JOURNAL OF MATERIALS SCIENCE 24 (1989) 2478–2482

Electrical conduction in γ-irradiated and unirradiated Fe_3O_4, $CdFe_2O_4$ and $Co_xZn_{1-x}Fe_2O_4$ $(0 \leqslant x \leqslant 1)$ ferrites

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The electrical conductivity of γ-irradiated and unirradiated finely divided ferrites of composition Fe_3O_4, $CdFe_2O_4$ and $Co_xFn_{1-x}Fe_2O_4 (0 \leqslant x \leqslant 1)$ was studied in a nitrogen atmosphere as a function of temperature. Fe_3O_4, $ZnFe_2O_4$ and $CdFe_2O_4$ showed n-type conduction, whereas $CoFe_2O_4$ showed p-type conduction. For $Co_xZn_{1-x}Fe_2O_4$ it was found that the type of conduction varies with the composition of ferrites. The electrical conduction in Fe_3O_4, and $Co_xZn_{1-x}Fe_2O_4 (0 < x \leqslant 1)$ was explained by a hopping mechanism, whereas the conduction in $ZnFe_2O_4$ and in $CdFe_2O_4$ is interpreted on the basis of the transfer of charge carriers through cation vacancies present on octahedral sites. The effect of γ-irradiation on the conductivity, activation energy, charge carriers and the conduction mechanism is discussed.

1. Introduction

The present investigations are part of a more extensive programme dealing with the effect of both composition and γ-irradiation on the electrical conduction of inorganic oxides having spinel crystal structure. These oxides are important in many branches of technology [1–3], e.g. ferrites, ferroelectric, solid state electrolytes, catalyst and nuclear fuels.

For a binary oxidic spinel containing divalent, X, and trivalent, Y, cations, two extreme distributions of cations are possible: the "normal" $(X)[Y_2]O_4$ and the "inverse" $(Y)[XY]O_4$ distribution [4], where the ions present on the octahedral sites are in square brackets. Between these limiting cases intermediate distributions are possible. The cation distribution in spinels has been found to be an equilibrium function of temperature and pressure [5] as well as other factors concerning the ions, such as the ionic charge, ionic radius, anion polarization, etc. [6].

In the present work we investigated the electrical conductivities of γ-irradiated and unirradiated Fe_3O_4, $Co_xZn_{1-x}Fe_2O_4 (0 \leqslant x \leqslant 1)$ and $CdFe_2O_4$ ferrites with the aim to investigate the effect of composition on the type of charge carrier and its transport mechanism. Moreover, the effect of γ-irradiation on the conduction in these ferrites was also one of our targets.

2. Experimental details

"Analar grade" CdO, CoO, ZnO and Fe_2O_3 were used as starting materials to prepare $CdFe_2O_4$ and $Co_xZn_{1-x}Fe_2O_4 (0 \leqslant x \leqslant 1)$ ferrites under investigation. The oxides were mixed intimately in stoichiometric proportion and preheated under nitrogen at 1100 K for 8 h and then at 1500 K for 10 h. Fe_3O_4 was prepared by heating tablets of Fe_2O_3 at 1700 K in air for 30 h. In all cases, the product was quenched in water.

The chemical analysis was done using the atomic absorption technique for determining the amounts of zinc, cobalt, cadmium and iron in the prepared samples. X-ray analysis confirmed the spinel phase formation in both γ-irradiated and unirradiated samples.

The ferrites investigated were irradiated with γ-rays using a ^{60}Co-cell with a dose rate of 3.6 krad h^{-1} for 344 h. Infrared spectra for γ-irradiated and unirradiated ferrites were recorded using a Pye Unicam Model SP3-100 spectrophotometer, KBr discs and Nujol oil nulls. The d.c. electrical conductivity, σ, was measured on pellets (diameter 7 mm and thickness 2 mm) using a two-probe method with silver electrodes. The conductivity measurements were carried out under a nitrogen atmosphere in the temperature range 300 to 550 K. The Seebeck coefficient, θ, measurements

