

STUDIES ON THERMAL STABILITY OF TITANIUM SUBSTITUTED IRON MOLYBDENUM SPINEL OXIDE

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Abstract

The thermal stability of the solid solutions of $\text{Fe}_2\text{Mo}_{1-x}\text{Ti}_x\text{O}_4$ for $x=0.0$ to 1.0 in air, had been investigated in the temperature range 303 – 1173 K using differential thermal analysis and thermogravimetry (DTA and TG). The products obtained by heating the sample in air, at different temperatures, have been characterized by X-ray diffraction and IR-studies. The results show that all the ferrite samples undergo surface oxidation during initial heating. On heating to 823 K, the samples undergo oxidation of the octahedral site cations only and form a cation deficient spinel phase. On further heating in air, the ferrites undergo complete oxidation.

Keywords: molybdenum ferrite, spinel oxide, thermal stability, titanium substitution

Introduction

Fe_2MoO_4 and Fe_2TiO_4 are inverse spinel oxides, with Mo and Ti ions on the octahedral sites, and Fe, distributed between the octahedral and tetrahedral sites of the spinel lattice [1, 2]. Thermal stability studies on these ferrites, in air, have shown that Fe_2MoO_4 undergoes surface oxidation followed by bulk oxidation above 723 K [3]. Derivative thermogravimetry (DTG) studies on Fe_2MoO_4 have shown that the B site ions (Fe^{2+} and $\text{Mo}^{3+}/\text{Mo}^{4+}$) are oxidized more readily than the A site ions (Fe^{2+}) [4]. In air, Fe_2TiO_4 undergoes surface oxidation below 573 K, and at higher temperatures, it undergoes bulk oxidation in three stages [5], and similar to Fe_2MoO_4 , the B-site ions (Fe^{2+}) are oxidized more readily than the A site ions. The present work was taken up to study the thermal stability of Fe_2MoO_4 when Mo is progressively replaced by Ti.

Experimental

The $\text{Fe}_2\text{Mo}_{1-x}\text{Ti}_x\text{O}_4$ ($x=0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0) samples were prepared by the method followed by Roy *et al.* [6].

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X-ray diffraction analyses of all the samples ($x=0.0$ to 1.0) were carried out in a Philips X-ray diffraction unit (Model PW-1710) using CoK_α radiation ($\lambda=1.79 \text{ \AA}$) with Ni-filter.

Thermal analyses of the samples were carried out in air with the thermal analyzer (model Shimadzu DT-30) in the temperature region 303 to 1173 K. A linear heating rate of 10 K min^{-1} was maintained during all the measurements.

Infrared (IR) spectra of the samples were recorded in KBr pellets in the $1000\text{--}200 \text{ cm}^{-1}$ region with a Perkin Elmer spectrophotometer (model 883). The pellets used in these measurements were made by mixing the sample with KBr in the mass ratio of 1:200. A pellet of KBr ($\approx 200 \text{ mg}$) was used as a reference.

Results

X-ray diffraction patterns of the titanium substituted samples i.e. $\text{Fe}_2\text{Mo}_{1-x}\text{Ti}_x\text{O}_4$ samples, show that for all the values of x , a single phase cubic spinel oxide is formed. The sample composition, code name and calculated lattice parameter values are given in Table 1.

Table 1 Sample composition, code name and lattice parameter for $\text{Fe}_2\text{Mo}_{1-x}\text{Ti}_x\text{O}_4$ samples

Sample composition	Code name	Lattice parameter, $a \pm 0.002/\text{\AA}$
Fe_2MoO_4	FTM10	8.5030
$\text{Fe}_2\text{Mo}_{0.8}\text{Ti}_{0.2}\text{O}_4$	FTM8	8.5080
$\text{Fe}_2\text{Mo}_{0.6}\text{Ti}_{0.4}\text{O}_4$	FTM6	8.5135
$\text{Fe}_2\text{Mo}_{0.4}\text{Ti}_{0.6}\text{O}_4$	FTM4	8.5185
$\text{Fe}_2\text{Mo}_{0.2}\text{Ti}_{0.8}\text{O}_4$	FTM2	8.5225
Fe_2TiO_4	FTM0	8.5275

Figures 1 and 2 show the DTA and TG curves of the $\text{Fe}_2\text{Mo}_{1-x}\text{Ti}_x\text{O}_4$ samples ($x=0.0$ to 0.8). For all the samples the DTA curve shows more than one peak in the studied temperature range. The first DTA peak is small, and appears around 573 K accompanied with a gradual mass gain, as shown in the TG curve. The second DTA peak is broad, appearing immediately after the first peak, and is accompanied with mass gain.

