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Studies on Some Titanium-Substituted Fe_2MoO_4 Spinel Oxides

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Electrical resistivity (ρ) and thermoelectric power (α) measurements were carried out in inert atmosphere on $Fe_2Mo_{1-x}Ti_xO_4$ ($0.0 \leq x \leq 1.0$) spinel oxides in the temperature ranges 100–600 and 300–600 K, respectively. Thermal activation energy (E_a), carrier concentration (n), activation energy for carrier concentration generation (E_n), and mobility (μ) values have been calculated from resistivity and thermoelectric power data. The results show that conduction in titanium-substituted Fe_2MoO_4 samples, i.e., $Fe_2Mo_{1-x}Ti_xO_4$, is carried out through the hopping of charge carriers, and the linear ln (ρ) vs $1/T$ plots show a break at the magnetic phase transition temperature. Progressive substitution of molybdenum by titanium in Fe_2MoO_4 shows that the ratio of Fe^{3+}/Fe^{2+} decreases and in Fe_2TiO_4 the ratio is very small. The decrease in the amount of Fe^{3+} with increasing x results in the high resistivity and large lattice parameter of Fe_2TiO_4.

INTRODUCTION

Fe_2MoO_4 is a cubic spinel showing some very interesting magnetic properties and has been studied by various groups for the past three decades (1–7). The most controversial point in all these studies has been the valence state of the cations and their distribution between the tetrahedral and octahedral sites of the spinel lattice. Studies by Ramdani *et al.* (8) and Domenichini *et al.* (9) have shown that the cations present in the ferrite are Fe^{2+}, Fe^{3+}, Mo^{3+}, and Mo^{4+} and the formal valence assignment can be best represented by the equilibrium reactions (8)

$$Fe_B^{2+} + Fe_A^{3+} + Mo^{3+} = Fe_B^{3+} + Fe_A^{2+} + Mo^{3+} = Fe_B^{2+} + Fe_A^{2+} + Mo^{4+}.$$

Recently, Roy *et al.* (10) carried out some magnetic measurements on titanium-substituted Fe_2MoO_4, i.e., $Fe_2Mo_{1-x}Ti_xO_4$ samples. The results confirmed the presence of Fe^{2+} and Fe^{3+} ions in the ferrites.

The present work was taken up to study the effect of titanium substitution on the electrical transport properties of Fe_2MoO_4.

EXPERIMENTAL

Solid solutions of $Fe_2Mo_{1-x}Ti_xO_4$ ($x = 0.0$, 0.2, 0.4, 0.6, 0.8, and 1.0) were prepared by thoroughly mixing stoichiometric amounts of Fe_2O_3 (specpure, Johnson–Mathey), Fe (electrolytic grade, Sarabhai Chemicals), MoO_2 (reduced from specpure MoO_3), and TiO_2 (analytic grade, S.D. Fine chemicals) and grinding in an agate mortar for several hours. The samples in the pellet form were placed inside quartz tubes, which were then degassed under vaccum and sealed under 10^{-5} Torr. The sealed tubes were heated to 1170°C for 2 h and then quenched in liquid nitrogen.

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 Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å) with Ni filter.

Resistivity measurements were carried out by four-probe technique in an inert atmosphere in the temperature range 100–600 K using silver paste for ohmic contact. Thermoelectric power measurements of all the polycrystalline samples were carried out in argon atmosphere in the temperature range 300–600 K following the procedure described elsewhere (11). The samples were heated at a rate of 200°C/h to avoid any phase separation during the measurements (8).

RESULTS AND DISCUSSION

Figure 1 shows the plot of lattice parameter **a** and the ferrimagnetic Curie temperature $\mathbf{T}_c$ against the titanium content of the $Fe_2Mo_{1-x}Ti_xO_4$ solid solution samples. With increasing x, the lattice parameter **a** increases linearly following Vegard's law. Such a change in the lattice parameter was also observed by Abe *et al.* (12). The Curie temperature however shows a gradual decrease as the molybdenum content in the ferrite is reduced.

