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Direct current electrical conductivity of doped gamma ferric oxide

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The data of the temperature variation of the direct current electrical conductivity and Seeback voltage, X-ray diffraction patterns and infrared spectra of eighteen doped samples of γ-Fe_2O_3 are analysed for the effect of dopants on the hydrogen ferrite phase present in γ-Fe_2O_3. The contribution of hydrogen ferrite phase in doped γ-Fe_2O_3 containing small amounts of cobalt (0.3%), nickel (0.5%) and gadolinium (0.3%) is negligible. The concentration of negative charge carriers is large in cobalt and nickel doped γ-Fe_2O_3.

1. Introduction

From the direct current electrical conductivity, σ, measurements of γ-Fe_2O_3 in the different atmospheres supplimented with the X-ray diffraction data it has been suggested that the sample stored under the static air (sample III) absorbs the atmospheric constitutents such as O_2 and H_2O [1], and it contains both H^+ and Fe^{2+} ions also. Such hydrogen ferrite phase may be considered as a hydrogen doped γ-Fe_2O_3, and the magnetic moment retained by γ-Fe_2O_3 after a heating cycle in a helium atmosphere [2] is probably associated with the hydrogen ferrite phase. The study of the physical properties of the doped samples of γ-Fe_2O_3 will be therefore profitable to throw a further light on the nature of the hydrogen ferrite phase. This paper reports our results obtained on the doped γ-Fe_2O_3 samples containing the different concentrations of cobalt, nickel, gadolinium and terbium.

2. Experimental procedure

The procedures used for the measurements of direct current electrical conductivity, infrared spectra, X-ray diffraction patterns and magnetic properties are similar to that reported earlier [1, 3]. The details of the measurements of Seeback voltage and synthesis of γ-Fe_2O_3 by dehydration of γ-FeOOH are also given earlier [1]. The details of synthesis of doped γ-Fe_2O_3 by synthetic method are given below.

2.1. Preparation of cobalt doped γ-Fe_2O_3

γ-Fe_2O_3 doped with the different concentration of cobalt were prepared using synthetic method. It involves the simultaneous precipitation of γ-FeOOH and hydroxide of dopant.

100 ml of ammonium chloride solution (0.1 M) were added to a mixture of $CoCl_2 \cdot 6H_2O$ (3.8×10^{-5} to 1.28×10^{-4} M, volume of solution is so adjusted that cobalt concentration lies in the range 0.3 to 1.0 wt% of Fe_2O_3) and 150 ml $FeCl_2$ (0.025 M) solution. The precipitation of oxyhydroxide was then carried out following the procedure given earlier [1]. The dry sample of cobalt doped γ-FeOOH was heated in air oven at 250° C for about an hour yielding the doped γ-Fe_2O_3 (yield 1.0 g).

Other samples of doped γ-Fe_2O_3 were prepared by following the procedure given above. The additional relevant details are summarized below.

2.2. Preparation of nickel doped γ-Fe_2O_3

The solutions of $NiCl_2 \cdot 6H_2O$ (3.80×10^{-5} to 1.92×10^{-4} M) and $FeCl_2$ (0.025 M) were used. The concentration of dopant was adjusted in the wt % range 0.3 to 1.5.

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2.3. Preparation of gadolinium doped γ-Fe_2O_3

The solutions of $GdCl_3 \cdot 6H_2O$ (1.42×10^{-5} to 7.20×10^{-5} M) and $FeCl_2$ (0.025 M) were used. The concentration of dopant was adjusted in the wt% range 0.3 to 1.5.

2.4. Preparation of terbium doped γ-Fe_2O_3

The solutions of $TbCl_3 \cdot 6H_2O$ (1.40×10^{-5} to 1.34×10^{-4} M) and $FeCl_2$ (0.025 M) were used. The concentration of dopant was adjusted in wt% range 0.3 to 1.5.

The apparent density of doped γ-Fe_2O_3 were determined by specific gravity bottle method [4, 5].

3. Results and discussion

Some of the interesting observations derived from the log σ against T^{-1} plots of doped γ-Fe_2O_3 samples are summarized below. (The typical nature of the results is examplified in Figs. 1 and 2; for sample numbers please refer Tables I to IV.)

(a) The doped samples of γ-Fe_2O_3 containing 0.3% cobalt (sample XVII), 0.5% nickel (sample XXII), or 0.3% gadolinium (sample XXVI) do not show any observable change in σ in the temperature range 120 to 180° C. The Seeback voltage of these samples is also practically independent of temperature in this temperature range.

