

THERMAL EFFECT ON FORMATION AND CONDUCTION MECHANISM OF MnFe_2O_4

S.A. MAZEN

Physics Department, Faculty of Science, Zagazig University, Zagazig (Egypt)

B.A. SABRAH

Chemistry Department, Faculty of Education, Cairo University, Fayoum (Egypt)

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ABSTRACT

Polycrystalline samples of MnFe_2O_4 were prepared at three different sintering temperatures: 1100, 1150 and 1200°C. X-ray analysis was carried out and it was found that the formation of MnFe_2O_4 was affected by the sintering temperature. The perfect structure was formed at 1150°C. The d.c. electrical conductivity was also studied. Discussion of conductivity was taken from the viewpoint of the hopping mechanism. The effect of sintering temperature on the Curie point, T_c , was explained through the oxidation process which leads to a shift in the Curie point towards higher temperatures.

INTRODUCTION

Nearly all ferrites belong to a class of semiconductors, the electrical conduction of which is much less completely understood than that of the classical semiconductors, such as Si and Ge. This is mainly due to the fact that the band model does not generally give a good description of the properties of ferrites. In the past twenty years, a number of theoretical developments have been made which promise to further our understanding of the conduction mechanism in these compounds [1–3].

Ferrites, which crystallize in the spinel structure, form a group of materials of great technological importance, especially as magnetic materials with a variety of special properties. Manganese–zinc ferrite and nickel–zinc ferrite were developed for a wide range of applications where high permeability and low loss were the main requirements [4]. The control of resistivity in ferrites is a serious problem. There are two general approaches to this problem: (1) controlling firing temperature and atmosphere; (2) addition of minor constituents to increase or decrease the conductivity. The aim of this paper is to study thermal effects on the structure and conduction mechanism of MnFe_2O_4 .

EXPERIMENTAL

Polycrystalline samples of MnFe_2O_4 were prepared at three different sintering temperatures: 1100, 1150 and 1200°C using a ceramic technique. Details of the preparation are given elsewhere [5].

The conductivity measurements were carried out using the two-terminal d.c. method over a wide range of temperature (from room temperature up to 673 K). Indium-amalgam was used to make a low contact resistance to the ferrite samples. The applied d.c. voltage (2 V) was measured by a digital multimeter (Keithly 131). The current was measured in two directions by a multimeter (LEVEL TM9BP) with a range of 10^{-3} to 10^{-12} A with an error of $\leq 1\%$. The temperature of the sample was measured using a calibrated iron-constantan thermocouple which was connected to an indicator (SIH $3\frac{1}{2}$ digit) with an accuracy of about $\pm 0.1^\circ\text{C}$.

The samples were ground to the finest particle size of powder form. X-ray diffraction patterns were made of the powder samples. A Philips recording diffractometer was used and CuK_α radiation source was applied with an iron filter to obtain the spectrum. The diffractometer was adjusted to rotate at a rate of 1° min^{-1} .

RESULTS AND DISCUSSION

X-ray analysis

The X-ray diffraction patterns for the fully formed MnFe_2O_4 at the three different sintering temperatures are shown in Fig. 1. The X-ray patterns show the existence of the spinel structure of MnFe_2O_4 with the reflection planes (311), (222), (400), (422) and (511). It was found that the plane (111) disappeared in all samples, but the planes (220) and (440) appeared only in the sample sintered at 1150°C. The d -spacings for the recorded peaks are calculated according to Bragg's law. The lattice parameter (a) can be calculated directly using the following relation:

$$a = d_{(hkl)}(h^2 + k^2 + l^2)^{1/2} \quad (1)$$

The graphs of measured lattice parameters against the function $F(\theta) = \frac{1}{2}[(\cos^2 \theta / \sin \theta) + (\cos^2 \theta / \theta)]$ were plotted as shown in Fig. 2. A straight line should result. The value of a_0 (the true value of a) can be found by extrapolating this line to $F(\theta) = 0$ as $\theta \rightarrow 90$. The lattice parameters, a_0 , as a function of sintering temperature are tabulated in Table 1. We see that the best value of a_0 is 8.55 Å, corresponding to a sintering temperature of 1150°C. This value deviates by 0.6% from the value on the ASTM card (8.499 Å).