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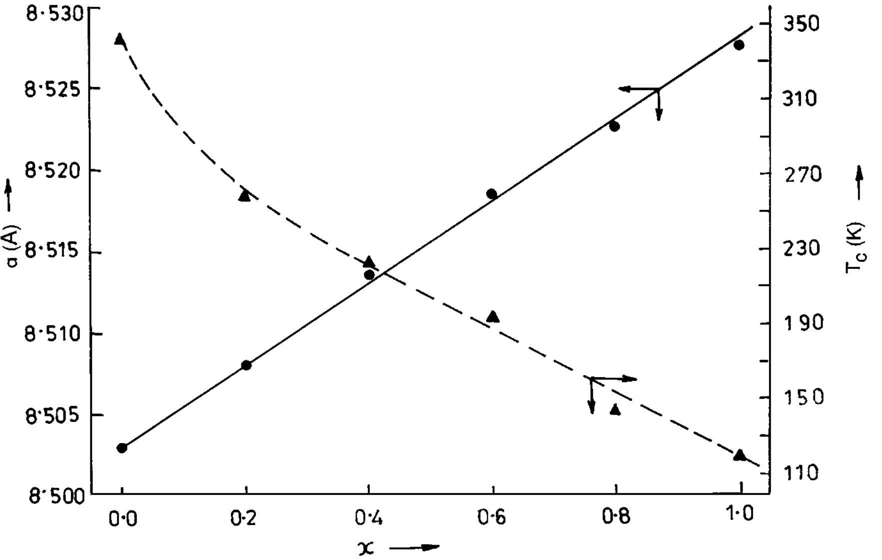

FIG. 1. Plots of a and T_c vs x for the $Fe_2Mo_{1-x}Ti_xO_4$ samples.

An increase in the lattice parameter (Fig. 1) with the substitution of Mo^{4+} by Ti^{4+} is rather surprising since the size of Mo^{4+} (65 pm) is larger than the size of the substituting ion, Ti^{4+} (60.5 pm). Earlier studies have shown that in Fe_2MoO_4, molybdenum is present both in the trivalent (Mo^{3+}) and tetravalent (Mo^{4+}) states and consequently, for oxygen stoichiometry, iron is present in the divalent and trivalent states, i.e., Fe^{2+} and Fe^{3+}. This implies that when molybdenum is substituted by titanium the amount of Fe^{3+} in the ferrite is reduced. Thus, substitution of Mo by Ti^{4+} effectively leads to the replacement of Fe^{3+} (55 pm) by Fe^{2+} (78 pm); i.e., a smaller Fe^{3+} ion is replaced by a larger Fe^{2+} ion, and so the lattice parameter of $Fe_2Mo_{1-x}Ti_xO_4$ samples is expected to increase with increasing x, which is actually shown in the results in Fig. 1.

Figure 2 shows the room temperature resistivity vs composition plot of $Fe_2Mo_{1-x}Ti_xO_4$ samples. The results show that up to $x = 0.6$, the resistivity increases very slightly, but on further increase of x, the resistivity of the samples increases by almost two orders of magnitude. This is expected since substitution leads to a decrease in the Fe^{3+}/Fe^{2+} ratio, and as will be discussed later, this leads to a decrease in the number of charge carriers.

The results of the temperature variation of resistivity show linear plots of $\ln(\rho)$ vs $1/T$ for all samples between 300 and 600 K. The plots at lower temperatures however show slight deviation from linearity (Figs 5 and 6). Using Arrhenius equation

$$\rho = \rho_0 \exp[E_a/kT] \qquad [1]$$

(where ρ is the resistivity, T is the absolute temperature, k is the Boltzmann constant, and E_a is the thermal activation energy), the E_a values were calculated from the linear plots, which are given in Table 1. The chemical composition of various titanium-substituted Fe_2MoO_4 samples and their code names are also given in Table 1. Similar to the reported values (8, 13), the E_a values of Fe_2MoO_4 and Fe_2TiO_4 are very small, implying hopping conduction in these ferrites.

