JOURNAL OF MATERIALS SCIENCE 23 (1988) 2917–2920

# Effect of $Mg^{2+}$–$Fe^{3+}$ replacement on physical and electrical properties of the system $Mg_xZn_{0.3}Fe_{(2.7-x)}O_{4\pm\delta}$

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X-ray analysis and d.c. electrical resistivity have been studied for the system $Mg_xZn_{0.3}Fe_{(2.7-x)}O_{4\pm\delta}$. The apparent density, X-ray density and porosity were also studied. It was found that the lattice parameter is independent of the substitution of iron ions with magnesium ions. Density, X-ray density and porosity do depend on replacement of the iron ions by magnesium ions. Two regions of resistivity were found; one region indicates the p-type and another one the n-type. This behaviour depends on the excess or deficiency and type of valency of the iron ions in the composition.

## 1. Introduction

It is known that the physical properties (e.g. structural and electrical) of spinel ferrites are modified by the introduction of known impurities. Discussion of the transfer phenomenon in ferrites is usually based on the model of thermally activated hopping between local electron states [1–3]. It is assumed that the electron exchange takes place between metal ions of different valency arranged on the octahedral (B) sites of the spinel lattice. In general one would expect ferrites with a simple composition to show a low conductivity, which can be increased by the formation of a solid solution with excess iron oxide in the form of $Fe_3O_4$ or with excess metal (Me) oxide in the form of $Me_3O_4$.

The present work is a systematic attempt to investigate the electrical resistivity of $Mg_xZn_{0.3}Fe_{(2.7-x)}O_{4\pm\delta}$ with an excess or a deficiency of oxygen. Ferrites with this composition can be used in the production of soft ferrites for many applications.

## 2. Experimental procedure

Experiments were performed on polycrystalline samples of mixed ferrite $Mg_xZn_{0.3}Fe_{(2.7-x)}O_{4\pm\delta}$, where $x$ changes from 0.4 to 1.1 while $0 \leqslant \delta \leqslant 0.2$. These samples were prepared by the ceramic technique from pure oxide powders of $\alpha$-$Fe_2O_3$, MgO and ZnO. The oxides were mixed in stoichiometric proportion and fired at 1200° C for 5 h and slowly cooled to room temperature.

The d.c. electrical resistivity was measured by using the two-terminal method in a wide range of temperatures (from room temperature up to 673 K). The measurements were carried out under equilibrium conditions on samples of pellet form with diameter 12 mm and thickness $\approx$ 3 mm. Silver paste was used in the contacts of electrodes. More details of the measurements and preparation are given elsewhere [4, 5].

The densities of the samples were determined using the method of hydrostatic weighting in toluene. A single crystal of germanium was used as a reference material. These measurements were carried out using an electrical balance with a sensitivity of $10^{-4}$ g.

X-ray diffraction patterns were recorded for the finest powder samples. A Phillips recording diffractometer was used and a Co$K\alpha$ radiation source was applied with an iron filter to obtain the spectrum.

## 3. Results and discussion

### 3.1. X-ray analysis and density

X-ray diffraction patterns were obtained for $Mg_xZn_{0.3}Fe_{(2.7-x)}O_{4\pm\delta}$ (where $0.4 \leqslant x \leqslant 1.1$ and $0 \leqslant \delta \leqslant 0.2$). The X-ray patterns show the existence of the spinel structure of each composition with the main reflection planes (220), (311), (400), (422), (333), (511) and (440). According to Ohnishi and Teranishi [6] and Mazen *et al.* [7] the intensity ratio $I(hkl)/I(400)$ is considered to be sensitive to the cation distribution which depends on the parameter $x$. It was found that the intensity ratios $I(220)/I(400)$, $I(422)/I(400)$ and $I(333)/I(400)$ were most sensitive to the parameter $x$ or $y$, where $y = 2.7 - x$ for the iron. These ratios are plotted against the composition in Fig. 1. We notice generally that the relation is a linear relationship. This relationship depends on the replacement of $Mg^{2+}$ ions by $Fe^{3+}$ ions.

The precise values of the lattice parameters were calculated using the extrapolation function $F(\theta)$ [4, 8]. These results are given in Table I and represented in Fig. 2a. It is clear that the lattice parameters are independent of the variation of $Mg^{2+}$ or $Fe^{3+}$ ions. This behavior may be attributed to the replacement

