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# THERMAL STUDIES ON IRON TITANATE SPINEL

*D. Basak and J. Ghose* *

DEPARTMENT OF CHEMISTRY, INDIAN INSTITUTE OF TECHNOLOGY, KHARAGPUR,
PIN 721 302, INDIA

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Thermogravimetry and X-ray analysis show that the iron titanate spinel sample is non-stoichiometric and has the formula $Fe_{1.76}Ti_{1.12}O_4$. On heating in air below 573 K, it undergoes surface oxidation and on further heating DTA and TG show that it undergoes bulk oxidation in three stages. X-ray analysis and resistivity measurements show that while octahedral $Fe^{2+}$ ions are oxidised, the spinel structure is retained and during $Fe^{2+}_{tet}$ oxidation a metastable phase is formed and when the oxidation is complete, the pseudobrookite phase is formed.

Several studies have been carried out on the oxidation of fine-grained $Fe_3O_4$ substituted by different types of ions [1–2]. Gillot *et al.* have shown that during the oxidation of fine-grained $Fe_3O_4$ substituted by $Ti^{4+}$ ($0 < x < 0.82$), the octahedral site $Fe^{2+}$ ions are preferentially oxidised [3] and for the sample with larger substitution [4] the spinel structure becomes unstable only during the oxidation of the tetrahedral site $Fe^{2+}$ ions.

The present study is aimed at studying the oxidation of moderate grained iron titanate spinel which initially does not contain any $Fe^{3+}$ ions.

## Experimental

$Fe_2TiO_4$ was prepared by the following method: stoichiometric amounts of $Fe_2O_3$, Fe and $TiO_2$ powders (specpure) were mixed in an agate mortar by grinding under acetone for several hours, pressed into pellets under a pressure of 3 tons/sq. inch, sintered in sealed evacuated quartz tube ($10^{-5}$

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*To whom correspondence may be addressed.

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*Akadémiai Kiadó, Budapest*

mm of Hg) at 1413 K for 5 hours and then quenched in liquid $N_2$. The spinel oxide is formed according to the reaction

$$3TiO_2 + 2Fe_2O_3 + 2Fe \rightarrow 3Fe_2TiO_4$$

X-ray diffraction analysis of the samples were carried out with an X-ray diffraction unit model PW 1710 using $CuK_\alpha$ radiation ($\lambda$ = 1.5418Å) and Ni filter.

Thermal analysis of the samples was carried out with a Stanton Redcroft instrument between 300 to 1273 K. A linear rate of heating of 10 deg/min was maintained.

The electrical resistivity of the sample in air was measured by means of a two probe technique described elsewhere [5]. The resistivity measurements were carried out between 300 K to 853 K. The resistivity measurements with time were carried out at 393 K, 478 K, 598 K, 673 K and 803 K.

The thermoelectric power measurements were carried out between 300 K to 431 K. The experimental set up is described elsewhere [6].

Surface area measurements were carried out by BET method using quantasorb (quantachrome).

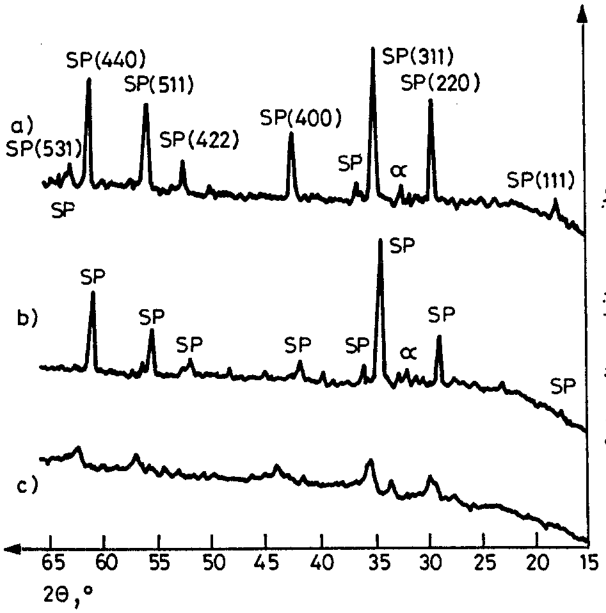

Fig. 1 X-ray diffractograms of $Fe_2TiO_4$ at (*a*) 300 K, (*b*) 803 K and 853 K Sp, spinel; *α*, *α*$-Fe_2O_3$

