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ELECTRICAL CONDUCTION IN SOME γ-IRRADIATED AND UNIRRADIATED METAL–ZINC FERRITES

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ABSTRACT

The electrical conductivity of some γ-irradiated and unirradiated metal–zinc ferrites, $M_{0.1}Zn_{0.9}Fe_2O_4$ ($M \equiv Mn^{2+}$, Co^{2+}, Ni^{2+}, Cu^{2+} or Mg^{2+}), was investigated as a function of temperature. The ferrites investigated showed n-type conduction. The electrical conduction in $M_{0.1}Zn_{0.9}Fe_2O_4$ ($M \equiv Co^{2+}$, Cu^{2+}, Mn^{2+} or Ni^{2+}), can be explained by a hopping mechanism, whereas the conduction in $ZnFe_2O_4$ and $Mg_{0.1}Zn_{0.9}Fe_2O_4$ is interpreted on the basis of the transfer of charge carriers through the cation vacancies present in octahedral sites. The effect of γ-irradiation on the conduction process is discussed.

INTRODUCTION

The spinel ferrites are among the most thoroughly investigated oxides. Their physical properties are largely influenced by the fact that they contain iron atoms in different oxidation states but in crystallographically equivalent positions. The study of such spinel ferrites is of great importance in both fundamental and applied research [1,2]. The interesting physical and chemical properties of spinel ferrites arise from the fact that they can distribute cations amongst the available tetrahedral (t) and octahedral (o) sites [3]. Because transition-metal ions exhibit variable oxidation states, cations of different valencies can occupy the same or different sites because of the fine balance in the respective preferences of the ion concerned [4]. $ZnFe_2O_4$ is

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one of the oxidic spinels possessing the cation distribution $(Zn^{2+})_t$-$(Fe_2^{3+})_oO_4^{2-}$. For the substituted $M_xZn_{1-x}Fe_2O_4$, a variation in the rate of charge transfer between ions of different valancies lying on equivalent sites [5,6] is expected. Therefore, the present work was designed to investigate the electrical conduction in γ-irradiated and unirradiated $M_{0.1}Zn_{0.9}Fe_2O_4$ (M ≡ Co^{2+}, Ni^{2+}, Mg^{2+}, Cu^{2+} or Mn^{2+}) ferrites. Such studies on mixed ferrites give information on the effect of γ-irradiation on each type of charge carriers and its transport mechanism.

EXPERIMENTAL

The ferrite samples were prepared from AnalaR grade Fe_2O_3, ZnO, CoO, CuO, NiO, MnO and MgO. Powders of these oxides were intimately mixed in stoichiometric proportions and pre-heated for 8 h at 1100 K and then for 30 h at 1600 K. The product was then cooled at the rate of 100 K h^{-1}.

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

The ferrites under investigation were irradiated with a dose of 18.7 Mrad using a ^{60}Co cell.

The d.c. conductivity was measured between 300 and 600 K using a published method [6]. The Seebeck coefficient measurements were made at temperature intervals of $\Delta T \approx 50$ K.

RESULTS

The variation of electrical conductivity σ with temperature for all unirradiated samples is shown in Fig. 1. Different trends can be distinguished from these plots. For $M_{0.1}Zn_{0.9}Fe_2O_4$ (M ≡ Co^{2+}, Cu^{2+}, Ni^{2+} or Mn^{2+}), two regions are seen with one break, while for $ZnFe_2O_4$ and $Mg_{0.1}Zn_{0.9}Fe_2O_4$, there is no break in the conductivity values in the measured temperature range. This change in slope at a certain temperature is known for many ferrites. The slope change can be attributed to a change in conduction mechanism or to the effect of magnetic ordering on the conduction process [6–9] in the ferrites. The activation energies E_a of the conduction processes were calculated from the plots in Fig. 1 using the Arrhenius equation and are listed with the conductivity values at 400 K (σ_{400}) and Seebeck coefficients θ in Table 1.

The effect of γ-irradiation on the electrical conductivity of the ferrite samples was throughly studied using a dose of 18.7 Mrad. The conductivity values obtained differ from those of unirradiated samples, while the plots of log σ versus $1/T$ for irradiated samples showed the same behaviour as those

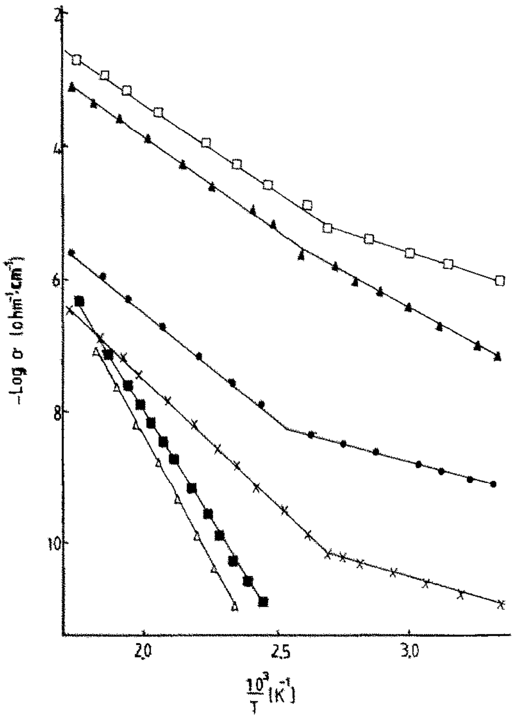

Fig. 1. Effect of temperature on the electrical conductivity values of unirradiated $M_{0.1}Zn_{0.9}Fe_2O_4$: □, Ni^{2+}; ▲, Cu^{2+}; ●, Mn^{2+}; ×, Co^{2+}; △, Mg^{2+}; and ■, $ZnFe_2O_4$.