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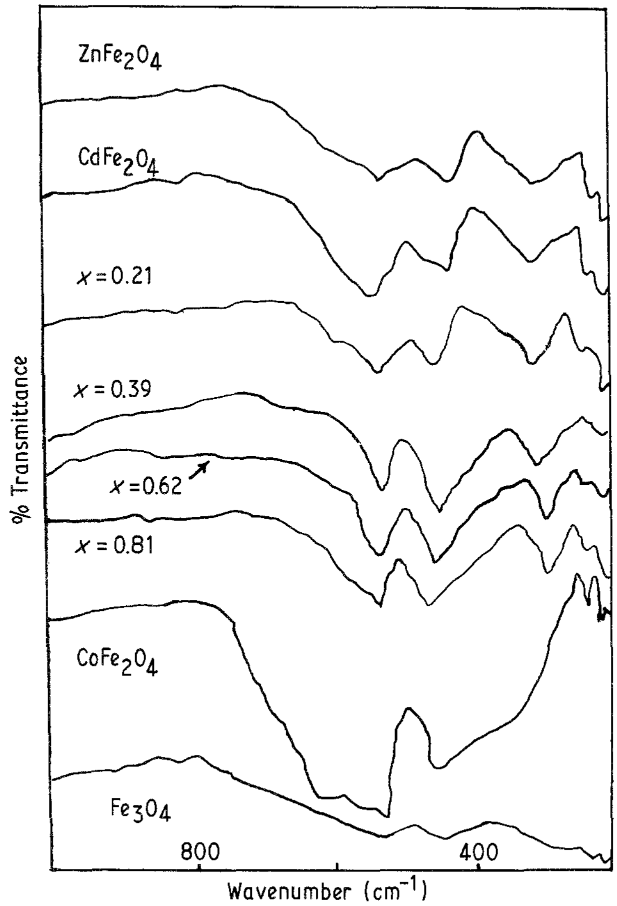

Figure 1 IR spectra of unirradiated Fe_3O_4, $CdFe_2O_4$ and $Co_xZn_{1-x}Fe_2O_4 (0 \leqslant x \leqslant 1)$.

were made at temperature intervals of $\Delta T \simeq 50$ K (against platinum).

3. Results

Fig. 1 shows the infrared (IR) spectra of the unirradiated ferrites; Fe_3O_4, $CdFe_2O_4$ and $Co_xZn_{1-x}Fe_2O_4$ $(0 \leqslant x \leqslant 1)$. From which it can be seen that for unirradiated Fe_3O_4, there are two frequency bands, ν_1 at $\simeq 550\,cm^{-1}$ and ν_2 at $\simeq 450\,cm^{-1}$, and a poorly defined band at $\sim 290\,cm^{-1}$. However, for unirradiated $CdFe_2O_4$, $Co_xZn_{1-x}Fe_2O_4 (0 \leqslant x \leqslant 1)$ the IR spectra presented in Fig. 1 show shifts in both the ν_1 and ν_2 bands in addition to the appearance of new band, ν_3, at 350 to 330 cm^{-1}. The shift in the ν_1 and ν_2 bands was found to be dependent on the composition of the ferrites. The IR bands of all the ferrites under investigation are given in Table I. The ν_1 and ν_2 bands are assigned to the intrinsic vibration of tetrahedral and octahedral groups, respectively [7, 8], whereas the ν_3 band can be assigned to the Zn^{2+} or Cd^{2+} tetrahedral vibration.

Gamma irradiation of the ferrite samples causes shifts in the three frequency bands ν_1, ν_2 and ν_3 to higher frequencies. However, for $CdFe_2O_4$ the shift in the ν_3 band has not been observed. Moreover, the IR spectra of irradiated Fe_3O_4 showed an increase in the development of the poor band appearing at $\sim 290\,cm^{-1}$.

The variation of electrical conductivity (σ) with temperature over the range 300 to 550 K for all unirradiated ferrites is shown in Fig. 2. A log σ against $1/T$ plot yields straight lines without any break for $CdFe_2O_4$, $CoFe_2O_4$ and $ZnFe_2O_4$ samples while the plot for $Co_xZn_{1-x}Fe_2O_4 (0.21 \leqslant x \leqslant 0.81)$ show straight lines with breaks at a certain temperature (T_c). These breaks may be due to the change in the conductivity mechanism or to the Curie temperature [9–11]. From Fig. 2, it can be seen that as the cobalt concentration increases, T_c moves towards higher temperatures. The activation energies of the conduction process (E_a) are calculated using the Arrhenius equation [12], from the plots given in Fig. 2, and listed with conductivity values (σ_{400}) at 400 K and Seebeck coefficient, θ, in Table II.