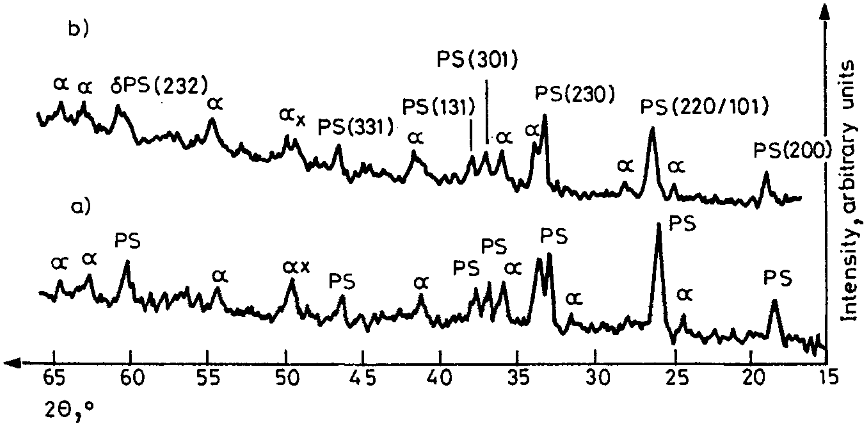

Fig. 2 X-ray diffractograms of $Fe_2TiO_4$ at (*a*) 973 K, and (*b*) 1273 K Sp, spinel; *α*, *α*–$Fe_2O_3$; X, $TiO_2$; *δ*, FeO; PS, pseudobrookite

## Results

X-ray pattern of the prepared $Fe_2TiO_4$ sample in Fig. 1 (a) shows the presence of a spinel phase along with traces of *α*-$Fe_2O_3$. Lattice parameter has been calculated and shows a value of $a_o$ = 849.5 ± 000.5 Pm. Average size of the particles is found to be between 50 μm and 70 μm. The DTA plot (Fig. 3) shows the presence of the two broad exothermic peaks in the temperature regions 473 K to 623 K and 673 K to 923 K. The first exothermic DTA peak is accompanied by a slow weight gain from 473 K to 623 K as shown in the TG curve (Fig. 3). From 706 K onwards, the TG curve shows a rapid weight gain accompanying the second exothermic peak. Above 923 K, the weight gain occurs slowly upto ≈ 11150 K. The second DTA peak shows three humps. At the temperature of the start of the second hump i. e. ~ 803 K, the TG curve shows a slight increase in slope. The X-ray diffractogram of the sample heated to 803 K showed the presence of broadened $Fe_2TiO_4$ lines (Fig. 1(b)). The X-ray diffractogram of the sample heated to 853 K, where the second hump is complete, however shows the presence of a large number of broad peaks which could not be identified with either the spinel phase or the pseudobrookite phase (Fig. 1(c)). Fig. 2(a) shows the X-ray diffractogram of the sample heated to 973 K, the temperature at which the second DTA peak is complete. The diffractogram shows the presence of a large number of lines corresponding to the pseudobrookite phase, *α*-$Fe_2O_3$ and $TiO_2$. The TG curve shows a weight gain above 973 K, up to ~1150 K. The X-ray diffractogram of the sample heated to a temperature above the

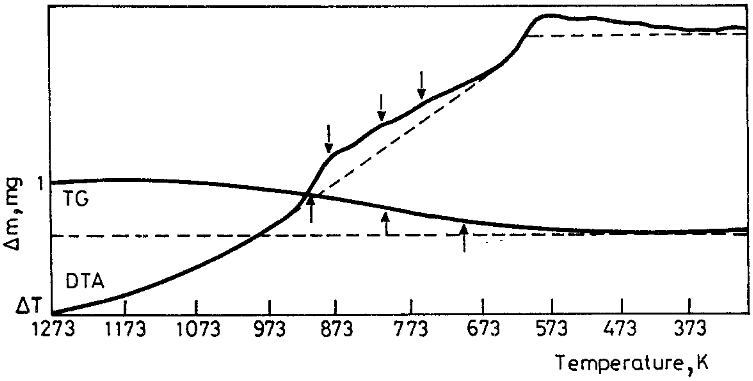

Fig. 3 DTA and TG of $Fe_2TiO_4$

completion of the weight gain temperature i. e. 1273 K shows the presence of the pseudobrookite phase along with traces of $\alpha$-$Fe_2O_3$, $TiO_2$ and FeO (Fig. 2(b)). The lines of the pseudobrookite phase are relatively larger than those of the other phases.