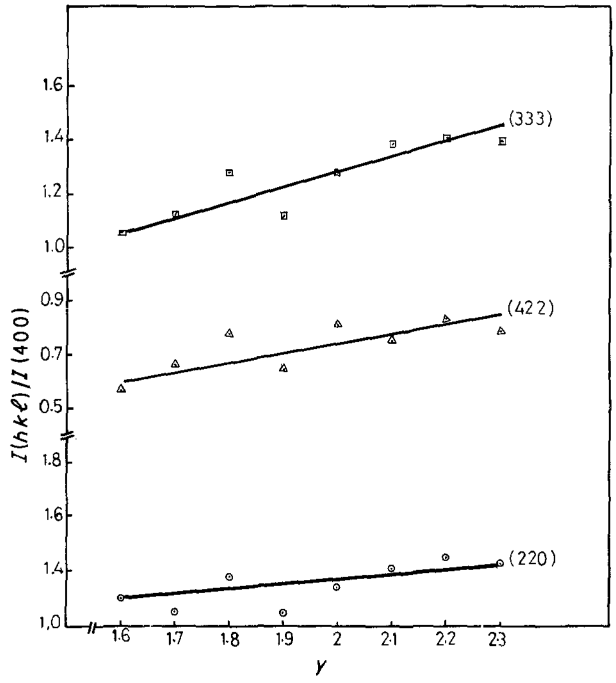

*Figure 1* The relation between the intensity ratios $I(hkl)/I(400)$ and iron content $y = 2.7 - x$.

between two nearly similar ionic radii which occurs between the iron and magnesium ($Mg^{2+} = 0.075\,nm$ and $Fe^{3+} = 0.073\,nm$) [9].

The apparent density $d$ was measured and is represented in Fig. 2b. Also, the X-ray density for each composition was calculated according to the relation [8]

$$d_X = \frac{ZM}{NV} \tag{1}$$

where $Z$ is the number of molecules per unit cell ($Z = 8$), $M$ is the molecular weight, $N$ is Avogadro's number and $V$ is the volume of the cell ($V = a^3$). Figs 2b and c show the variation of density $d$ and X-ray density $d_X$ with iron concentration for each composition. It is clearly shown that both densities increase with the iron content. This has been ascribed to the large density ($7.9\,g\,cm^{-3}$) associated with the iron ions which replace the less dense magnesium ions ($1.74\,g\,cm^{-3}$).

The percentage porosity was also calculated using the relation [10]

$$P = 100\left(1 - \frac{d}{d_X}\right) \tag{2}$$

The change of $P$ with the iron content is shown in Fig. 2d. Since the rate of increase of $d_X$ with the iron content is bit larger than that of $d$, then one can expect the porosity to increase with an increase of iron content.

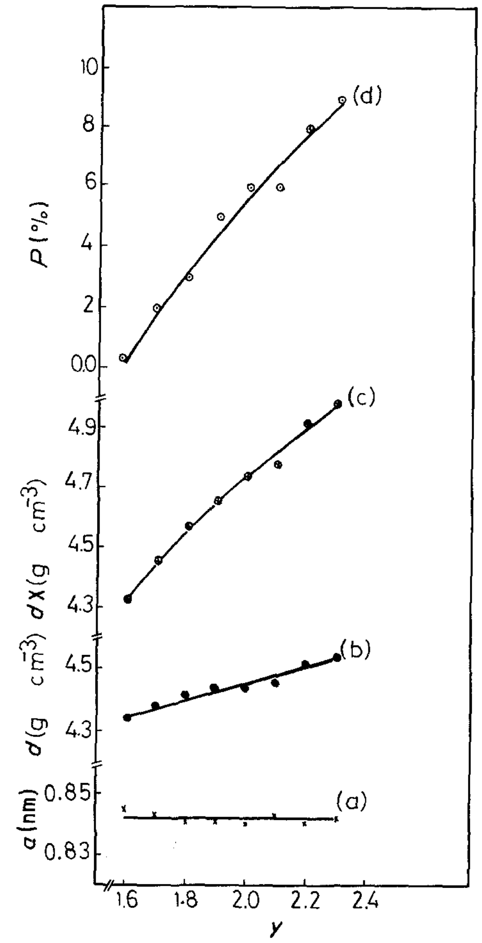

*Figure 2* The relation between some physical properties and the iron content $y = 2.7 - x$ of $Mg_xZn_{0.3}Fe_{(2.7-x)}O_{4\pm\delta}$: (a) lattice parameter, (b) density, (c) X-ray density, (d) porosity.