TABLE I IR absorption bands of the ferrites investigated

Composition of ferrite	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	Other bands (cm^{-1})
Fe_3O_4	550	450	290	290
$ZnFe_2O_4$	560	430	345	285
$CoFe_2O_4$	550	470		
$Co_{0.21}Zn_{0.79}Fe_2O_4$	555	455	345	
$Co_{0.39}Zn_{0.61}Fe_2O_4$	555	455	340	
$Co_{0.62}Zn_{0.38}Fe_2O_4$	560	460	335	
$Co_{0.81}Zn_{0.19}Fe_2O_4$	560	465	330	
$CdFe_2O_4$	570	430	350	280
Irradiated ferrites				
Fe_3O_4	555	455		290
$ZnFe_2O_4$	570	440	350	285
$CoFe_2O_4$	555	475		
$Co_{0.21}Zn_{0.79}Fe_2O_4$	560	460	350	
$Co_{0.39}Zn_{0.61}Fe_2O_4$	560	460	350	
$Co_{0.62}Zn_{0.38}Fe_2O_4$	565	465	345	
$Co_{0.81}Zn_{0.19}Fe_2O_4$	570	470	335	
$CdFe_2O_4$	580	440	350	280

The effect of γ-irradiation on the electrical conductivity of the ferrites has been well studied using a dose of 1.24 Mrad. The plots of log σ against $1/T$ for the irradiated ferrites showed the same behaviour as those of unirradiated ones. The conductivity data of the irradiated samples are summarized and also given with unirradiated ones in Table II. The following points can be shown: (i) a change occurs in the σ and E_a values of Fe_3O_4 and $Co_xZn_{1-x}Fe_2O_4 (0 < x \leqslant 1)$ ferrites after irradiation – σ decreases and E_a increases in the case of Fe_3O_4, whereas the σ values increase and E_a decreases in the $Co_xZn_{1-x}Fe_2O_4$ ferrites; (ii) T_c moves towards higher temperatures for irradiated ferrites compared with that of the corresponding unirradiated ones; (iii) a change occurs in Seebeck coefficient values (θ) – they become more negative in the case of irradiated Fe_3O_4 and more positive for irradiated $Co_xZn_{1-x}Fe_2O_4 (0 < x \leqslant 1)$ compared with those of unirradiated ones; (iv) no change occurs in the conductivity data of $ZnFe_2O_4$ and $CdFe_2O_4$ after irradiation process.

4. Discussion

Fe_3O_4, can be described as the parent compound in the ferrites $M_xM'_{1-x}Fe_2O_4 (0 \leqslant x \leqslant 1)$ where M and M′ represent different divalent cations (Co^{2+}, Zn^{2+} and Cd^{2+}). The ferrite, Fe_3O_4, possesses an inverse spinel structure [13] with the cation distribution $(Fe^{3+})_t[Fe^{2+}Fe^{3+}]_oO_4$, where “t” and “o” represent

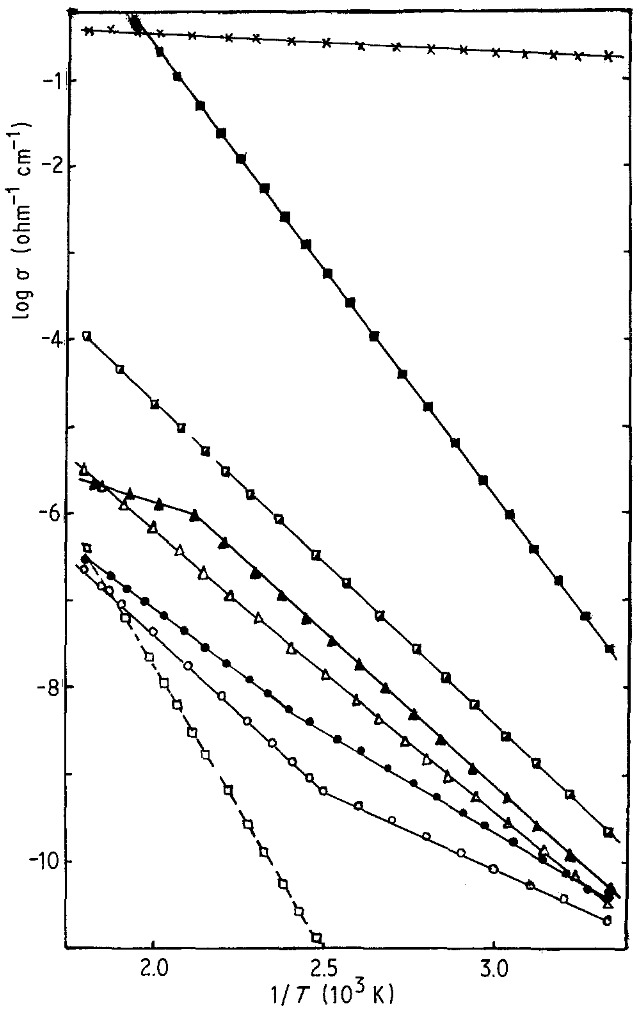

Figure 2 Effect of temperature on the electrical conductivity values of unirradiated Fe_3O_4, $CdFe_2O_4$ and $Co_xZn_{1-x}Fe_2O_4 (0 \leqslant x \leqslant 1)$: (x) Fe_3O_4; (□) $ZnFe_2O_4$; (◪) $CoFe_2O_4$; (■) $CdFe_2O_4$; (○) $Co_{0.21}Zn_{0.79}Fe_2O_4$; (●) $Co_{0.39}Zn_{0.61}Fe_2O_4$; (△) $Co_{0.62}Zn_{0.38}Fe_2O_4$ and (▲) $Co_{0.81}Zn_{0.19}Fe_2O_4$.