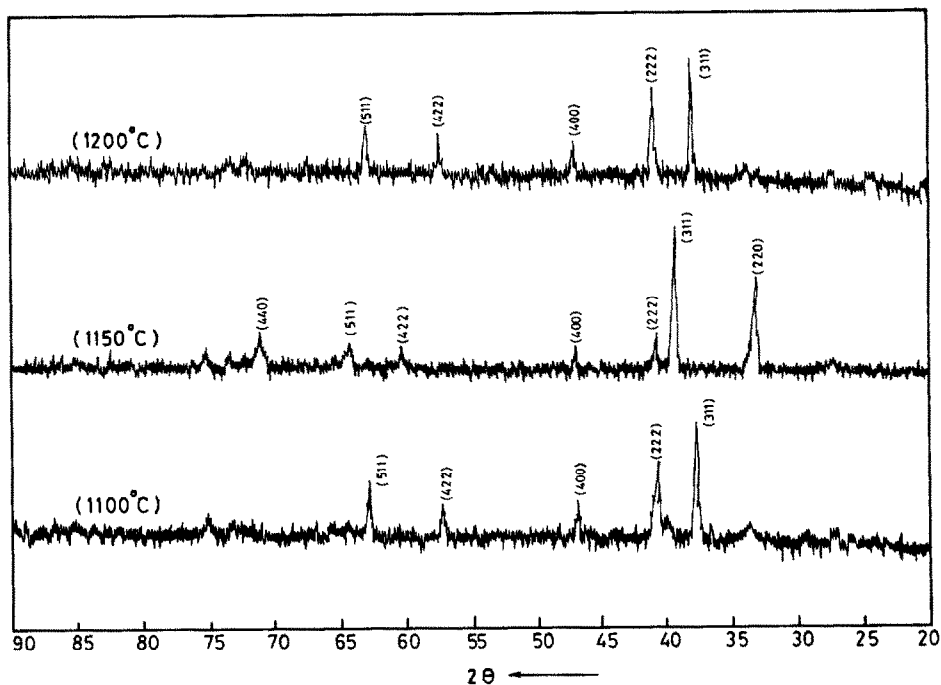


Fig. 1. X-ray diffraction patterns for MnFe_2O_4 sintered at 1100, 1150 and 1200 °C.

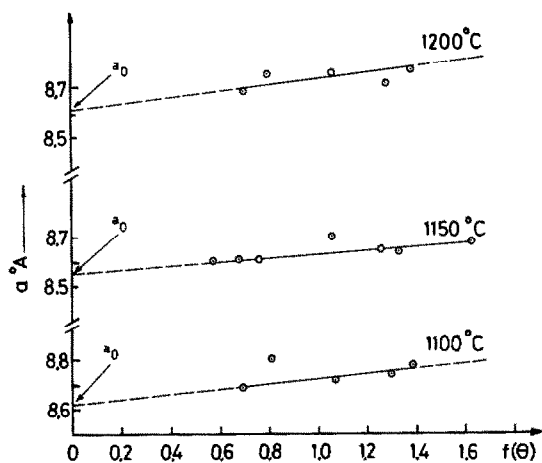


Fig. 2. The lattice parameter a_0 (Å) of MnFe_2O_4 vs. the function $F(\theta) = 1/2[(\cos^2\theta/\sin\theta) + (\cos^2\theta)/\theta]$.

TABLE 1

The lattice parameter a_0 (Å) values of MnFe_2O_4 as a function of sintering temperature

| Sintering temp. (°C) | 1100 | 1150 | 1200 |
|----------------------|------|------|------|
| $a_0 \pm 0.01$ (Å) | 8.62 | 8.55 | 8.61 |

Our result is in approximate agreement with that reported by Vanugopal Reddy and Seshagiri Rao [6], Harrison et al. [7] and Hastings and Corliss [8] (8.5078, 8.515 and 8.517 Å, respectively).

According to the X-ray results, it could be concluded that all MnFe_2O_4 compounds were formed in the spinel cubic structure. Also, we can conclude that improved homogenisation and a perfect structure are formed at 1150°C in our preparation.

D.c. electrical conductivity

We made a thermal study on the electrical conductivity of MnFe_2O_4 . The conductivity measurements were performed from room temperature (RT \approx 300 K) to \sim 673 K. Temperature variation of conductivity was studied at temperatures over the Curie point (T_c), where T_c of MnFe_2O_4 is about 573 K [9].

Since ferrite materials are semiconductors, the temperature dependence of the conductivity of a band-semiconductor is given by the expression [9]:

$$\sigma = \sigma_0 \exp - \frac{E_\sigma}{KT} \quad (2)$$

where σ_0 is a constant independent of temperature and E_σ is the energy dependent on the nature of the charge carriers. Figure 3 shows the temperature dependence of d.c. conductivity of MnFe_2O_4 according to eqn. (2). As expected for semiconductors, the conductivity of manganese ferrite was observed to increase with rising temperature.

Figure 4 shows the relation between sintering temperature and logarithm of conductivity at 300 K. It can be seen that the conductivity increases with an increase in sintering temperature.