Figure 4 shows the temperature variation of thermoelectric power from 300 K to 431 K. The $\alpha e/K \rightarrow 1/T$ plot shows that the sample is n-type upto 388 K, and above this temperature it becomes *p*–type. The values of a show $\alpha$ show a continuous change in the studied temperature range.

The change in electrical conductivity of the sample with temperature is shown in the Fig. 5. The results show that with increasing temperature, the conductivity grandually increases from $1.818 \times 10^{-6}\ \Omega^{-1}\,\mathrm{cm}^{-1}$ (300 K) to $0.57 \times 10^{-4}\ \Omega^{-1}\,\mathrm{cm}^{-1}$ (613 K). Between 612 K to 680 K it shows a small decrease and on heating above this temperature, the conductivity rises rapidly to the value of $7.69 \times 10^{-4}\ \Omega^{-1}\,\mathrm{cm}^{-1}$ (853 K).

The change in conductivity of the sample with time at various temperatures are shown in the Fig. 6. At 393 K, the conductivity does not show any change with time and at 478 K, a small increase occurs. At 598 K, the conductivity value shows an initial rapid increase and then becomes constant after 50 minutes. At 673 K, the conductivity continually decreases with time. At 803 K, after an initial decrease $\sigma$ increases with time.

The surface area measurement shows that about 0.0682 mg of oxygen is required to form a monolayer on the sample surface.

## Discussion

The prepared sample shows the presence of the spinel phase along with traces of $\alpha$-$Fe_2O_3$ as was found by Gillot *et. al.* [4] in the titanium substituted $Fe_3O_4$ samples. This probably indicates that non-stoichiometric spinel phase is formed which is iron deficient and may be represented as $Fe_{2-2x}Ti_{1+x}O_4$. The two exothermic peaks in the DTA plot are not sharp and both are accompanied by weight gain. The first DTA peak shows a gradual increase upto 573 K and above this temperature a sharp fall. Surface area measurements show that the weight gain up to 573 K quantitatively corresponds to oxygen which can form a monolayer on the surface of the sample. This implies that on heating, surface oxidation occurs upto 573 K which is manifested in the first DTA peak accompanied by a very small weight gain. Further evidence that the first DTA peak corresponds to surface oxidation is also obtained from thermoelectric power ($\alpha$) and conductivity ($\sigma$) measurements at various temperatures. Figure 4 shows that at the onset temperature