Figure 3 shows the X-ray diffraction patterns of Fe_2MoO_4 samples heated in air for 30 min at 623, 823 and 1023 K respectively. The X-ray diffraction pattern of Fe_2MoO_4 sample heated to 623 K (Fig. 3b), shows lines of spinel phase along with some characteristic lines of $\text{Fe}_2\text{Mo}_3\text{O}_8$, present in very small amounts. On further heating to 823 K, X-ray pattern shows additional lines along with the spinel phase lines (Fig. 3c). These lines could be identified with $\alpha\text{-Fe}_2\text{O}_3$, MoO_2 and $\text{Fe}_2\text{Mo}_3\text{O}_8$ phases. On heating Fe_2MoO_4 to 1023 K, X-ray pattern shows that it is completely oxidized to the respective oxides (Fig. 3d). The various phases present in samples FTM8, FTM6, FTM4, FTM2 and FTM0 heated to 623 K are shown in Table 2. The different phases obtained on heating these samples to 823 and 1023 K are also shown in Table 2. The change in lattice parameter (a) of the spinel phase, on heating the samples

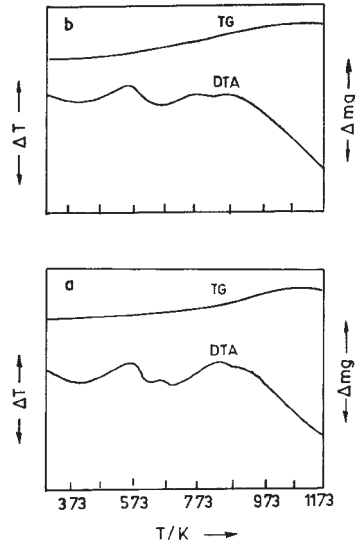


Fig. 1 DTA and TG curves of a – FTM10 and b – FTM8

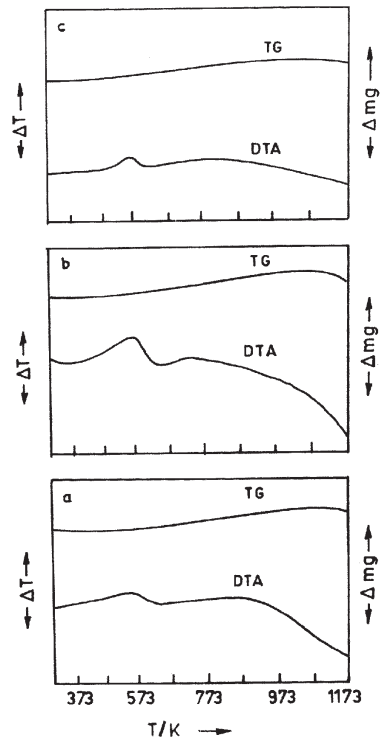


Fig. 2 DTA and TG curves of a – FTM6; b – FTM4 and c – FTM2

to different temperatures, is shown in Fig. 4. The IR spectra of all the samples heated to different temperatures are shown in Figs 5 and 6.