### 3.2. D.C. electrical resistivity

Fig. 3 shows the observed variation of $\log \varrho$ with $10^4/T$ from room temperature up to 400° C. As expected for semiconductors, the resistivities of the ferrites were observed to fall with rising temperature. The observed curves of all samples are best represented by straight lines. The resistivity characteristics are given by

$$\varrho = \varrho_\infty \exp(E_\varrho/kT) \tag{3}$$

where $E_\varrho$ represents the activation energy of the conduction mechanism. Fig. 4 shows the activation energy and logarithm of resistivity at room temperature, which vary systematically from iron deficiency ($y < 2$) to iron excess ($y > 2$). The activation energy and electrical resistivity decreases as the substitution ratio of magnesium decreases or the iron content increases. We shall discuss these results in connection with data reported by van Uitert [11] and Jonker [12] for $Ni_{0.3}Zn_{0.7}Fe_xO_{4\pm\delta}$ and $Co_{1+x}Fe_{2-x}O_4$, respectively, and also in connection with the results for $Co_{0.5}Zn_{0.5}Fe_xO_{4\pm\varepsilon}$ [5]. In $Mg_xZn_{0.3}Fe_{(2.7-x)}O_{4\pm\delta}$, for

TABLE I Variation of the lattice parameter $a$ for $Mg_xZn_{0.3}Fe_{(2.7-x)}O_{4\pm\delta}$

| $y = 2.7 - x$ | 1.6 | 1.7 | 1.8 | 1.9 | 2.0 | 2.1 | 2.2 | 2.3 |
|---|---|---|---|---|---|---|---|---|
| $a$ (nm) ±0.001 | 0.845 | 0.843 | 0.841 | 0.841 | 0.841 | 0.844 | 0.841 | 0.842 |

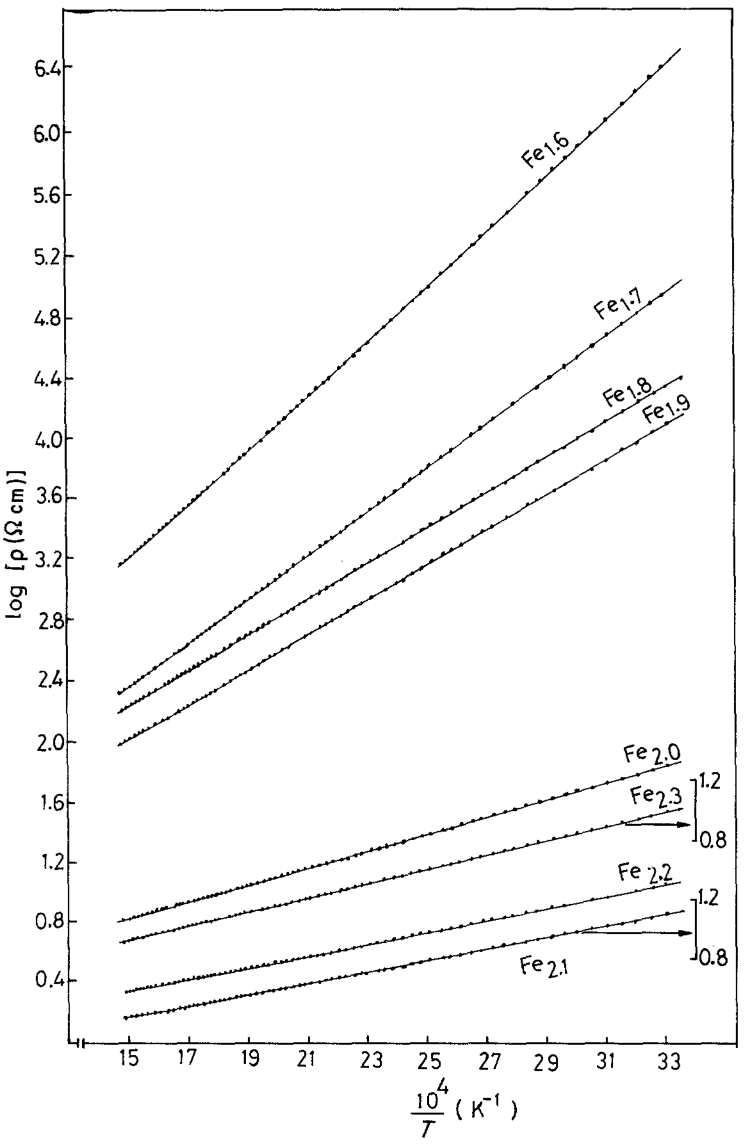

*Figure 3* The relation between $\log \varrho$ and $10^4/T$ for composition $\mathrm{Mg}_x\mathrm{Zn}_{0.3}\mathrm{Fe}_{(2.7-x)}\mathrm{O}_{4\pm\delta}$.