(b) Above 180° C the log σ against T^{-1} plots for samples XVII, XXII and XXVI are comparable with that for a sample III in a static air [1]. This observation suggests that presence of lattice water in this temperature range in samples XVII, XXII and XXVI. Infrared spectra of these samples heated at 180° C for 12 h and cooled in the nitrogen atmosphere do show the characteristic bands

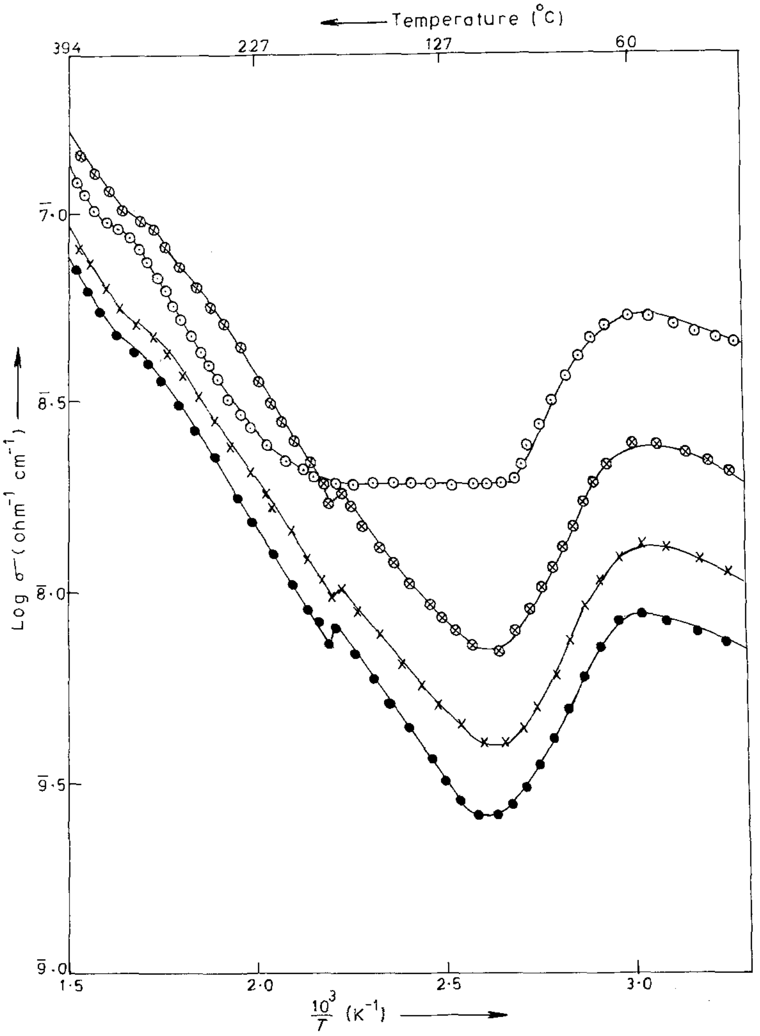

Figure 1 Plot of log σ against T^{-1} of cobalt-doped γ-Fe_2O_3. Curve (XVII), ⊙ 0.3%; curve (XVIII), ⊗ 0.5%; curve (XIX), × 0.75%; curve (XX), ● 1.0%.

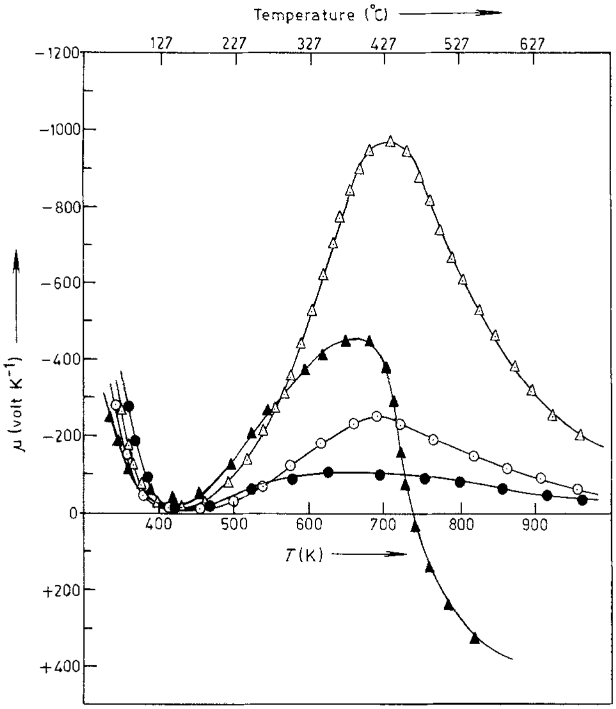

Figure 2 Plot of Seeback voltage, μ (volt K^{-1}) against T (K) of doped γ-Fe_2O_3. △ Sample XVIII; ▲ samples XXIII; ⊙ sample XXVII; ● sample XXXII.