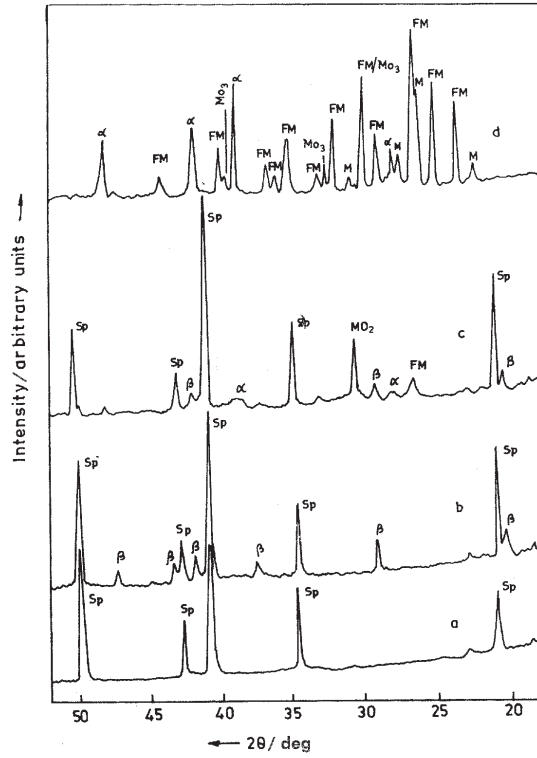


Fig. 3 X-ray diffractograms of Fe_2MoO_4 sample at a – 300 K and heated to b – 623 K; c – 823 K and d – 1023 K; Sp–spinel, FM– $\text{Fe}_2\text{Mo}_3\text{O}_{12}$, MO3– MoO_3 , MO2– MoO_2 , M– Mo_4O_{11} , α – $\alpha\text{-Fe}_2\text{O}_3$ and β – $\text{Fe}_2\text{Mo}_3\text{O}_8$

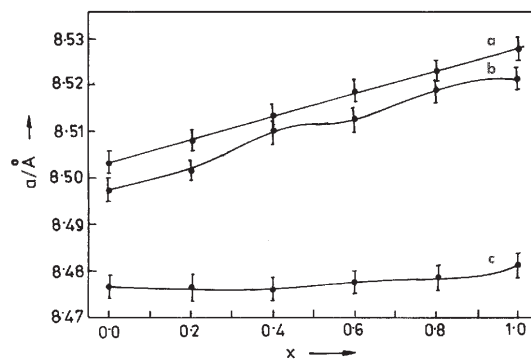


Fig. 4 Variation of lattice parameter, $a(\text{\AA})$ with composition (x) for $\text{Fe}_2\text{Mo}_{1-x}\text{Ti}_x\text{O}_4$ samples at a – 300 K; b – 623 K and c – 823 K

Table 2 Phases identified by XRD, after heating $\text{Fe}_2\text{Mo}_{1-x}\text{Ti}_x\text{O}_4$ samples to different temperatures

Sample code	Temperature/K			
	300	623	823	1023
FTM10	spinel	spinel, $\text{Fe}_2\text{Mo}_3\text{O}_8$	spinel, $\alpha\text{-Fe}_2\text{O}_3$, $\text{Fe}_2\text{Mo}_3\text{O}_{12}$, $\text{Fe}_2\text{MoO}_3\text{O}_8$, MoO_2 , MoO_3	$\text{Fe}_2\text{Mo}_3\text{O}_{12}$, $\alpha\text{-Fe}_2\text{O}_3$, Mo_4O_{11} , MoO_3
FTM8	spinel	spinel	spinel, $\text{Fe}_2\text{Mo}_3\text{O}_{12}$, $\alpha\text{-Fe}_2\text{O}_3$, MoO_2	$\text{Fe}_2\text{Mo}_3\text{O}_{12}$, $\alpha\text{-Fe}_2\text{O}_3$, Mo_4O_{11} , MoO_3 , Fe_2TiO_5
FTM6	spinel	spinel	spinel, $\alpha\text{-Fe}_2\text{O}_3$	$\text{Fe}_2\text{Mo}_3\text{O}_{12}$, $\alpha\text{-Fe}_2\text{O}_3$, Mo_4O_{11} , Fe_2TiO_5 , TiO_2
FTM4	spinel	spinel	spinel, $\alpha\text{-Fe}_2\text{O}_3$	$\text{Fe}_2\text{Mo}_3\text{O}_{12}$, $\alpha\text{-Fe}_2\text{O}_3$, Mo_4O_{11} , Fe_2TiO_5 , TiO_2
FTM2	spinel	spinel	spinel, $\alpha\text{-Fe}_2\text{O}_3$	$\text{Fe}_2\text{Mo}_3\text{O}_{12}$, $\alpha\text{-Fe}_2\text{O}_3$, Mo_4O_{11} , Fe_2TiO_5 , TiO_2
FTM0	spinel	spinel	spinel, $\alpha\text{-Fe}_2\text{O}_3$	$\alpha\text{-Fe}_2\text{O}_3$, Fe_2TiO_5 , TiO_2

