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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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ABSTRACT

The electrical conductivity of γ irradiated and unirradiated finely divided ferrites of composition Fe_3O_4, $CdFe_2O_4$ and $Co_xZn_{1-x}Fe_2O_4$ ($0 \leqslant x \leqslant 1$) 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 was discussed.

INTRODUCTION

The present investigations are part of a more extensive programme dealing with the effect of both composition and γ irradiation on the

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electrical conduction of inorganic oxides having a spinel crystal structure. These oxides are important in many branches of technology [1–3] for example, ferrites, ferroelectrics, solid state electrolytes, catalysts and nuclear fuels.

For binary oxidic spinels 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] and to depend on 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 in order to determine the effect of composition on the type of charge carrier and its transport mechanism. In addition, the effect of γ irradiation on conduction in these ferrites was investigated.

EXPERIMENTAL

AnalaR grade CdO, CoO, ZnO and Fe_2O_3 were used as starting materials to prepare the $CdFe_2O_4$ and $Co_xZn_{1-x}Fe_2O_4$ $(0 \leqslant x \leqslant 1)$ ferrites under investigation. The oxides were intimately mixed in the stoichiometric proportions 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 granulated Fe_2O_3 at 1700 K in air for 30 h. In all cases, the product was quenched in water.

Atomic absorption analysis was used to determine the quantities of zinc, cobalt, cadmium and iron in the prepared samples. X-ray analysis confirmed the formation of the spinel phase in both γ irradiated and unirradiated samples.

The investigated ferrites were irradiated with γ rays using a ^{60}Co cell with a dose rate of 3.6 krad h^{-1} for 344 h.

IR spectra for γ irradiated and unirradiated ferrites were recorded using a Pye–Unicam Model SP3-100 spectrophotometer, KBr disks and Nujol oil mulls.

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 a temperature range of 300–550 K. The Seebeck coefficient, θ, measurements were made at temperature intervals of $\Delta T \simeq 50$ K (against platinum).

RESULTS

Figure 1 shows the IR spectra of the unirradiated ferrites Fe_3O_4, $CdFe_2O_4$ and $Co_x\,Zn_{1-x}Fe_2O_4$ $(0 \leqslant x \leqslant 1)$. It can be seen that for unirradiated Fe_3O_4 there are two frequency bands, ν_1 at $\simeq 550$ and ν_2 at $\simeq 450$ cm^{-1}, and a poorly defined band at ~ 290 cm^{-1}. However, for unirradiated $CdFe_2O_4$ and $Co_xZn_{1-x}Fe_2O_4$ $(0 \leqslant x \leqslant 1)$, the IR spectra presented in Fig. 1 show shifts in the ν_1 and ν_2 bands, in addition to the appearance of a new band ν_3 at 350–330 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 1. The ν_1 and ν_2 bands are assigned to the intrinsic vibration of the tetrahedral and octahedral groups, respectively [7,8]. The ν_3 band can be assigned to the Zn^{2+} or Cd^{2+} tetrahedral vibration.

γ irradiation of the ferrite samples causes shifts in the three frequency bands ν_1, ν_2 and ν_3 to higher frequencies. However, for $CdFe_2O_4$, a shift in the ν_3 band was not observed. Moreover, the IR spectra of irradiated Fe_3O_4

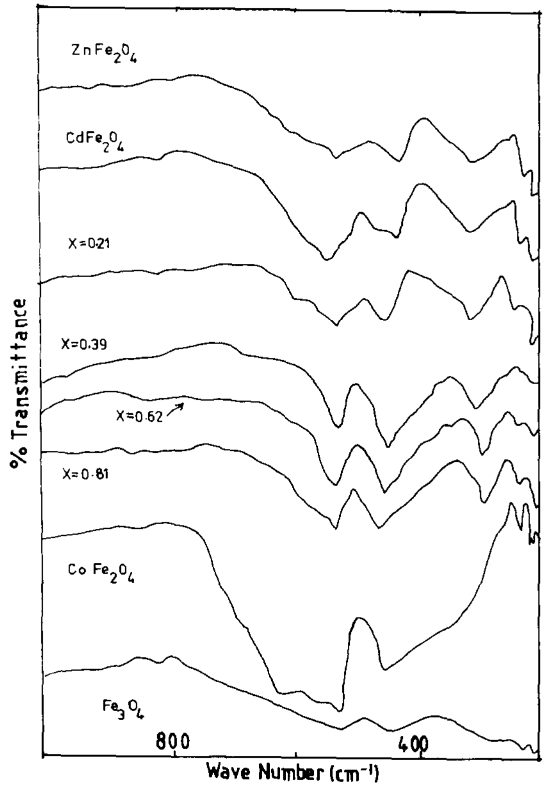

Fig. 1. IR spectra of unirradiated Fe_3O_4, $CdFe_2O_4$ and $Co_xZn_{1-x}Fe_2O_4$ $(0 \leqslant x \leqslant 1)$.

