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Some electrical and magnetic properties of γ-Fe_2O_3

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Abstract. γ-Fe_2O_3 synthesized from $FeC_4H_4O_4 \cdot 4H_2O$ has been studied using various techniques. The phase transformation observed by electrical conductivity measurements agrees well with the initial magnetization measurement. The magnetic hysteresis values compare with those of γ-Fe_2O_3 samples synthesized using established procedures. γ-Fe_2O_3 particles obtained were circular in shape showing a well resolved six narrow bands in Mössbauer spectrum. The presence of hydrogen ferrite phase was also confirmed by electrical and magnetic measurements.

Keywords. Electrical conductivity; Seebeck coefficient; ferrites; initial magnetization.

1. Introduction

γ-Fe_2O_3 is an important magnetic tape recording material and its synthesis has been studied in some detail (Kuo *et al* 1982; Karmazsin *et al* 1983; Ravindranathan and Patil 1986). However, studies on newer methods of synthesis and doping of γ-Fe_2O_3 to improve its magnetic properties are still being actively pursued (Rane *et al* 1981; Sharrock and Bonder 1985; White 1985; Venkataraman *et al* 1987a,b; Venkataraman *et al* 1989) because of its ideal combination of such magnetic hysteresis parameters as saturation magnetization (M_S), coercive force (H_C) and squareness ratio (M_R/M_S) (Bate 1975). Pure γ-Fe_2O_3 is a vacancy-ordered ferrite with a structural formula Fe_8^{3+} $[Fe^{3+}40/3\ \square_{1/8}]O_{32}$ where $\square$ indicates vacancy sites present in the lattice.

The occurrence of hydrogen ferrite phase with the structural formula $Fe_8^{3+}[Fe_{12}^{3+}H_4^+]\cdot O_{32}$ has been investigated by Rane *et al* (1981) and Venkataraman and Mukhedkar (1988) while synthesizing γ-Fe_2O_3 by thermal decomposition of ferrous oxalate dihydrate and ferrous fumarate half hydrate respectively. The magnetic properties of ferrites in general are influenced by the method of preparation, microstructure and crystal morphology (Schnettler 1972; Bate 1975; Manjula 1990; Vishwanadhan 1990). This paper reports studies on the magnetic behaviour of γ-Fe_2O_3 obtained by thermal decomposition of ferrous succinate tetrahydrate ($FeC_4H_4O_4 \cdot 4H_2O$), and its suitability as a potent magnetic tape recording material. DC electrical conductivity was studied to understand the irreversible phase transformation (γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$) temperature and the result obtained is supplemented with Seebeck coefficient measurement and magnetic studies. γ-Fe_2O_3 and other ferrites, apart from their many technological uses, are also useful as potent heterogeneous catalysts.

2. Experimental

The experimental procedure for measuring the d.c. electrical conductivity, Seebeck coefficient, initial magnetization with variation of temperature, high field magnetic hysteresis loop tracer (HLT) and Mössbauer parameters were reported earlier (Rane *et al* 1981).

2.1 *Synthesis*

γ-Fe_2O_3 was synthesized using thermal decomposition of $FeC_4H_4O_4 \cdot 4H_2O$ under a controlled atmosphere of dynamic air containing water vapour at 290°C (Venkataraman 1987).

3. Results and discussion

Figure 1 shows the plot of log σ vs $1/T$ for γ-Fe_2O_3 under static air atmosphere. After the observed maximum V, there was a decrease in conductivity σ up to 130°C as indicated by region B'. The σ value then increased showing a Kink. With further increase in temperature, the σ value rose till a phase transformation of γ-Fe_2O_3 to α-Fe_2O_3 was attained with broadening in the curve from the starting temperature T_D to the ending temperature $T_E(T_D - T_E)$. The cooling curve showed hysteresis in which σ did not exhibit any variation between 180°C and room temperature (30°C). The occurrence of V was due to the desorption of the adsorbed water molecules and the Kink was due to existence of hydrogen ferrite phase. It is also seen from figure 1 that hydrogen ferrite phase was present up to 190°C at which the hydrogen ferrite decomposed to give a vacancy-ordered γ-Fe_2O_3 i.e. $Fe_8^{3+}[Fe_{12}^{3+}H_4^+]O_{32}$ to $Fe_{8/3}^{3+}[Fe^{3+}40/3\,\square_{1/8}]O_{32}$. This transformation is confirmed by magnetic studies discussed later. On further raising the temperature from 190°C, there was a slow transformation of γ-Fe_2O_3 to α-Fe_2O_3 as indicated by temperature regions $T_D - T_E$(440° to 530°C).

The Seebeck coefficient measurements (figure 2) showed a fall in the number of

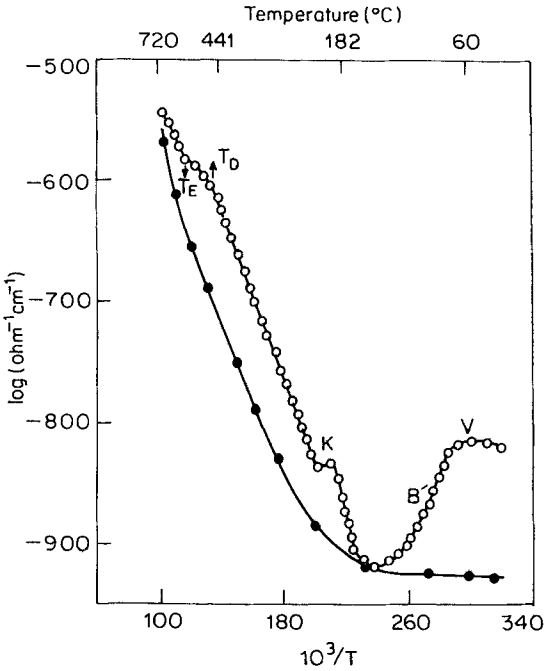

Figure 1. Plot of log σ vs T^{-1}(K) for γ-Fe_2O_3 heating curve; X, cooling curve.