of lattice water at 3400(s) and 1650(s) cm^{-1}. In addition the comparison of infrared spectra indicates that the band at 540 cm^{-1} associated with the Fe–O stretching mode is very broad for these three samples.

(c) The σ values for samples XVII and XXVI in the temperature range 120 to 180° C are characteristically higher than that of other samples in the same temperature range.

(d) The X-ray diffraction patterns of samples XVII, XXII and XXVI are as sharp as that of γ-Fe_2O_3 heated under nitrogen at 250° C for 20 h. The pattern in the high angle-region for these samples are also clearly obtained.

(e) The observations (a) and (d) suggest that the samples XVII, XXII and XXVI contain a negligible amount of the hydrogen ferrite phase.

(f) For other doped samples containing cobalt (samples XVIII–XX), nickel (samples XXI, XXIII–XXV), gadolinium (samples XXVII–XXX) and terbium (samples XXXI–XXXIV) the temperature-independent direct current electrical conductivity is not observed in any temperature range. We are, therefore, tempted to suggest that these samples do contain the hydrogen ferrite phase. The doped samples XVIII, XIX and XX containing cobalt show a definite kink corresponding to the kink **k** observed for the undoped sample of γ-Fe_2O_3 [1]. For other samples an overall broadening in the log σ against T^{-1} curves is observed in the temperature range 150 to 195° C and a definite kink corresponding to **k** could not be detected.

(g) It seems that the temperatures correspond-

TABLE I Cobalt-doped γ-Fe_2O_3

Sample number	Concentration of dopants (%)	Temperature corresponding to the desorption of adsorbed O_2 and H_2O (°C)	Temperature corresponding to γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$ transformation			Seeback voltage, highest value, μ (volt K^{-1})
			Electrical conductivity measurement (°C)	Initial magnetic susceptibility measurement (°C)	Seeback voltage measurement (°C)	
XVII	0.3	105	395	400	405	−1025
XVIII	0.5	110	395	400	408	−965
XIX	0.75	108	398	395	405	−920
XX	1.0	115	395	400	408	−745

TABLE II Nickel-doped γ-Fe_2O_3

Sample number	Concentration of dopants (%)	Temperature corresponding to the desorption of adsorbed O_2 and H_2O (°C)	Temperature corresponding to γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$ transformation			Seeback voltage, highest value, μ (volt K^{-1})
			Electrical conductivity measurement (°C)	Initial magnetic susceptibility measurement (°C)	Seeback voltage measurement (°C)	
XXI	0.3	108	395	405	400	−630
XXII	0.5	110	390	403	400	−540
XXIII	0.75	110	395	398	402	−460
XXIV	1.0	112	395	400	405	−430
XXV	1.5	105	390	400	400	−400

ing to the completion of the desorption of adsorbed oxygen and water depend on the nature and concentration of the dopant (Tables I to IV). A small concentration of the dopant shows an increase in these temperatures, and these temperatures increase with an increase in the dopant concentration.

(h) The phase transformation γ-Fe_2O_3 to α-Fe_2O_3 in nickel-doped γ-Fe_2O_3 (samples XXI to XXV) is clearly shown by a well resolved kink in the log σ against T^{-1} curves. However for other doped samples a mere change in the slope of this plot has been observed at the phase transformation temperature. The activation energy determined from the log σ against T^{-1} curves of these doped samples lie between 0.35 and 0.78 eV in the temperature range 130 to 295° C.

(i) From the data of the Seeback voltage (μ) the cobalt-doped samples have the largest number of negative carriers as compared to other doped samples (Tables I to IV). The temperature variation of μ for the nickel-doped samples is similar to that for the undoped γ-Fe_2O_3 (Fig. 2). The negative values of μ for the gadolinium and terbium doped samples are small. A sharp decrease in μ is observed at a temperature corresponding to the phase change γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$ for the cobalt- and nickel-doped γ-Fe_2O_3. It is interesting to note that the nickel-doped α-Fe_2O_3 shows a positive value of μ at a high temperature ($> \sim 480°$ C).