the tetrahedral and the octahedral sites, respectively. The divalent ions, Zn^{2+} and Cd^{2+}, have a preferential occupation for the tetrahedral sites [14, 15], whereas the Co^{2+} prefer to occupy octahedral sites in the ferrites investigated [16].

The electronic behaviour of unirradiated Fe_3O_4, $(Fe^{3+})_t[Fe^{2+}Fe^{3+}]_oO_4^{2-}$, has been widely investigated and frequently reviewed [11, 17]. Fast electron exchange is considered to occur among the Fe^{2+} and Fe^{3+} ions on octahedral sites. The decrease in the σ-values of Fe_3O_4 after irradiation is attributed to the decrease in Fe^{2+}/Fe^{3+} ratio present on the octahedral sites as a

TABLE II Electrical conductivity of γ-irradiated and unirradiated ferrites: Fe_3O_4, $CdFe_2O_4$ and $Co_xZn_{1-x}Fe_2O_4 (0 \leqslant x \leqslant 1)$

Composition of ferrites	Unirradiated			Irradiated		
	σ_{400} (Ω^{-1} cm^{-1})	E_a (eV)	θ (μV K^{-1})	σ_{400} (Ω^{-1} cm^{-1})	E_a (eV)	θ (μV K^{-1})
Fe_3O_4	0.26	0.038	−53	9.0×10^{-2}	0.048	−61
$ZnFe_2O_4$	8.2×10^{-12}	1.32	−490	8.0×10^{-12}	1.33	−492
$CoFe_2O_4$	3.4×10^{-7}	0.76	222	3.8×10^{-6}	0.60	350
$Co_{0.21}Zn_{0.79}Fe_2O_4$	6.0×10^{-10}	0.35 for $T < 400$ 0.74 for $T > 400$	−206	1.3×10^{-9}	0.30 for $T < 410$ 0.74 for $T > 410$	−176
$Co_{0.39}Zn_{0.61}Fe_2O_4$	2.1×10^{-9}	0.41 for $T < 415$ 0.67 for $T > 415$	−71	8.5×10^{-9}	0.36 for $T < 425$ 0.66 for $T > 425$	−16
$Co_{0.62}Zn_{0.38}Fe_2O_4$	1.4×10^{-8}	0.63 for $T < 450$ 0.67 for $T > 450$	54	8.6×10^{-8}	0.55 for $T < 460$ 0.66 for $T > 470$	120
$Co_{0.81}Zn_{0.19}Fe_2O_4$	4.2×10^{-8}	0.71 for $T < 470$ 0.24 for $T > 470$	139	3.4×10^{-7}	0.66 for $T < 495$ 0.24 for $T > 495$	235
$CdFe_2O_4$	5.5×10^{-4}	1.02	−100	5.3×10^{-4}	1.03	−102

consequence of the following interaction [11]

$$\gamma + Fe^{2+} \rightleftharpoons Fe^{3+} + e \qquad (1)$$

This decrease in Fe^{2+}/Fe^{3+} ratio leads to a decrease in the rate of the electron exchange between Fe^{2+}/Fe^{3+} by the hopping mechanism.

The electrical conduction in $Co_xZn_{1-x}Fe_2O_4$, $(Zn^{2+}_{1-x}Fe^{3+}_x)_t[Co^{2+}_xFe^{3+}_{2-x}]O_4^{2-}$, where $0 < x \leqslant 1$, arises from the presence of Co^{2+} on the octahedral sites which favour the following mechanism