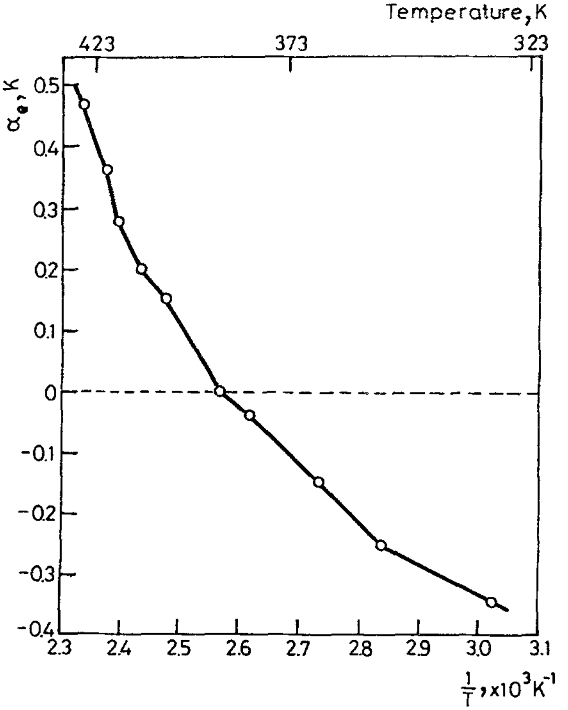

Fig. 4 Variation of thermoelectric power with temperature of $Fe_2TiO_4$

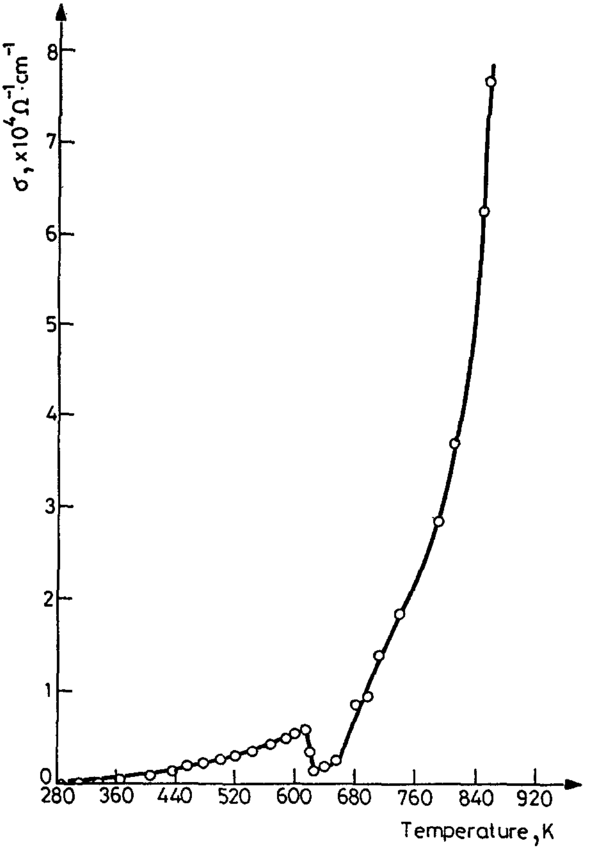

Fig. 5 Variation of resistivity with temperature of $Fe_2TiO_4$

of the first DTA peak, $\alpha$ changes from $n$-type to $p$-type. Figure 5 shows that the conductivity rises very slowly up to ~ 600 K and Fig. 6 shows that the conductivity does not change much with time upto about 500 K. At 598 K, it increases only for a short period and then becomes constant. These results, clearly show that on heating $Fe_2TiO_4$ initially, surface oxidation occurs upto ~573 K. Above this temperature, the weight gain shows a more rapid increase which could be due to diffusion of oxygen beyond the surface layer of the sample. Diffusion of ions into the bulk is also evident in the $\sigma \rightarrow$ time plots (Fig. 6). At 598 K, diffusion probably occurs to a small extent as the conductivity shows a constant value after an initial rise with time. Above this temperature however, $\sigma$ shows a sudden decrease between 612 K to 680 K and then an increase with temperature and decrease with time which implies

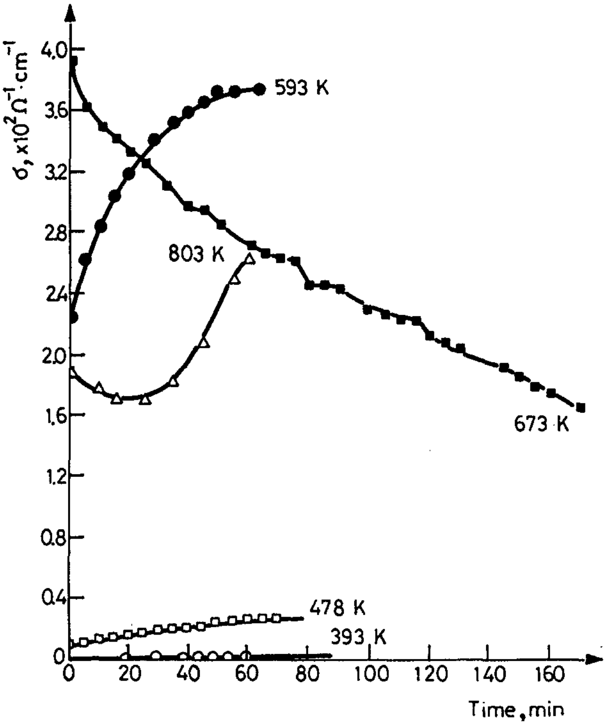

Fig. 6 Variation of resistivity with time of $Fe_2TiO_4$

bulk oxidation and this is also supported by a rapid weight gain in the TG curve. Bulk oxidation probably gives rise to the second DTA peak.

