase in weight. The γ-Fe$_2$O$_3$ upto 300°C is in the form of hydrogen ferrite having the structural formulae Fe$_8^{3+}$[Fe$_{12}^{3+}$[H$^+$]$_4$]O$_{32}$ [6]. The existence of hydrogen ferrite at higher temperature 300°C, when compared to 190°C as shown by electrical conductivity data [6] may be cautiously understood by considering the nature of experimental set-up and the sample nature used in these two types of studies. On further rise in temperature the sample weight slightly increases indicating the conversion of γ-Fe$_2$O$_3$ to α-Fe$_2$O$_3$.

The DTA curve does not show any clear distinction between any of these stages, as represented in Eq. (1). The peak around 330°C would correspond to
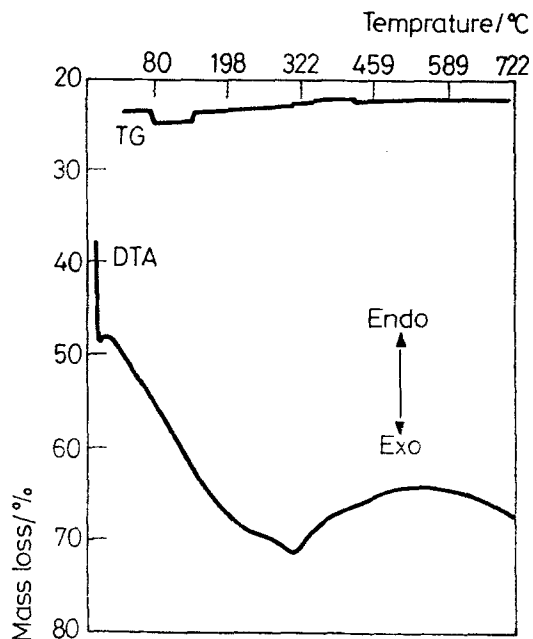
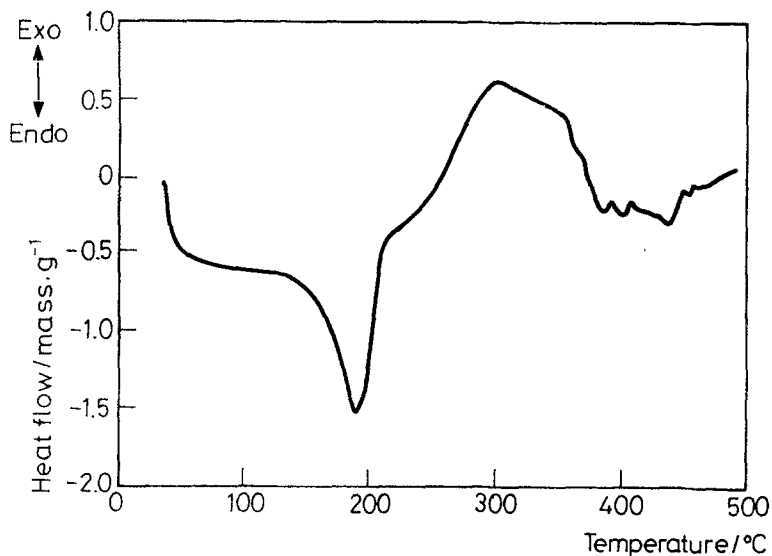**Fig. 1** TG/DTA trace of γ-Fe$_2$O$_3 \cdot x$H$_2$O under static air atmosphere

Fig. 2 DSC trace of γ-Fe$_2$O$_3 \cdot x$H$_2$O under N$_2$ atmosphere

the curie transformation temperature, T_c, (γ-Fe$_2$O$_3$–α-Fe$_2$O$_3$). One possible reason for these processes, for not being distinguished may be that they are accom-

panied by very close range of ΔH values. However the DTA trace predicts to some extent the steps shown in Eq. (1), that is the irregular broadness up to peak at 330°C and than a slow tailing to the base line. The tailing indicates that γ-Fe_2O_3 → α-Fe_2O_3 is a slow process, further our earlier report [6] on electrical conductivity and initial magnetisation supplement this behaviour.