$$Co^{2+} + Fe^{3+} \rightleftharpoons Co^{3+} + Fe^{2+} \qquad (2)$$

The increase in σ values with increasing the concentration of cobalt in $Co_xZn_{1-x}Fe_2O_4$ may be attributed to the presence of a larger number of cobalt ions on octahedral sites, which favour the hopping mechanism between Co^{2+} and Co^{3+} ions. Also this mechanism may explain the shifts occurring in T_b with increasing concentration of cobalt in $Co_xZn_{1-x}Fe_2O_4$ ferrites. However, the lower conductivity values in $CoFe_2O_4$ compared with that found for Fe_3O_4 can be attributed to the high activation energy of the hopping mechanism in the case of $CoFe_2O_4$, because the hopping between ions of different metals is likely to be more highly activated than that for ions of the same metal, from orbital considerations. The results listed in Table II show that σ values of $Co_xZn_{1-x}Fe_2O_4$ go to more positive values with increasing concentration of cobalt. Thus p-type, i.e. hole hopping between $Co^{3\pm}$ and Co^{2+}, is the predominant conduction mechanism in the ferrites containing higher concentrations of cobalt. This hole hopping mechanism was also reported for other ferrites containing cobalt ions [16–18]. However, the Seebeck coefficient values of the ferrites containing lower concentrations of cobalt, show that the predominant conduction mechanism is n-type, i.e. electron hopping between Fe^{2+} and Fe^{3+} ions. This mechanism was also reported for other similar ferrites [17, 18].

The increase in the electrical conduction of $Co_xZn_{1-x}Fe_2O_4$, $(0 < x \leqslant 1)$, ferrites by gamma irradiation can be explained according to the following interaction

$$Co^{2+} + \gamma \rightleftharpoons Co^{3+} + e \qquad (3)$$

The electron released in the above interaction can recombine with the higher valency form of iron and cobalt, i.e. Co^{3+} and Fe^{3+}. This interaction will lead to an increase in the ratios Fe^{3+}/Fe^{2+} and Co^{3+}/Co^{2+} lying on octahedral sites and in turn increases the hopping rate after irradiation; consequently, the electrical conductivity increases and the activation energy decreases. This is supported by IR spectra results as γ-irradiation shifts ν_1 and ν_2 to higher frequencies, due to the creation of a large ionic radius of Fe^{2+} induced by γ-radiation on both octahedral and tetrahedral sites. ν_1 is responsible for (Fe^{3+}–O) vibration on tetrahedral sites and ν_2 for (Fe^{3+}–O) vibration on octahedral sites [7, 8]. As mentioned above, the ions lying on tetrahedral sites do not make a large contribution to the conduction process due to their isolation states, compared to those found on octahedral sites.

The results of Seebeck coefficient measurements show that θ values of $Co_xZn_{1-x}Fe_3O_4 (0 < x \leqslant 1)$ assume more positive values after irradiation (Table II). This indicates that the increase in σ values by positive holes, i.e. $Co^{3+} \rightarrow Co^{2+}$, is higher than that obtained by hopping electrons, i.e. $Fe^{2+} \rightarrow Fe^{3+}$, in irradiated ferrites. Thus the irradiation causes a higher increase in the Co^{3+}/Co^{2+} ratio than that produced in the Fe^{3+}/Fe^{2+} ratio. Also, the shift in T_b to higher temperatures after the irradiation of $Co_xZn_{1-x}Fe_2O_4$ $(0 < x < 1)$ can be explained on the basis of the increase in the Co^{3+}/Co^{2+} ratio in irradiated samples, compared to unirradiated ones, as mentioned above.

Our results listed in Table II show that $ZnFe_2O_4$, $(Zn^{2+})_t[Fe^{3+}Fe^{3+}]_oO_4^{2-}$, and $CdFe_2O_4$, $(Cd^{2+})_t[Fe^{3+}Fe^{3+}]_oO_4$, behave as n-type semiconductors. The absence of divalent ions on the octahedral sites indicates that the hopping mechanism could be excluded here. This can also be shown from the high activation energies obtained in these ferrites compared with those observed in the other ferrites investigated in which the hopping mechanism is predominant, as shown in Fe_3O_4 and $Co_xZn_{1-x}Fe_2O_4$, $(0 < x \leqslant 1)$. The electrical conduction in $ZnFe_2O_4$ and $CdFe_2O_4$ could also be explained here on the basis of the transport of charge carriers through cation vacancies present on octahedral sites. These cation vacancies may be created in these ferrites during their preparation at higher temperatures [19]. The cation vacancy mechanism was also reported for other ferrites having similar composition [11, 17]. The agreement between the conductivity data of the irradiated and unirradiated $ZnFe_2O_4$ and $CdFe_2O_4$ ferrites indicates that the concentration of the cation vacancies has not been altered by the radiation dose used in this work, 1.24 Mrad. However, a slight variation in the concentration of the cation vacancies in $ZnFe_2O_4$ was observed on using a dose of 22.5 Mrad [11].

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Received 4 May
and accepted 9 September 1988