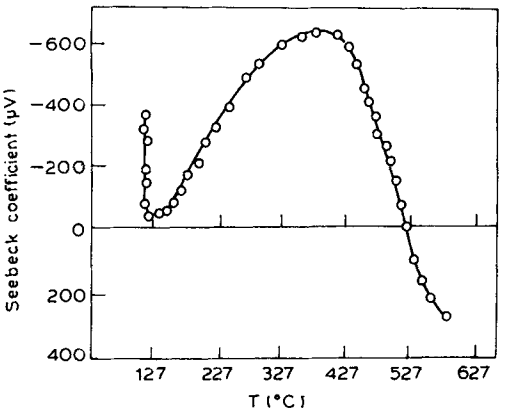

Figure 2. Plot of Seebeck voltage (μVK^{-1}) vs T^{-1}(°C) for γ-Fe_2O_3.

Table 1. Magnetic parameters.

Sample	Saturation magnetization (M_S emu g^{-1})	Coercive force H_C (Oe)	Squareness ratio (M_R/M_S)
Hydrogen ferrite phase	65·0	250·0	0·53
Vacancy ordered γ-Fe_2O_3	72·0	350·0	0·58

charge carriers (negative type) in the temperature region 115–145°C and then remained almost constant up to 190°C. A further increase in temperature showed a rise in the number of charge carriers up to phase transformation ($\gamma \rightarrow \alpha$) temperature, after which the nature of charge carriers changed from negative to positive type.

The magnetic hysteresis parameters for hydrogen ferrite and that of vacancy ordered γ-Fe_2O_3 (obtained by heating hydrogen ferrite under dynamic nitrogen atmosphere at 200°C for 4 h) are given in table 1. The M_S value for vacancy ordered γ-Fe_2O_3 was higher than that observed for hydrogen ferrite. Such behaviour is expected when non-magnetic dopants are present in the crystal lattice (Venkataraman and Mukhedkar 1988). As expected all the magnetic parameters observed compare well with expected values (Bate 1975).

It was believed that permeability K or susceptibility X_i of a magnetic material having SD grains always increased on heating and showed a peak (Hopkinson's peak) just before T_C and then fell to zero rapidly (Bate 1975; Nagarajan and Murthy 1981). Figure 3 shows the normalized $X_i - T$ curve obtained for vacancy ordered γ-Fe_2O_3. The normalized X_i values varied with respect to temperature before Hopkinson's peak indicating SD behaviour of the sample, after this the X_i value decreased to zero T_C with some tailing.

The Mössbauer spectra of γ-Fe_2O_3 and that of hydrogen ferrite were found very similar with a well-resolved six narrow lines (half bandwidth of 0·285 mms^{-1}) in the intensity ratio 3:2:1:1:2:3. This spectra suggested that the effective magnetic fields at A and B sites of γ-Fe_2O_3 were comparable and the magnetic SD grains were randomly oriented (Venkataraman 1987). The hyperfine field for vacancy-ordered γ-Fe_2O_3 and hydrogen ferrite phase was found to be 493·8 KOe. Hence it can be

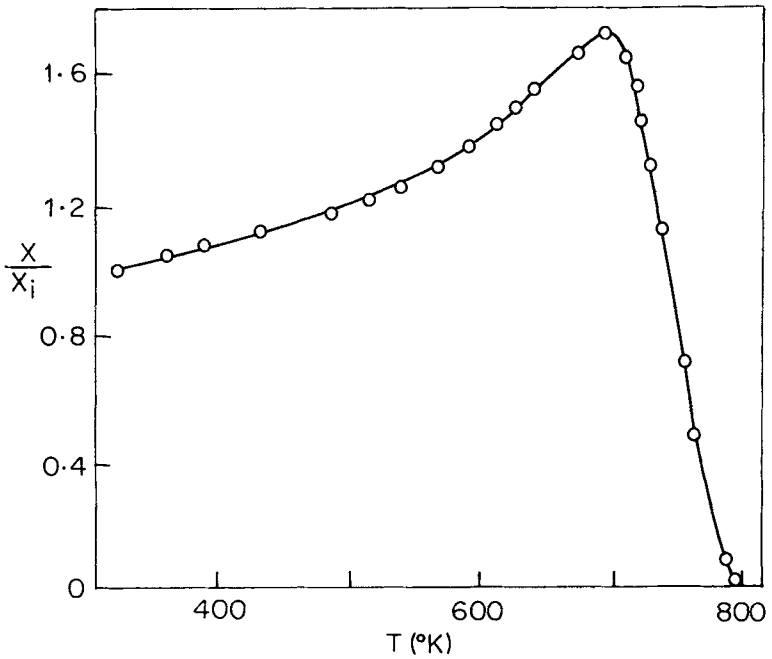

Figure 3. Plot of normalized susceptibility (X/X_i) vs T(°C) for γ-Fe_2O_3.

stated that the presence of nonmagnetic dopant like H^+ leading to the formation of hydrogen ferrite does not affect the magnetic fields at A and B sites. γ-Fe_2O_3 thus obtained showed spherical particles bound together to give particles of 1–6 nm diam. (Venkataraman 1987).

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