In order to confirm hopping conduction in these ferrities, $\ln(\rho/T)$ was plotted against $1/T$. Figures 3 and 4 show the $\ln(\rho/T)$ vs $1/T$ plots in the temperature range 300–600 K. As is expected in semiconductors with hopping conduction, all the plots were found to be linear. However, the plot of FTM6 shows that between 400 and 476 K the resistivity remains almost constant. On repeating the measurements, reproducible results were obtained (Fig. 3, inset). Further studies on FTM6 must be carried out to explain this anomalous result.

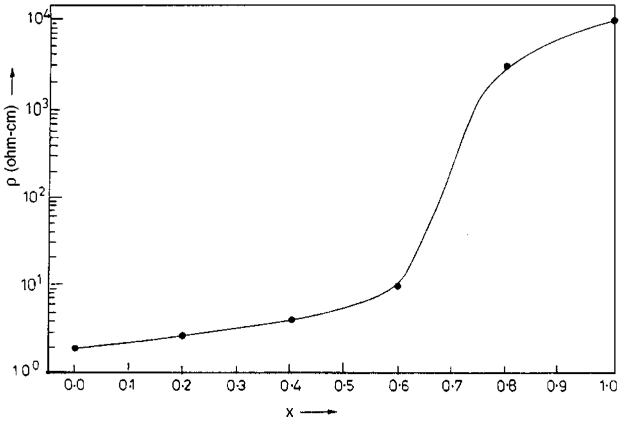

FIG. 2. Plots of room temperature resistivity ρ vs x for the $Fe_2Mo_{1-x}Ti_xO_4$ samples.

TABLE 1

Sample Composition, Code Name, Thermal Activation Energy (E_a), Optical Phonon Frequency (γ_0), and Mobility (μ) at 550 K for $Fe_2Mo_{1-x}Ti_xO_4$ Samples

Sample composition	Code name	E_a (eV) 300–573 K	$\gamma_0 \times 10^{11}$ (sec^{-1})	$\mu_{550\,K}$ (cm^2 V^{-1}sec^{-1})
Fe_2MoO_4	FTM10	0.052	0.89	2.68×10^{-4}
$Fe_2Mo_{0.8}Ti_{0.2}O_4$	FTM8	0.127	4.00	2.90×10^{-4}
$Fe_2Mo_{0.6}Ti_{0.4}O_4$	FTM6	0.103	1.91	3.00×10^{-4}
$Fe_2Mo_{0.4}Ti_{0.6}O_4$	FTM4	0.133	1.65	1.23×10^{-4}
$Fe_2Mo_{0.2}Ti_{0.8}O_4$	FTM2	0.165	0.16	6.82×10^{-6}
Fe_2TiO_4	FTM0	0.250	0.11	8.50×10^{-7}

Studies on Fe_2MoO_4 by Ramdani *et al.* (8) have shown that the ferrite is a semiconductor in which conduction is carried out through the hopping of charge carriers between Fe^{2+}–Fe^{3+} and Mo^{3+}–Mo^{4+}. During substitution of Mo by Ti in the solid solutions, $Fe_2Mo_{1-x}Ti_xO_4$, the amounts of both Mo^{3+} and Fe^{3+} are likely to be reduced and hence with increasing x, resistivity should increase. The results in Fig. 2 show this increase, which indirectly confirms the presence of Fe^{3+} and Mo^{3+} in Fe_2MoO_4. It also shows a sudden increase in resistivity between FTM4 and FTM2. Spinel oxides usually show hopping conduction, and the hopping of charge carriers can occur between (i) tetrahedral sites, (ii) octahedral sites, and (iii) tetrahedral and octahedral sites of the spinel lattice. The contribution from (i) and (iii) toward the total conduction of the spinel may be neglected, because the distance between two adjacent tetrahedral sites is larger than that between two adjacent octahedral sites and the hopping between two crystallographically nonequivalent sites is energetically unfavorable (14). However, Ramdani *et al.* (8) have suggested that in Fe_2MoO_4, the low resistivity can be explained by taking the hopping of charge carriers between the tetrahedral sites into consideration. Thus, during substitution of Mo by Ti as the Fe^{3+} content decreases, the probability of hopping of charge carriers between $Fe^{2+}_{tet.}$ and $Fe^{3+}_{tet.}$ becomes smaller and on going from FTM4 to FTM2 the contribution from tetrahedral site hopping becomes negligible, and this is manifest in the sharp rise in the room temperature resistivity between FTM4 and FTM2.