The manganese ferrite is a nearly normal spinel, about 80% manganese ions occupy the tetrahedral sites (A-sites); these ions are Mn^{2+} ions. However, on the octahedral sites (B-sites) Mn^{3+} ions occur, which are connected by the presence of Fe^{2+} ions on these sites [10]. So, the cation distribution can be represented by:



Therefore, the electrical conductivity in the ferrite, which behaves according to the hopping process of electrons between Fe ions on the octahedral sites, is given by the formula [11]:

$$\sigma = \frac{\text{const}}{T} \exp - \frac{E}{KT} \quad (4)$$

where E (eV) is the activation energy of the conductivity process. According to eqn. (4), the relation between $\log \sigma T$ versus T^{-1} is shown in Fig. 5. From eqns. (2) and (4), E_σ/K and E/K represent the slope of $\log \sigma$ vs. T^{-1} and

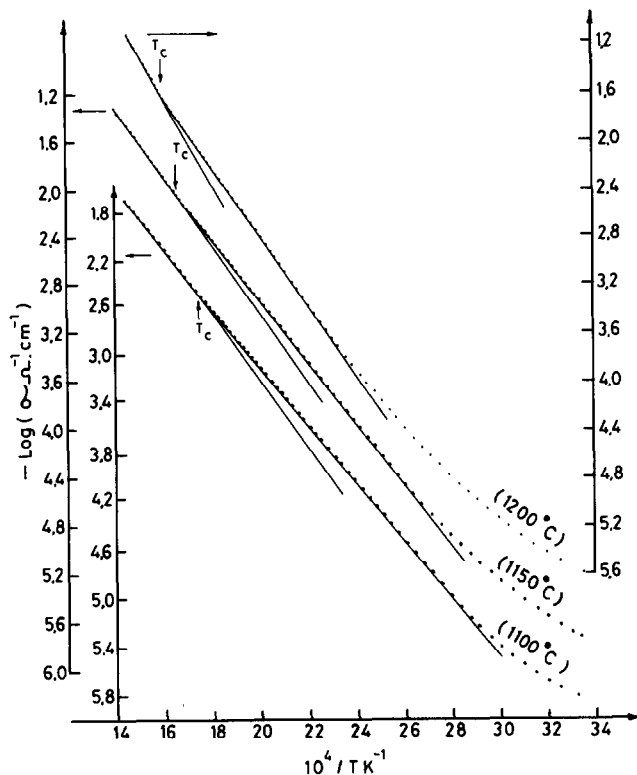


Fig. 3. Plot of $\log \sigma$ vs. $10^4/T$ for MnFe_2O_4 at three different sintering temperatures.

$\log \sigma T$ vs. T^{-1} , respectively. The values of the activation energies E_a and E estimated from Figs. 3 and 4 are tabulated in Table 2. It can be seen that the mean value of the difference between the activation energies of the corre-

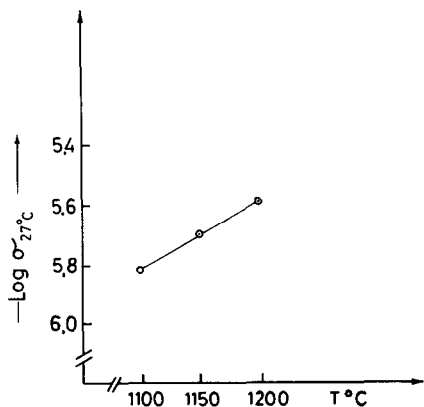


Fig. 4. Relation between logarithm of conductivity at room temperature and sintering temperature.

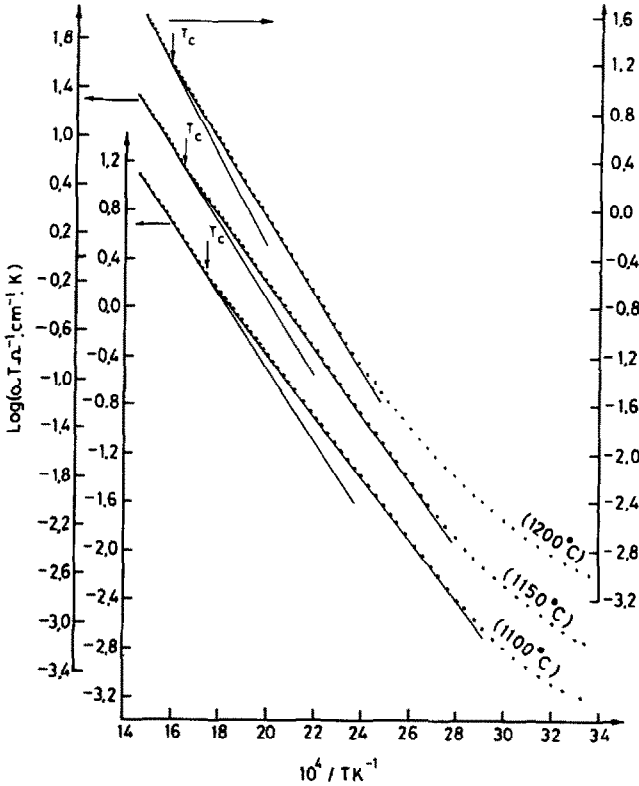


Fig. 5. Plot of $\log \sigma T$ vs. $10^4/T$ for MnFe_2O_4 at three different sintering temperatures.