The spinel structure is retained during oxidation upto about 803 K as is shown by the presence of only spinel lines in the X-ray pattern of the sample heated to 803 K. This is also the temperature where the first hump in the DTA peak is complete. It has been reported by Gillot *et al.* [3] that the spinel structure becomes unstable only during the oxidation of the tetrahedral $Fe^{2+}$ ions and hence it may be suggested that the temperature below which the spinel structure is retained, i. e. 803 K, only octahedral $Fe^{2+}$ ions are oxidised. Furthermore, the decrease in conductivity between 612 K to 680 K probably suggests, that in this temperature region more $Fe^{3+}$ ions are present on the octahedral sites. The temperature variation of conductivity, shown in Fig. 4 is different for these observed by Gillot *et al.* for their sample $Fe_{2.18}Ti_{0.82}O_4$. This difference could be due to the presence of $Fe^{3+}$ ions in their sample and also due to different grain boundary effects on finely grained samples and the samples in the present work.

Above 803 K, the tetrahedral site $Fe^{2+}$ ions are probably oxidised and may be giving rise to a hump in the second DTA peak. Also the $\sigma$ *vs* time plot at 803 K, shows an initial decrease followed by increase of conductivity with time. Gillot *et al.* [3] suggested that conductivity should increase as $Fe^{3+}$ ions are formed and then decrease when more than half of $Fe^{2+}$ ions on the octahedral site are oxidised. An increase in the conductivity following a decreasing trend is due to the beginning of oxidation of $Fe^{2+}$ ions on the tetrahedral site. Thus the results indicate that the tetrahedral site $Fe^{2+}$ ions start getting oxidized only above 803 K. Further evidence of the oxidation of $Fe^{2+}_{tet}$ above 803 K is obtained from the X-ray pattern (Fig. 1(c)). The pattern does not have the spinel lines but very broad lines which could be due to a metastable phase formed during oxidation of the spinel. It is not a very sharp transition as it appears only as a hump in the DTA curve.

The appearance of the third hump in the DTA peak is probably due to the change from the metastable to the pseudobrookite phase. To confirm the formation of the pseudobrookite phase the X-ray pattern of the sample heated to a temperature where the DTA peak is complete i. e. 973 K was taken. It shows the presence of a crystalline phase with sharp lines corresponding to pseudobrookite and $\alpha$-$Fe_2O_3$. This indicates that the oxidation of $Fe_2TiO_4$ to pseudobrookite occurs below 973 K. The TG curve however shows a weight gain even above 973 K and the X-ray pattern of the sample heated to 1273 K (after the weight gain is complete) shows the presence of sharper lines of $TiO_2$, $\alpha$-$Fe_2O_3$ and pseudobrookite. This probably indicates that although at 973 K, the pseudobrookite is formed by oxidising $Fe_2TiO_4$, the oxidation process is not complete bleow 1130 K. The presence of $TiO_2$ lines in the completely oxidised sample and its absence in the spinel sample, further suggests the presence of stoichiometrically excess titanium in the iron titanate sample.

On complete oxidation, the total weight gain corresponds to the oxidation of 1.76 atoms of $Fe^{2+}$ in one molecule of the spinel. If the sample had been $Fe_2TiO_4$, 2 atoms of $Fe^{2+}$ should have been oxidised. From these results, it may be suggested that the spinel sample is iron deficient and as was suggested in the earlier part of the discussion, the sample may be represented by the formula $Fe_{2-2x}Ti_{1+x}O_4$. From thermogravimetry results it seems that the spinel should be represented by the formula $Fe_{1.76}Ti_{1.12}O_4$ and then the oxidation to pseudobrookite may be represented as

$$Fe_{1.76}Ti_{1.12}O_4 \xrightarrow{O_2} Fe_{1.76}Ti_{0.88}O_{4.4} + 0.24\ TiO_2$$

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**Zusammenfassung** — Durch TG und Röntgendiffraktion zeigte sich, daß eine Eisentitanat-Spinellprobe keine stöchiometrische Zusammensetzung, sondern die Formel $Fe_{1.76}Ti_{1.12}O_4$ besitzt. Bei Erhitzen in Luft wird die Probe unterhalb 573 K an der Oberfläche oxidiert. Bei weiterem Erhitzen zeigen DTA- und TG-Daten eine dreistufige Oxidation im gesamten Volumen. Röntgendiffraktions- und Widerstandsuntersuchungen zeigen, daß bei der Oxidation von oktaedrischen $Fe^{2+}$-Ionen die Spinellstruktur beibehalten wird und bei der $Fe^{2+}_{tet}$-Oxidation eine metastabile Phase und nach vollständiger Oxidation eine Pseudobrookitphase gebildet wird.