The plot of Fe_2MoO_4, (Fig. 3a) shows a break near 400 K which is its magnetic phase transition temperature $\mathbf{T_c}$. Similar results have been reported by Ramdani *et al.* (8). Breaks in the plots of $\ln(\rho)$ vs $1/T$ were also observed near the magnetic phase transition temperature of the substituted samples (Figs. 5 and 6).

Taking the best fit of the linear plot of $\ln(\rho/T)$ vs $1/T$ (Figs. 3 and 4), the optical phonon frequency (γ_0) and mobility values (μ) at different temperatures were calculated following the method of Metselaar *et al.* (15). The values are given in Table 1. The values of the optical phonon frequency (γ_0) confirm hopping conduction in these samples. The values of mobility, μ, show a decrease with increasing x. This is expected, since both Fe^{3+} and Mo^{3+} are removed by titanium substitution, which implies that the number of hopping centers is reduced and as a consequence the distance through which the charge carrier can hop is increased, resulting in a decrease in the mobility.

The results of the thermoelectric power measurements show that all the samples are p-type and the magnitude of

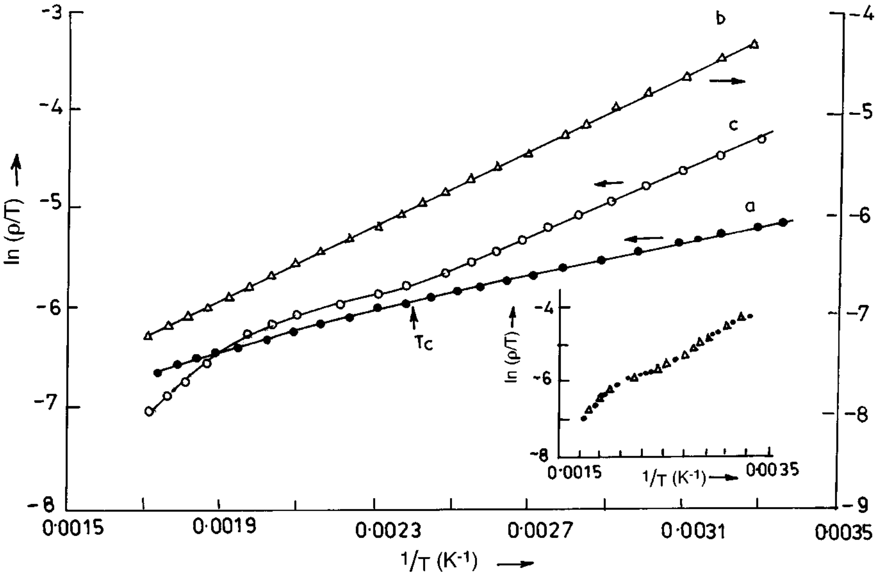

FIG. 3. Plots of $\ln(\rho/T)$ vs $1/T$ for (a) FTM10, (b) FTM8, and (c) FTM6. (Inset) Repeat plot of FTM6.