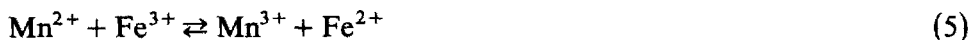
sponding region (calculated from Figs. 3 and 5 and using eqns. 2 and 4) is ~ 0.05 eV. We may attribute this value to the activation energy of hopping (E_μ) which is a reasonable value and in good agreement with the result of Miroshkin et al. [12]. For manganese ferrous ferrite, the electrical conductivity is caused by the hopping process of electrons between octahedral Fe ions [11]. Thus it can be assumed that in manganese ferrites, the carriers are

TABLE 2

Values of activation energies E_σ and E (for ferri- and paramagnetic regions), Curie point, T_c , and exchange energy, E_{ex} , for MnFe_2O_4 as a function of sintering temperature

| Sintering temp. ($^\circ\text{C}$) | E_σ (eV) | | E (eV) | | Curie point $T_c \pm 5$ (K) | E_{ex} (eV) |
|--------------------------------------|-----------------|-------|----------|-------|-----------------------------|----------------------|
| | ferri. | para. | ferri. | para. | | |
| 1100 | 0.48 | 0.53 | 0.53 | 0.58 | 571 | 0.049 |
| 1150 | 0.50 | 0.61 | 0.55 | 0.68 | 602 | 0.052 |
| 1200 | 0.58 | 0.72 | 0.62 | 0.75 | 625 | 0.054 |

created by the following reaction of electron exchange on octahedral sites (B-sites) of the spinel lattice:



The activation energy E_σ is the energy necessary for generation of the charge carriers by $\text{Mn}^{2+} + \text{Fe}^{3+}$ pairs. This leads us to think that the activation energy of the conductivity process becomes

$$E = E_\sigma + E_\mu \quad (6)$$

where E_μ represents the additional part due to the thermal activation energy of mobility (hopping activation energy between $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$ or $\text{Mn}^{2+} \rightleftharpoons \text{Mn}^{3+}$ on the B-sites).

Magnetic ordering effect

All samples exhibit an exponential temperature dependence of conductivity, eqn. (4), but it is known that the slope of the $\log \sigma T$ vs. T^{-1} curve changes at the Curie point. The conductivity activation energy increases on passing from the ferrimagnetic (E_f) to the paramagnetic (E_p) phase, $E_p > E_f$ (see Table 2). This is the anomaly of the temperature dependence of conductivity at the Curie point (T_c). It is proof of the influence of magnetic ordering upon the conductivity process in ferrites. According to most theories based on nearest-neighbour interaction, the critical temperature (Curie point, T_c) is proportional to the exchange interaction energy at this point (KT_c) [13]:

$$E_{\text{ex}} = KT_c \quad (7)$$

where K is Boltzmann's constant. By comparing values of the exchange interaction energy (see Table 2) with the activation energy of hopping due to ferrimagnetic ordering (the hopping is due to an exchange of energy with phonons [1]), both are in good agreement where $E_{\text{ex}} \approx E_\mu \approx 0.05$ eV.

The Curie temperature of MnFe_2O_4 depends on the sintering temperature, as seen in Table 2. It was found that the Curie point increases with an increase in sintering temperature. This behaviour is explained in the following way. According to cation distribution of MnFe_2O_4 , as seen in formula (3), the A-sites (tet.) will be occupied by all of the Mn^{2+} with some Fe^{3+} , but Mn^{3+} and Fe^{2+} and most of the Fe^{3+} occupy B-sites (oct.). The oxidation process (which increases with an increase in sintering temperature) as a result of the oxidation $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ leads to a shift in the Curie point towards higher temperatures. Also, this process could change the ratio $(\text{Fe}^{3+})^{\text{B}}/(\text{Fe}^{2+})^{\text{B}}$ which is accompanied by an increase in iron concentration in the B-sites. When the concentration of a magnetic ion, such as Fe^{3+} , with higher spin (magnetic moment) than Fe^{2+} is increased in the B-sites by replacement of Fe^{2+} (lower spin), magnetisation will be increased leading to an increased Curie point (T_c).

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