TABLE 1

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

TABLE 2

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

Composition of ferrites	Unirradiated			γ-Irradiated		
	σ_{400} (ohm^{-1} cm^{-1})	E_a (eV)	θ ($\mu V\ k^{-1}$)	σ_{400} (ohm^{-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

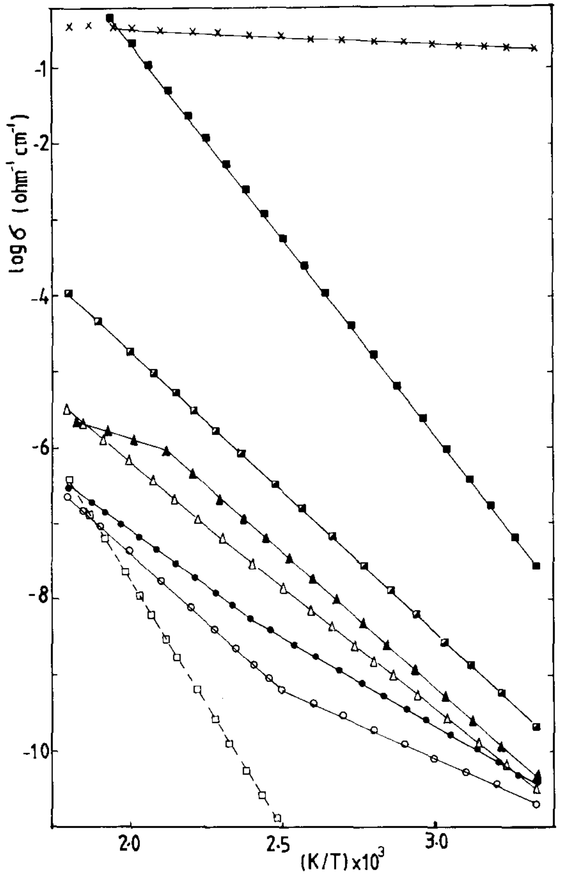

Fig. 2. Effect of temperature on the electrical conductivity values of unirradiated Fe_3O_4. $CdFe_2O_4$ and $Co_xZn_{1-x}Fe_2O_4$ ($0 \leqslant x \leqslant 1$); (×) Fe_3O_4; (□) $ZnFe_2O_4$; (◪) $CoFe_2O_4$; (■) $CdFe_2O_4$; (○) $Co_{0.21}Zn_{0.79}Fe_2O_4$; (●) $Co_{0.39}Zn_{0.61}Fe_2O_4$; (△) $Co_{0.62}Zn_{0.38}Fe_2O_4$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

showed an increase in the development of the weak band appearing at ~ 290 cm^{-1}.

The variation of electrical conductivity (σ) with temperature over the range 300–550 K for all unirradiated ferrites is shown in Fig. 2. A log σ versus $1/T$ plot yields straight lines without any break for $CdFe_2O_4$, $CoFe_2O_4$ and $ZnFe_2O_4$, while the plot for $Co_xZn_{1-x}Fe_2O_4$ ($0.21 \leqslant x \leqslant 0.81$) has 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 shifts to higher temperatures. The activation energies of the conduction process (E_a) were calculated using the Arrhenius equation [12] from the plots given in Fig. 2, and are listed with conductivity values (σ_{400}) at 400 K and Seebeck coefficient θ in Table 2.

The effect of γ irradiation on the electrical conductivity of the ferrites has been extensively studied using a dose of 1.24 Mrad. The plots of log σ versus $1/T$ for the irradiated ferrites showed the same behaviour as those of the unirradiated ones. The conductivity data of the irradiated samples are summarized together with the unirradiated conductivity data in Table 2, from which the following observations can be made: there is a change 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 σ increases and E_a decreases in the $Co_xZn_{1-x}Fe_2O_4$ ferrites; T_c shifts to higher temperatures for irradiated ferrites compared with that of the corresponding unirradiated ones; there is a change in the 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 the values of unirradiated samples; and there is no change in the conductivity data of $ZnFe_2O_4$ and $CdFe_2O_4$ after the irradiation process.

DISCUSSION

Fe_3O_4 can be described as the parent compound of the ferrites $M_x M'_{1-x}Fe_2O_4$ $(0 \leqslant x \leqslant 1)$ 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 the tetrahedral and the octahedral sites, respectively. In the ferrites investigated, the divalent ions, Zn^{2+} and Cd^{2+} preferentially occupy the tetrahedral sites [14,15], whereas Co^{2+} prefers to occupy the octahedral sites [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 the octahedral sites. The decrease in the σ values of Fe_3O_4 after irradiation is attributed to the decrease in the Fe^{2+}/Fe^{3+} ratio present on the octahedral sites as a consequence of the following interaction [11]