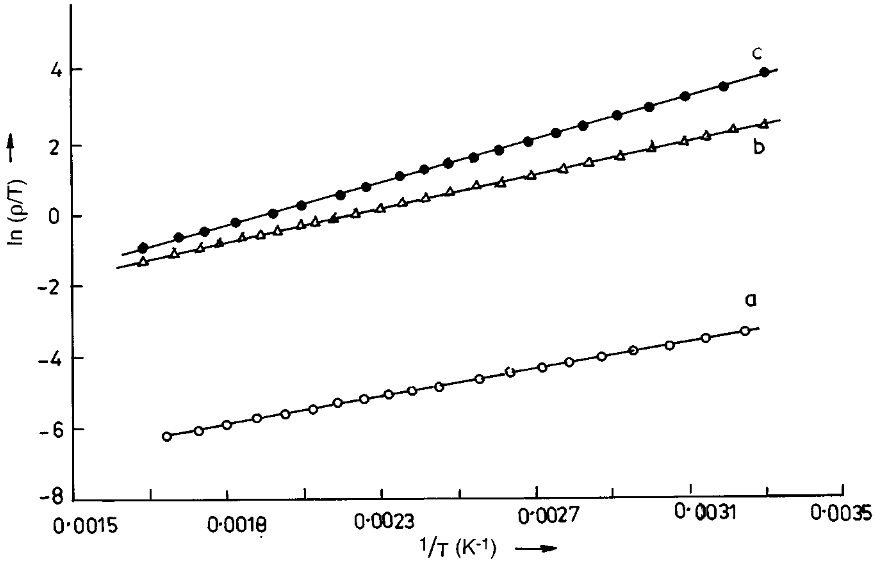

FIG. 4. Plots of $\ln(\rho/T)$ vs $1/T$ for (a) FTM4, (b) FTM2, and (c) FTM0.

Seebeck coefficient (α) decreases with increasing temperature. From the values of α, the values of carrier concentration **n** were calculated using

$$n = N_v \exp(-\alpha/k), \quad [2]$$

where N_v is the density of states involved in the conduction process and k is the Boltzmann constant. N_v values were calculated following the method of Metselaar *et al.* (15). The values of **n** are shown in Table 2 for all the $Fe_2Mo_{1-x}Ti_xO_4$ samples. From the results it is apparent that with increasing x, there is a decrease in the number of charge carriers. These results support the suggestions made earlier, that substitution of Mo by Ti leads to a decrease in the Fe^{3+}/Fe^{2+} ratio.

From the slope of the ln(**n**) vs $1/T$ plots in the temperature range 370–600 K (Fig. 7), E_n was calculated and the values are given in Table 2. In order to ascertain the conduction mechanism in these samples, E_n values were compared with E_a values. For all samples $E_a > E_n$, which is expected when conduction is by hopping of charge carriers (16). These results thus confirm that as in Fe_2MoO_4, in the $Fe_2Mo_{1-x}Ti_xO_4$ samples also conduction appears to be by the hopping of charge carriers between Fe^{3+} and Fe^{2+} ions.