(j) Infrared spectra of these doped samples of γ-Fe_2O_3 (heated for 12 h at 250° C and cooled in N_2 atmosphere) are similar to those of the undoped-sample of γ-Fe_2O_3. The bands observed in the Fe–O stretching region (370 to 710 cm^{-1}) are sharp. The band observed at 540 cm^{-1} shows a small blue shift on doping. The band observed at 370 cm^{-1} for the undoped γ-Fe_2O_3 is of the strong intensity and that for the doped samples is of the medium intensity.

(k) The apparent densities of the doped samples and that of the undoped sample lie in a narrow range $4870 \pm 10\,kg\,m^{-3}$. The X-ray diffraction Patterns of these doped samples are similar to that of the undoped sample of γ-Fe_2O_3, and correspond to a tetragonal configuration [6]. The X-ray diffraction patterns in the high angle-region for the samples XVII, XXII and XXVI have relatively higher intensity and are sharp.

TABLE III Gadolinium-doped γ-Fe_2O_3

Sample number	Concentration of dopants (%)	Temperature corresponding to the desorption of adsorbed O_2 and H_2O (°C)	Temperature corresponding to γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$ transformation			Seeback voltage, highest value, μ (volt K^{-1})
			Electrical conductivity measurement (°C)	Initial magnetic susceptibility measurement (°C)	Seeback voltage measurement (°C)	
XXVI	0.3	110	395	400	405	−230
XXVII	0.5	115	390	395	405	−255
XXVIII	0.75	120	395	390	402	−170
XXIX	1.0	130	390	400	400	−115
XXX	1.5	125	395	390	408	−75

TABLE IV Terbium-doped γ-Fe_2O_3

Sample number	Concentration of dopants (%)	Temperature corresponding to the desorption of adsorbed O_2 and H_2O (°C)	Temperature corresponding to γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$ transformation			Seeback voltage, highest value, μ (volt K^{-1})
			Electrical conductivity measurement (°C)	Initial magnetic susceptibility measurement (°C)	Seeback voltage measurement (°C)	
XXXI	0.3	120	390	395	400	−160
XXXII	0.5	130	390	400	407	−115
XXXIII	0.75	120	395	405	400	−110
XXXIV	1.5	120	398	395	402	−55

(1) The observations (f) and (k) suggest that the doped samples other than XVII, XXII and XXVI do have a significant contribution of the hydrogen ferrite phase.

In the previous work it has been proposed that the normal sample of γ-Fe_2O_3 (sample III) [1] has a formula intermediate between Relation 1 and 2.

$$Fe_8^{3+}[(Fe_{4/3}^{3+}\square_{8/3})Fe_{12}^{3+}]O_{32} \qquad (1)$$

$$Fe_8^{3+}[(H_4^{1+})Fe_{12}^{3+}]O_{32}. \qquad (2)$$

An intermediate composition (Relation 3) requires a part of iron in a lower oxidation state, the composition (Relation 4) being an extreme case.

$$Fe_8^{3+}[(Fe_x^{2+}H_{4-2x}^{1+}\square_x)Fe_{12}^{3+}]O_{32} \qquad (3)$$

$$Fe_8^{3+}[(Fe_2^{2+}\square_2)Fe_{12}^{3+}]O_{32}. \qquad (4)$$

A formula similar to Relation 4 can be used for γ-Fe_2O_3 doped with divalent metal ions. Its composition will be therefore represented by Relation 5.

$$Fe_8^{3+}[(Fe_{(2-x)}^{2+}M_x^{2+}\square_2)Fe_{12}^{3+}]O_{32}. \qquad (5)$$

Thus it is possible for some concentration of the divalent dopant the contribution of the hydrogen ferrite phase would be negligible. The observations (a) and (d) substantiate this prediction.