Discussion

The results in Figs 1 and 2 indicate, that as found with iron molybdate and iron titanate [3, 5], the titanium substituted molybdenum ferrite samples also undergo change on heating in air and the presence of two DTA peaks suggests that in these samples also, the thermal changes take place in two steps. The first DTA peak accompanied with a slow mass gain may be attributed to surface oxidation of the samples and the second peak may be due to bulk oxidation, which is also supported by the mass gain in the TG curve. These results appear to be similar to the thermal analysis data of Fe_2TiO_4 [5]. In order to ascertain the extent of bulk oxidation, quantitative analyses of the mass gain during heating, was carried out. The results show that for all the molybdenum containing samples, the total mass gain during heating is less than the expected mass gain for complete oxidation of all the Fe^{2+} and Mo^{4+} ions in the $\text{Fe}_2\text{Mo}_{1-x}\text{Ti}_x\text{O}_4$ samples. Calculations were also carried out to see if the experimental mass gain corresponds to oxidation of only Fe^{2+} ions or only Mo^{4+} ions. The results show that the total mass gain recorded in TG is more than the calculated mass gain for the oxidation of either of the ions alone. Furthermore, TG shows that the net mass gain decreases with increase in the titanium content of the ferrites, implying that both the cations i.e. Mo^{4+} and Fe^{2+} are oxidized during heating the sample in air. The kinetics of oxidation of the two cations however, may not be identical and to follow the details of the oxidation process, the samples were heated to different temperatures, held for 30 min, and then characterized by X-ray and IR.

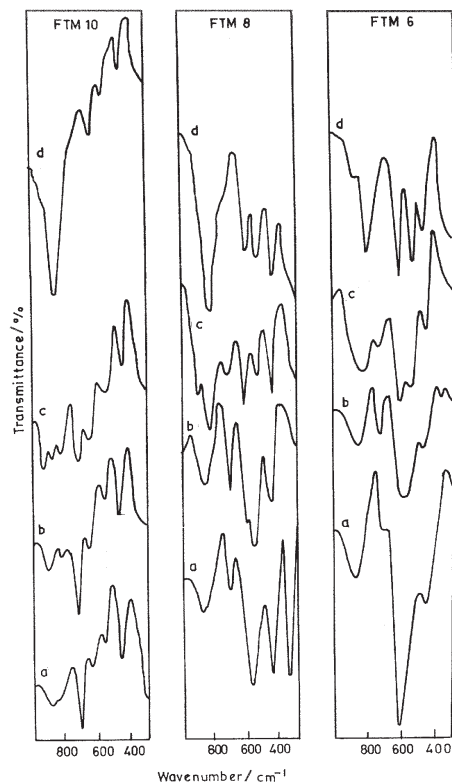


Fig. 5 IR spectra of FTM10, FTM8 and FTM6 samples at a – 300 K and heated to b – 623 K; c – 823 K and d – 1023 K

From the X-ray data, it appears that on heating Fe_2MoO_4 (FTM10) to 623 K, the spinel phase is retained and along with it an additional phase, identified as $\text{Fe}_2\text{Mo}_3\text{O}_8$ is formed (Fig. 3b). However, when the titanium substituted samples i.e. $\text{Fe}_2\text{Mo}_{1-x}\text{Ti}_x\text{O}_4$ ($x > 0.0$) are heated to 623 K, the X-ray patterns show the presence of a single spinel phase with an initial increase of the (111) peak intensity with increasing x . The calculated lattice parameter of the spinel phase shows that with increasing temperature the lattice parameter decreases (Fig. 4). The X-ray pattern of FTM10 heated to 823 K (Fig. 3c) shows the presence of the spinel phase along with $\text{Fe}_2\text{Mo}_3\text{O}_8$, MoO_2 , MoO_3 and $\alpha\text{-Fe}_2\text{O}_3$ and the $\text{Fe}_2\text{Mo}_3\text{O}_{12}$ phases, indicating that on heating FTM10 to 823 K Mo^{4+} and Fe^{2+} are oxidized to Mo^{6+} and Fe^{3+} respectively. Similar results were also observed with the $x=0.2$ (FTM8) sample. However, for the samples with $x \geq 0.4$ (FTM6 to FTM2) oxidation of Mo^{4+} cannot be detected in the X-ray patterns (Table 2). The X-ray patterns of FTM4 to FTM0 samples show characteristic lines of $\alpha\text{-Fe}_2\text{O}_3$ and the spinel phase along with some very low intensity lines, which could not be identified. Earlier studies [7] have shown that the presence of a large number of weak or very weak peaks in the X-ray pattern, may be due to the formation of a cation deficient spinel phase. Thus, the appearance of extra peaks in the X-ray