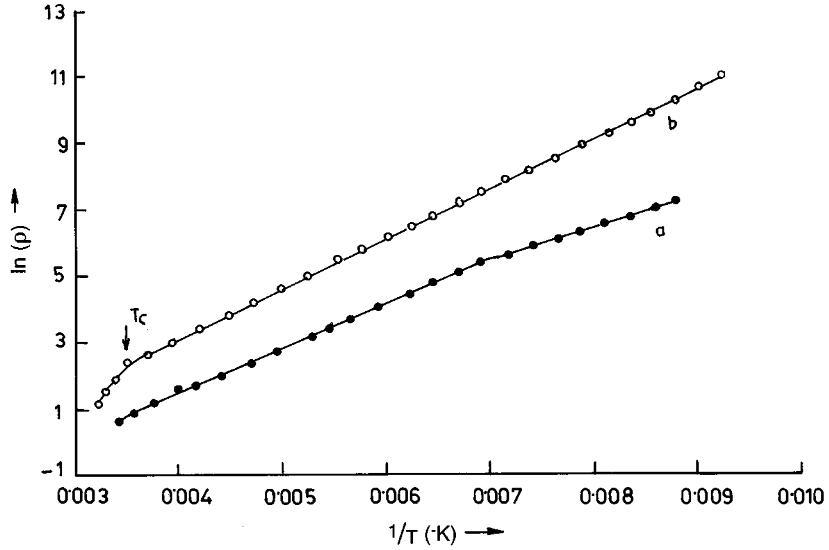

FIG. 5. Plots of $\ln(\rho)$ vs $1/T$ for (a) FTM10 and (b) FTM8.

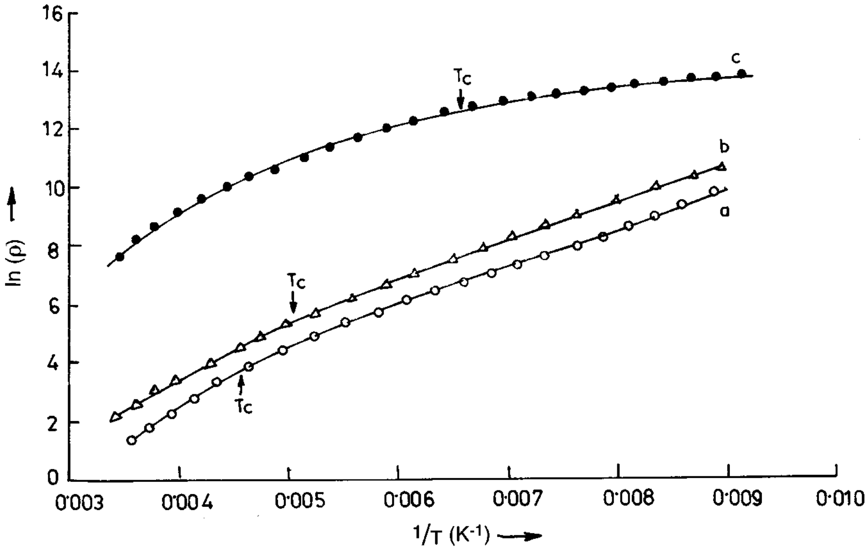

FIG. 6. Plots of ln(ρ) vs $1/T$ for (a) FTM6, (b) FTM4, and (c) FTM2.

For small polaron conduction, the Seebeck coefficient for the thermoelectric power is given by (17)

$$\alpha = \frac{k}{e}\left[\ln \beta \frac{[\mathrm{Fe}^{3+}_{\mathrm{oct}}]}{[\mathrm{Fe}^{2+}_{\mathrm{oct}}]} + A\right]. \qquad [3]$$

In all the samples under investigation a small activation energy of thermoelectric power is consistent with the small polaron hopping mechanism. Thus, using Eq. [3], the ratio of $[\mathrm{Fe}^{3+}_{\mathrm{oct}}]/[\mathrm{Fe}^{2+}_{\mathrm{oct}}]$ was calculated taking the value of $\beta = 2$ and neglecting the value of A as was suggested by Chang *et al.* (13) and Tuller *et al.* (18); the values are given in Table 2. The results in Table 2 show that the ratio decreases as molybdenum is progressively replaced by titanium, and in Fe_2TiO_4, the ratio is very small. These results again confirm that substitution of Mo by Ti in Fe_2MoO_4 reduces the amount of Fe^{3+} in the ferrite.

From these results the following cation distributions for Fe_2MoO_4 and Fe_2TiO_4 may be suggested: $\mathrm{Fe}^{3+}_{0.737}\mathrm{Fe}^{3+}_{0.263}[\mathrm{Fe}^{2+}_{0.737}\mathrm{Fe}^{3+}_{0.263}\mathrm{Mo}^{3+}_{0.526}\mathrm{Mo}^{4+}_{0.474}]\mathrm{O}_4$ and $\mathrm{Fe}^{2+}_{0.965}\mathrm{Fe}^{3+}_{0.035}[\mathrm{Fe}^{2+}_{0.965}\mathrm{Fe}^{3+}_{0.035}\mathrm{Ti}^{4+}]\mathrm{O}_{4.035}$.