values of $x < 0.7$ (i.e. $y > 2$), such mixed ferrites can be considered as consisting of a molecule $\mathrm{Mg}_x^{2+}\mathrm{Zn}_{0.3}^{2+}\mathrm{Fe}_2^{3+}\mathrm{O}_4^{2-}$ and $(0.7 - x)$ molecules of $\mathrm{Fe}^{2+}\mathrm{Fe}_2^{3+}\mathrm{O}_4^{2-}$, thus $(0.7 - x)$ represents the $\mathrm{Fe}^{2+}$ content per molecule. The dominant conductivity mechanism in the iron-deficient ferrites may thus be p-type, and n-type in the iron-excess ferrites. Therefore the general expression for the conductivity can be represented as

$$\begin{aligned} \sigma &= \sigma_n + \sigma_p \\ &= ne\mu_n + Pe\mu_p \qquad (4) \end{aligned}$$

where $n$ and $p$ represent the numbers of electrons and holes which are taken to be equal to the number of $\mathrm{Fe}^{2+}$ and $\mathrm{Fe}^{3+}$ ions, respectively. The difference between $n$ and $p$ is given by the chemical composition of each sample. From Fig. 4, the activation energy $E_\varrho$ and $\log \varrho_{27^\circ\mathrm{C}}$ decreases with increasing iron ion concentration. This indicates that the mobility $\mu$ increases with an increase of iron ion concentration, which was observed to occur slowly when the iron concentration exceeded 2. The region of excess iron ($y > 2$, i.e. $x < 0.7$) behaves as an n-type semiconductor while in the region of $y < 2$ the ferrite behaves as p-type. This can be clarified as follows.

Firstly, in the iron-deficient ferrites, the dominant conduction mechanism is due to hole-hopping and in this region the probability of $\mathrm{Fe}^{2+}$ ions existing is very small. Also, oxygen deficiency may cause some of the cations to occupy interstitial sites. These interstitial cations are assumed to act as holes on oxygen ions [13]. Also, it is obvious that in the first region ($y < 2$) of composition containing a high concentration of $\mathrm{Mg}^{2+}$ ions the conductivity is low. This is due to the obstruction of $\mathrm{Mg}^{2+}$ ions to the hopping process between iron ions.

Secondly, in the iron-excess ferrites, the $\mathrm{Fe}^{2+}$ concentration is appreciable and in such a case the predominant conduction process is due to the hopping of an electron from $\mathrm{Fe}^{2+}$ to $\mathrm{Fe}^{3+}$ [14], leading to a type of conductivity with relative low activation energy. In the compositions with $y > 2$ the iron ions shift to octahedral sites (B sites), increasing thereby the concentration of $\mathrm{Fe}^{3+}$ ions for charge compensation. The conduction due to electron hopping is modified as a consequence of the decrease in number of $\mathrm{Fe}^{3+}$ ions and an equal increase in that of $\mathrm{Fe}^{2+}$ ions in the B sublattice. This will increase the electronegativity of the samples, and in this case the compounds will probably behave as n-type semiconductors.

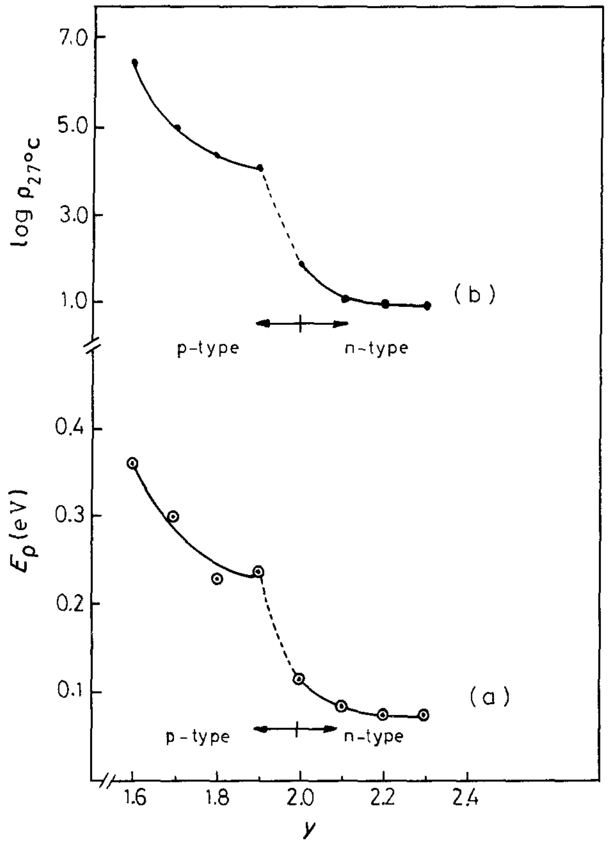

*Figure 4* The variation of (a) activation energy $E_\varrho$ and (b) $\log \varrho_{27°C}$ with iron content $y = 2.7 - x$ of composition $Mg_xZn_{j0.3}Fe_{(2.7-x)}O_{4\pm\delta}$.

From these data and from an analysis of the semiconductor properties of ferrites [15, 16], the charge carriers can be considered as localized at the ions or vacant sites and the results have generally been interpreted in terms of a conduction process that involves charge exchange between ions of different valency at equivalent sites.

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*Received 3 September*
*and accepted 1 December 1987*