patterns probably suggests that on heating $x \geq 0.4$ samples to 823 K, a cation deficient spinel phase is formed.

The room temperature IR pattern of FTM10 (Fig. 5, 1(a)) shows the presence of strong bands at 710, 625, 550 and 450 cm^{-1} , which are very similar to the reported IR spectra of Fe_2MoO_4 [4]. The presence of a strong band at $\sim 710 \text{ cm}^{-1}$ indicates that Mo^{4+} is present only in the octahedral site of the spinel lattice. However, the observed weak bands around 885 and 840 cm^{-1} suggests that some Mo^{6+} is also present on both octahedral and tetrahedral sites of the spinel lattice. This is in accordance with the results of Domenichini *et al.* [4]. They have shown that there is a possibility of Mo^{6+} formation on the surface of the samples during grinding. The other molybdenum containing samples i.e. FTM8, FTM6 and FTM4 also show an absorption band at $\sim 720 \text{ cm}^{-1}$ whose intensity decreases with increase in titanium content of the ferrite. This band is however, very weak in FTM4 and is completely absent in FTM2. This is expected, since both in FTM4 and in FTM2, a very small amount of molybdenum is present. FTM8 and FTM6 samples show a band at $\sim 890 \text{ cm}^{-1}$ indicating the presence of a very small amount of Mo^{6+} on the octahedral site only (Fig. 5, 2(a) and 5, 5 (a)), and as in Fe_2MoO_4 , perhaps Mo^{6+} is present only on the surface.

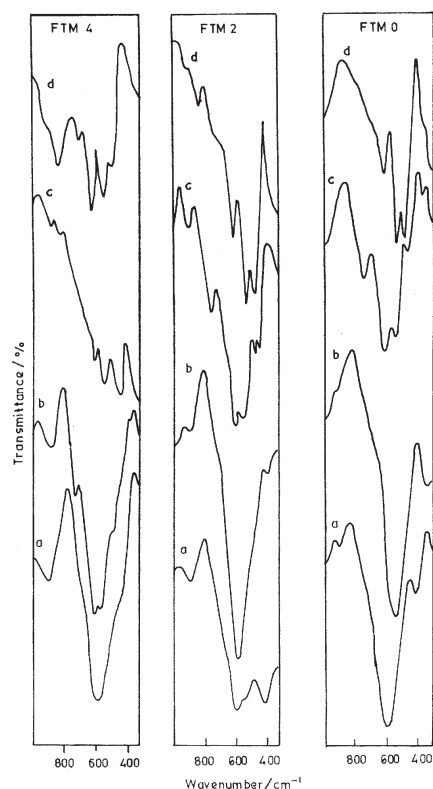


Fig. 6 IR spectra of FTM4, FTM2 and FTM0 samples at a – 300 K and heated to b – 623 K; c – 823 K and d – 1023 K

The IR spectra of the FTM10 sample (Fig. 5, 1 (b)) heated to 623 K show a slight shift in the band positions but extra bands do not appear. Thus, similar to the X-ray data, the IR data also indicates that by heating molybdenum ferrite to 623 K in air, the sample is not oxidized. In the titanium substituted samples, however, along with a shift in the band positions, some additional bands appear (Figs 5, 2 to 6, 3). A large number of additional bands may be due to the formation of vacancies in the spinel lattice during heating, as has been indicated in earlier studies [7, 8].