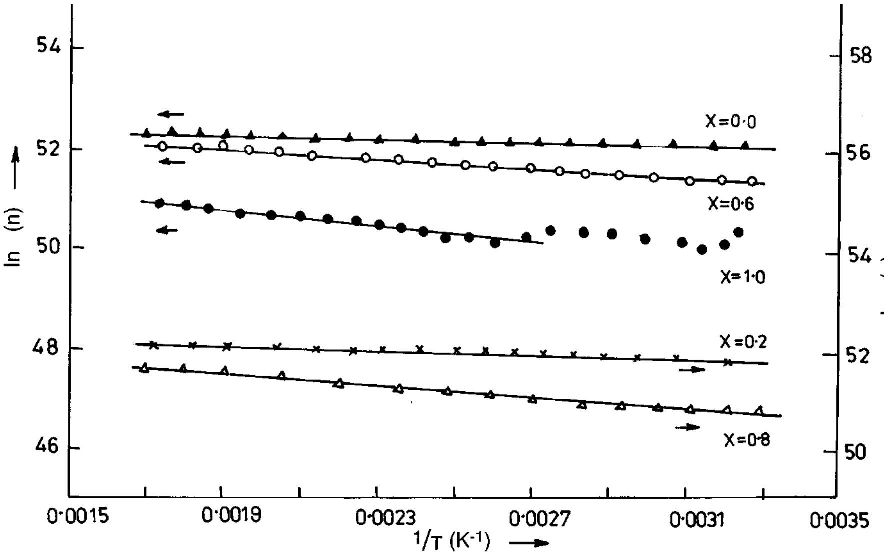

FIG. 7. Plots of ln(**n**) vs $1/T$ for $Fe_2Mo_{1-x}Ti_xO_4$ samples.

TABLE 2

Charge Carrier Concentration (*n*), Activation Energy for Charge Carrier Generation (E_n), and Octahedral Iron Valence Ratio ($[Fe^{3+}_{oct}]/[Fe^{2+}_{oct}]$) for $Fe_2Mo_{1-x}Ti_xO_4$ Samples

Code name	$\mathbf{n} \times 10^{22}$ 300 K	E_n(eV) 370–573 K	$E_a - E_n$ (eV)	$[Fe^{3+}_{oct}]/[Fe^{2+}_{oct}]$ 300 K
FTM10	3.70	0.013	0.039	0.357
FTM8	2.80	0.021	0.106	0.270
FTM6	2.09	0.047	0.056	0.202
FTM4	1.78	0.035	0.098	0.172
FTM2	1.36	0.048	0.117	0.131
FTM0	0.21	0.072	0.178	0.036

CONCLUSION

From the results it may be concluded that similar to Fe_2MoO_4, all the titanium-substituted $Fe_2Mo_{1-x}Ti_xO_4$ samples are p-type semiconductors in which conduction takes place by the hopping of charge carriers between Fe^{2+}–Fe^{3+} and between Mo^{3+}–Mo^{4+}. Near the ferrimagnetic to paramagnetic phase transition temperature, T_c all the $Fe_2Mo_{1-x}Ti_xO_4$ samples show a change in slope in the $\ln(\rho)$ vs $1/T$ plots. The substitution of molybdenum by titanium in Fe_2MoO_4 results in a decrease in the charge carrier concentration, **n**, charge carrier mobility, μ, and the ratio of $[Fe^{3+}_{oct}]/[Fe^{2+}_{oct}]$. All these results confirm that both Fe^{3+} and Fe^{2+} ions are present in Fe_2MoO_4, and in Fe_2TiO_4 a very small amount of Fe^{3+} appears to be present.

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