To understand the effect of atmosphere on the thermal curves of γ-$Fe_2O_3\cdot$ xH_2O sample, TG/DSC studies were undertaken under dynamic N_2 (nitrogen) atmosphere. The TG curve showed 2.0% weight loss from 70 to 180°C and remained constant up to 600°C. The loss of weight is attributed to the partial dehydration taking place in the sample. However the decomposition of H–F and formation of γ-Fe_2O_3 is not noticed here, but when the parent sample was heated isothermally under N_2 atmosphere for 0.5 h, formation of γ-Fe_2O_3 is confirmed on the basis of XRD and magnetic studies. The DSC study in N_2 atmosphere shows interesting results. There occurs an endotherm at 192°C, a broad exotherm at 300°C and an endotherm again at 460°C along with some other weak endotherms. The first endotherm has ΔH, value of 207 J/g and heat capacity (C) of 2.6 J/g°C. As the heat capacity is very much less than that for pure H_2O (4 J/g°C) this difference may be explained on the basis of partial dehydration of the sample. The occurrence of broad exotherm at 300°C having ΔH values of 120.3 J/g and C value of 1.4 J/g°C, may be due to decomposition of H–F phase into γ-Fe_2O_3. The third endotherm at 460°C having ΔH, value of 45.10 J/g and C, value of 0.8 J/g°C, corresponds to T_c. The other peak near this endotherm may have resulted due to the tailing effect as mentioned earlier. To understand the changes observed in DSC, a first and second derivatives with re-
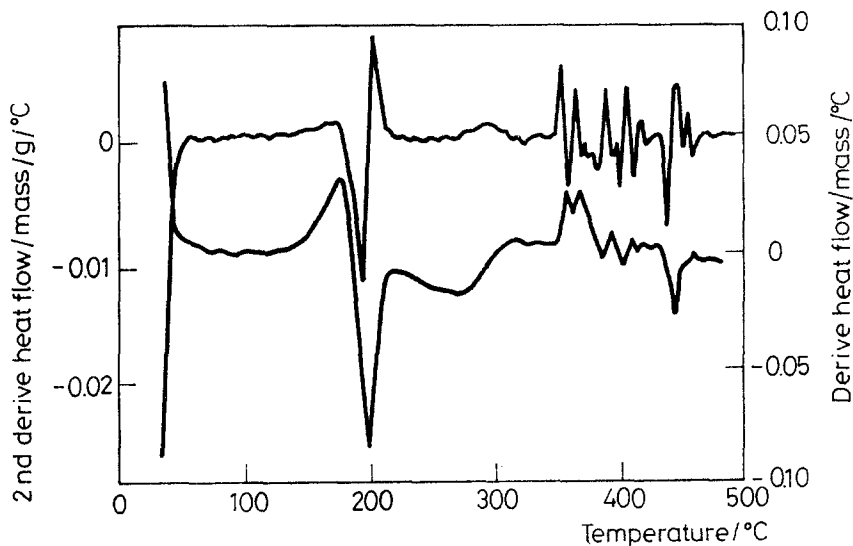

Fig. 3 1st and 2nd derivative of γ-$Fe_2O_3\cdot xH_2O$ of Fig. 2

spect to temperature of the normal curve is also recorded for the sample, this is shown in Fig. 3. It is noticed here that at the temperature as observed at the exotherm (300°C) in the normal curve, the first and second derivatives had no peaks, this phenomena indicates that the decomposition of H–F phase is not accompanied by either the first order or the higher order transition. The conversion of γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$ has number of peaks on second derivative along with a few peaks on the first derivative thereby clearly indicating the tailing nature of the sample near T_c is a second order phase transformation.

To ascertain the effect of magnetic hysteresis parameters on the H–F phase and γ-Fe_2O_3 samples, the measurements were conducted for these samples at liquid N_2 and room temperature. The values obtained are as given in Table 1. It is observed that the coercive force, H_c for H–F at both the temperatures is less than that of γ-Fe_2O_3 sample at the two temperatures. However the squareness ratio M_R/M_S, and saturation magnetisation, M_S, values vary slightly. The variation in H_c values depends on the orientation of easy axis along the direction of magnetisation. On the basis of H_c values for H–F and γ-Fe_2O_3 samples it can be understood that there is hinderance for magnetisation along the easy axis in case of H–F when compared to γ-Fe_2O_3.

Table 1 Magnetic properties of γ-Fe_2O_3 and H–F samples at room and liquid N_2 temperatures

Sample and temperature of measurement / °C	Coercive force H_c / O_e	Squareness ratio M_R/M_S	Saturation magnetisation M_S / e.m.u./g^{-1}
Room temperature (30)			
γ-Fe_2O_3	300.0	0.56	71.0
H–F	200.0	0.51	62.0
Liquid N_2 temperature			
γ-Fe_2O_3	285.0	0.51	66.0
H–F	215.0	0.48	62.0

The infrared spectral study for γ-Fe_2O_3 and H–F samples gave the following observation. In case of γ-$Fe_2O_3 \cdot xH_2O$, bands associated with the presence of lattice water are broad and are observed at 3400(s) and 1650(s) cm^{-1}. The simultaneous presence of these two bands excludes the possibility of the presence of a detectable amount of OH(8), in addition to these two bands, comparatively weak but much less broad bands are observed at 2720 and 2660 cm^{-1}. The intensities of these bands decrease on heating and disappear after heating for 5 h at 300°C under nitrogen atmosphere, and at this temperature H–F is lost. More than seven peaks are observed in the region 710 to 370 cm^{-1} due to metal oxygen vibrational modes. The IR spectrum obtained for γ-$Fe_2O_3 \cdot xH_2O$ samples

heated under N_2 atmosphere resembles to much extent the γ-$Fe_2O_3 \cdot xH_2O$ sample heated under static air at 300°C.

<div align="center">*   *   *</div>

References

1 A. Venkataraman, Bull. Mater. Sci., India, 16 (1993) 51.
2 A. Venkataraman, V. A. Mukhedkar, M. M. Rahman, A. K. Nikumbh and A. J. Mukhedkar, Thermochim. Acta, 115 (1987) 215.
3 V. Moya, K. S. Rane and V. N. Kamat Dalal, J. Mater. Sci., Materials in Electronics, 1 (1990) 212.
4 P. Ravindranathan and Kashinath C. Patil, Am. Ceram. Soc. Bull., 66 (1987) 688.
5 K. Suresh, N. R. S. Kumar and K. C. Patil, Advanced Materials Communication, 30 (1991) 148.
6 A. Venkataraman and A. J. Mukhedkar, J. Mater. Sci., 23 (1988) 3505.
7 A. K. Nikumbh, K. S. Rane and A. J. Mukhedkar, J. Mater. Sci., 17 (1982) 2503.
8 K. S. Rane, A. K. Nikumbh and A. J. Mukhedkar, J. Mater. Sci., 16 (1981) 2387.