For the trivalent dopant a formula similar to Relation 5 requires the presence of a monovalent ion such as hydrogen for the charge balance. The extreme case is represented by Relation 6.

$$Fe_8^{3+}[(M_x^{3+}H_{4-3x}^{1+}\square_{2x})Fe_{12}^{3+}]O_{32} \qquad (6)$$

The formula similar to Relation 1 is given below.

$$Fe_8^{3+}[(Fe_x^{3+}M_{4/3-x}^{3+}\square_{8/3})Fe_{12}^{3+}]O_{32} \qquad (7)$$

Since γ-Fe_2O_3 prepared under the static air is always associated with the hydrogen ferrite phase, the doped sample containing trivalent metal ion under similar conditions will also be associated with the hydrogen ferrite phase.

Among all the samples of γ-Fe_2O_3 doped with gadolinium and terbium only one sample containing 0.3% gadolinium indicates an absence of hydrogen ferrite phase. One may say with caution that this observation may be considered as one of the rare examples in which Gd^{2+} with the probable electronic configuration $4f^7 5d^1$ is stabilized in a crystal lattice of γ-Fe_2O_3.

The Seeback voltage of γ-Fe_2O_3 and doped γ-Fe_2O_3 is negative. Thus the samples are n-type semiconductor similar to ZnO [7, 8]. The probable hopping mechanism of the direct current electrical conductivity of these samples requires the presence of Fe^{2+} so that there will be an electron transfer between the Fe^{2+} to Fe^{3+} ions on the octahedral sites. A contribution of the configurations 3 and 5 to γ-Fe_2O_3 doped with the divalent metal ions will be the origin of iron(II) ions. Thus the number of charge carriers in γ-Fe_2O_3 doped with divalent metal ions will be more than that in γ-Fe_2O_3 doped with trivalent metal ions. The observation (i) substantiates this prediction. It may be noted here that the expected concentration of iron(II) in the samples studied in the present work is expected to be very small, and one should not compare the values of direct current electrical conductivity of these compounds with that of the metallic semiconductors Fe_3O_4 which contains an equal number of iron(II) and iron(III) ions on the octahedral sites.

The study of the effect of the oxygen partial pressure on the irreversible transformation γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$ has indicated that the transformation temperature depends on the number of vacancies. The transformation temperature decreases with an increase in the number of vacancies [2]. The transformation temperatures for γ-Fe_2O_3 and doped γ-Fe_2O_3 in static air determined from the data of the temperature variation of direct current electrical conductivity, Seeback voltage and initial magnetic susceptibility lie in a narrow range (Tables I to IV). It seems therefore that the low concentrations of dopants as used in the present work do not change the effective number of vacancies in γ-Fe_2O_3.

There is no observable change in the lattice parameters of the doped samples studied in the present work. The concentrations of dopants in these samples are low. The data of direct current electrical conductivity under controlled atmosphere of samples containing the higher concentrations of dopants are necessary to ascertain a delicate balance of different formulae and its correlation with the hydrogen ferrite phase.

4. Conclusions

The effect of dopants on the hydrogen ferrite phase present in γ-Fe_2O_3 is decidedly shown from the following observations:

(a) Since there is no observable temperature variation of direct current electrical conductivity of doped samples of γ-Fe_2O_3 containing 0.3% cobalt (sample XVII), 0.5% nickel (sample XXII) and 0.3% gadolinium (sample XXVI) in the temperature range 120 to 180° C, a negligible contribution of hydrogen ferrite phase has been suggested in these samples. This suggestion has been substantiated on the basis of X-ray diffraction patterns.

(b) Other doped samples containing cobalt, nickel, gadolinium, and terbium do have a definite contribution of the hydrogen ferrite phase. The position and shape of $\nu_{\text{Fe—O}}$ observed in the region 370 to 710 cm^{-1} can also be used to decide the presence of the hydrogen ferrite phase.

(c) The Seeback voltage of these samples are of negative sign. The magnitude of Seeback voltage for cobalt-doped and nickel-doped samples are higher as compared to that for γ-Fe_2O_3 doped with gadolinium and terbium.

(d) The following general formulas are suggested for doped γ-Fe_2O_3.

$$\text{Fe}_8^{3+}[(\text{Fe}_{(2-x)}^{2+}\text{M}_x^{2+}\square_2)\text{Fe}_{12}^{3+}]\text{O}_{32}$$

$$\text{Fe}_8^{3+}[(\text{M}_x^{3+}\text{H}_{4-3x}^{1+}\square_{2x})\text{Fe}_{12}^{3+}]\text{O}_{32}.$$

The observed physical properties of doped γ-Fe_2O_3 are explained using these fomulae. The data of sample XXVI containing a low gadolinium dopant concentration suggest that this sample contains Gd^{2+}.

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