$$\gamma + Fe^{2+} \rightleftharpoons Fe^{3+}e \tag{1}$$

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

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

$$Co^{2+} + Fe^{3+} \rightleftharpoons Co^{3+} + Fe^{2+} \tag{2}$$

The increase in σ values with increasing 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 the 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 cobalt concentration in $Co_xZn_{1-x}Fe_2O_4$ ferrites. However, the lower conductivity values in $CoFe_2O_4$ compared with those 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 between ions of the same metal, because of orbital considerations. Results listed in Table 2 show that σ values of $Co_xZn_{1-x}Fe_2O_4$ become more positive with increasing concentration of cobalt. This means that p-type i.e. hole hopping between Co^{3+} and Co^{2+} is the predominant conduction mechanism in those ferrites containing higher concentrations of cobalt. This hole hopping mechanism was also reported for other ferrites containing cobalt ions [16–18]. However, the Seebeck coefficent 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 following γ irradiation can be explained according to the following interaction

$$Co^{2+} + \gamma \rightleftharpoons Co^{3+} + e \tag{3}$$

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

The results of the measurement of the Seebeck coefficient show that θ values of $Co_xZn_{1-x}Fe_3O_4$ $(0 < x \leqslant 1)$ become more positive after irradiation, see Table 2. This indicates that in irradiated ferrites, the increase in σ values by positive holes i.e. $Co^{3+} \rightarrow Co^{2+}$ is higher than that obtained by hopping electron i.e. $Fe^{2+} \rightarrow Fe^{3+}$. This means that the irradiation causes a higher increase in the Co^{3+}/Co^{2+} ratio than in the Fe^{3+}/Fe^{2+} ratio. Also, the shift in T_b to higher temperatures following irradiation of $Co_xZn_{1-x}Fe_2O_4$ $(0 < x < 1)$ can be explained on the basis of the increase in

Co^{3+}/Co^{2+} ratio in irradiated samples as compared to unirradiated ones, as mentioned above.

Our results listed in Table 2 show that $ZnFe_2O_4$ $[(Zn^{2+})_t[Fe^{3+}Fe^{3+}]_oO_4^{2-}]$ and $CdFe_2O_4[(Cd^{2+})_t[Fe^{3+}Fe^{3+}]_oO_4^{2-}]$ behave as n-type semiconductors. The absence of divalent ions on the octahedral sites indicates that the hopping mechanism can be excluded here. This can also be demonstrated from the high activation energies obtained in these ferrites as compared with those observed in the other investigated ferrites 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 $CdFe_2O_4$ can 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 vacancy has not been varied by the radiation dose applied here i.e. 1.24 Mrad. However, a slight variation in the concentration of the cation vacancy in $ZnFe_2O_4$ was observed on using a dose of 22.5 Mrad [11].

REFERENCES

1 J.B. Goodenough, Prog. Solid State Chem., 5 (1971) 145.
2 J.A. Wilson, Adv. Phys., 21 (1972) 143.
3 C.P. Poole and H.A. Farach, Z. Phys. B, 47 (1982) 55.
4 T.F. Barth and E. Posnjak, Z. Krist., 82 (1923) 325.
5 P. Porta, F.S. Stone and R.G. Turner, J. Solid State Chem., 11 (1974) 135.
6 J.B. Goodenough and A.L. Loeb, Phys. Rev., 98 (1955) 391.
7 R.D. Waldron, Phys. Rev., 99 (1955) 1727.
8 S. Hafner, Z. Krist., 115 (1961) 331.
9 A.P. Komar, Bull. Acad. Sci. USSR Ser. Phys., 18 (1954) 122.
10 R. Parker and C.J. Tinsley, in Y. Hoshino, S. Iida and M. Sugimota (Eds.), Proc. Int. Conf. of Ferrites, Japan, 1970, University Park Press, Tokyo, 1970, p. 591.
11 M.A. Mouse and M.A. Ahmed, Thermochim. Acta, 125 (1988) 379.
12 C. Kittel, Solid State Physics, 3rd edn., Wiley, New York, 1960, p. 349.
13 R. Bauminger and S.G. Cohen, Phys. Rev., 122 (1961) 743.
14 H.B. Mathur, A.P.B. Sinha and C.M. Yagnik, Indian J. Pure Appl. Phys., 5 (1967) 155.
15 A. Rousset, J. Paris and P. Mollard, Ann. Chim., 7 (1972) 119.
16 G.H. Jonker, J. Phys. Chem. Solids, 9 (1959) 165.
17 B. Gillot, R.M. Benloucif and A. Rousset, Phys. Status Solidi A, 65 (1981) 205 and references therein.
18 O.S. Josyulu and J. Sobhanadri, Phys. Status Solidi A, 59 (1980) 323.
19 J.A. Kulkarni, K. Muraleedharan, J. Srivastava, V.R. Marathe, V.S. Darshane, C.R.K. Murty and R. Vijayaraghavan, J. Phys. C: Solid State Phys., 18 (1985) 2593.