TABLE 1

Electrical conductivity data of γ-irradiated and unirradiated ferrites

Composition of ferrites	Unirradiated			γ-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 [a]	0.26	0.038	−53	3×10^{-2}	0.051	−70
$ZnFe_2O_4$	8.2×10^{-12}	1.32	−526	3.0×10^{-12}	1.33	−550
$Co_{0.1}Zn_{0.9}Fe_2O_4$	3.99×10^{-10}	0.75 ($T > 370$) 0.23 ($T < 370$)	−370	1.2×10^{-9}	0.75 ($T > 385$) 0.18 ($T < 385$)	−300
$Mn_{0.1}Zn_{0.9}Fe_2O_4$	7.58×10^{-9}	0.64 ($T > 390$) 0.21 ($T < 370$)	−370	1.2×10^{-9}	0.66 ($T > 385$) 0.18 ($T < 385$)	−300
$Cu_{0.1}Zn_{0.9}Fe_2O_4$	5.75×10	0.57 ($T > 385$) 0.45 ($T < 385$)	−260	2.87×10^{-5}	0.61 ($T > 395$) 0.36 ($T < 395$)	−200
$Ni_{0.1}Zn_{0.9}Fe_2O_4$	2.29×10^{-5}	0.54 ($T > 370$) 0.33 ($T < 370$)	−190	1.60×10^{-4}	0.53 ($T > 390$) 0.21 ($T < 390$)	−130
$Mg_{0.1}Zn_{0.9}Fe_2O_4$	7.61×10^{-13}	1.51	−620	1.12×10^{-12}	1.56	−680

[a] $ZnFe_2O_4$ data obtained from ref. 5.

of unirradiated ones. The results of irradiated samples are also summarised in Table 1, from which the following conclusions can be drawn: there is a shift in the temperature at which the conductivity break occurs; and there are changes in each of the activation energies E_a and Seebeck coefficient θ values compared with those obtained for unirradiated samples.

DISCUSSION

Ferrite, Fe_3O_4, has high conductivity values which has been explained by an electron hopping mechanism between the Fe^{2+} and Fe^{3+} ions present on the octahedral sites [5,10]. The change in the conductivity of Fe_3O_4 caused by replacing Fe^{2+} ions with M^{2+} cations ($M \equiv Co^{2+}$, Zn^{2+}, Ni^{2+}, Mg^{2+}, Cu^{2+} or Mn^{2+}) in the spinel-ferrite lattice can be attributed to the distribution of the introduced cations over different sites in the spinel structure. This distribution may lead to a change in both the concentration and the mobility of charge carriers in the ferrite lattice. The results listed in Table 1 show a change in each conductivity value and Seebeck coefficient value when the ferrite composition was changed. The conductivity values of the irradiated and unirradiated ferrites lie in the semiconductor range. The negative Seebeck coefficient values show that the investigated spinels are n-type semiconductors. The γ-irradiation effect does not change the sign of the Seebeck voltage and leads to a slight change in the activation energies of the electrical conduction in the lower temperature range, while for the high temperature range (after the break in σ values, see Fig. 1) the activation energies did not appreciably change. This means that the conduction mechanism in the investigated ferrites is not changed by irradiation.

The conductivity data obtained for the mixed metal–zinc ferrites, $(Zn^{2+}_{0.9}Fe^{3+}_{0.1})_t(M^{2+}_{0.1}Fe^{3+}_{1.9})_oO_4^{2-}$ ($M^{2+} \equiv Co^{2+}$, Ni^{2+}, Mn^{2+} or Cu^{2+}), can be explained by charge transfer between the octahedral electrons by hopping of localised d-electrons. In the $ZnFe_2O_4$ ferrites, the Zn^{2+} ions prefer to occupy tetrahedral sites [11]. The presence of M^{2+} ions on the octahedral sites of the spinel lattice lead to an increase in the conductivity values via the hopping mechanism

$$M^{2+} + Fe^{3+} \rightleftharpoons M^{3+} + Fe^{2+}$$

The increase in the electrical conduction of the above ferrites, $M_{0.1}Zn_{0.9}Fe_2O_4$ caused by irradiation can be explained according to

$$M^{2+} \rightleftharpoons M^{3+} + e$$

The electrons released in this interaction can recombine with Fe^{3+} ions. This interaction will lead to an increase in the Fe^{2+}/Fe^{3+} and M^{3+}/M^{2+} ratios in octahedral sites which in turn, will increase the hopping rate after irradiation. Consequently, the electrical conductivity increases and the activation energy decreases.

The lower conductivity values and higher activation energies obtained for irradiated and unirradiated $ZnFe_2O_4$ and $Mg_{0.1}Zn_{0.9}Fe_2O_4$ samples indicate that the hopping mechanism is not applicable here. Electrical conduction in these ferrites can also be explained on the basis of the transport of charge carriers through the cation vacancies present on octahedral sites. These cation vacancies may be created during the preparation of ferrites at higher temperatures [12]. This mechanism has also been observed for other similar divalent-substituted ferrites [5,13,14]. The agreement between the conductivity data for irradiated and unirradiated $ZnFe_2O_4$ and $Mg_{0.1}Zn_{0.9}Fe_2O_4$ indicates that the concentration of cation vacancy was not changed by irradiation.

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