On heating the sample to 823 K, as indicated in the X-ray data, IR also shows partial oxidation of Mo^{4+} and Fe^{2+} ions. Molybdenum rich samples, FTM10 and FTM8, show bands near 370, 440, 520, 620, 700, 800, 840 and 900 cm^{-1} . The bands near 620, 800 and 900 cm^{-1} are associated with the presence of Mo^{6+} ions located on B-sites. The presence of bands near 840 and 440 cm^{-1} are due to the presence of some Mo^{6+} ions on tetrahedral sites. It has been shown in the X-ray patterns (Fig. 3) that $\text{Fe}_2\text{Mo}_3\text{O}_{12}$ phase is formed during heating FTM10 and 823 K and this is confirmed by the presence of the bands at 840 and 440 cm^{-1} respectively. The band at 370 cm^{-1} is due to $\alpha\text{-Fe}_2\text{O}_3$ formed by oxidation [9]. FTM6 and FTM4 samples also show bands around 840 and 440 cm^{-1} indicating oxidation of Mo^{4+} to Mo^{6+} in these samples during heating to 823 K. These oxidation products, however, could not be detected in the X-ray diffraction patterns. For the FTM6 to FTM0 samples, on heating to 823 K, there is a shift in the ~ 700 cm^{-1} band (also observed on heating the samples to 623 K) to higher frequency (~ 760 cm^{-1} for FTM0), which is due to the formation of defect structure. It has been shown by Gillot *et al.* [7], in their studies on titanomagnetites, that precipitation of $\alpha\text{-Fe}_2\text{O}_3$ leads to a decrease in iron and an increase in titanium content in the defect phase. This results in a decrease in mass of the central atom, increasing the force constant, which causes the shift of the 700 cm^{-1} band to higher frequency. The titanium rich samples also show bands around 620, 470 and 370 cm^{-1} , which are due to the presence of Fe_2TiO_5 and $\alpha\text{-Fe}_2\text{O}_3$ in the oxidized samples. From the IR and X-ray results it appears that on heating the samples (FTM6 to FTM0) to 823 K, in air, oxidation occurs, along with the formation of cation deficient spinel oxides.

On further heating the samples to 1023 K, complete oxidation of the Fe^{2+} and Mo^{4+} ions to Fe^{3+} and Mo^{6+} ions occurs. The X-ray patterns of the molybdenum rich samples however, show the presence of an additional Mo_4O_{11} phase (Fig. 3(d)), in which the valency of Mo is 5.5. This implies that all the Mo^{4+} ions are not completely oxidized to Mo^{6+} . Formation of Mo_4O_{11} phase is also supported by TG. This oxide is non stoichiometric and hence oxidation of Mo^{4+} to give Mo_4O_{11} phase will not lead to complete oxidation of all the Mo^{4+} present in $\text{Fe}_2\text{Mo}_{1-x}\text{Ti}_x\text{O}_4$ samples and hence the mass gain calculated from TG will always be smaller than the expected mass gain for complete oxidation of all the Mo^{4+} to Mo^{6+} . This probably explains the discrepancy in the calculated and experimental mass gain from TG. However, discrepancy in the mass gain calculation due to evaporation of some MoO_3 at higher temperatures [3] is also possible. In the IR patterns of the samples, FTM10 and FTM8, heated to 1023 K, bands around 960, 840 and 440 cm^{-1} appear which could be due to the $\text{Fe}_2\text{Mo}_3\text{O}_{12}$ phase. The samples FTM6 to FTM0, heated to 1023 K show a strong band at

$\sim 620\text{ cm}^{-1}$ which is due to the presence of the pseudobrookite phase. The other bands present in all the samples match with the IR spectrum of $\alpha\text{-Fe}_2\text{O}_3$ [9].

From these results it may be concluded that during heating in air all the samples undergo surface oxidation followed by bulk oxidation. At intermediate temperatures the samples form a cation deficient spinel oxide as indicated in the X-ray and IR studies. A small substitution of molybdenum by titanium stabilizes the spinel phase as none of the titanium substituted samples show the separation of the $\text{Fe}_2\text{Mo}_3\text{O}_8$ phase on heating to 623 K.

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