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ELECTRICAL CONDUCTION IN γ-IRRADIATED AND UNIRRADIATED ZINC–IRON FERRITES

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ABSTRACT

The electrical conductivity of γ-irradiated and unirradiated finely-divided spinels of composition $(Zn_x^{2+} Fe_{1-x}^{2+} Fe_2^{3+})O_4^{2-}$ was studied in nitrogen atmosphere as a function of temperature. The results of both γ-irradiated and unirradiated ferrites with compositions $x \leqslant 0.79$ showed that the electrical conduction occurred by fast electron exchange amongst Fe^{2+} and Fe^{3+} ions situated on octahedral sites in the spinel lattice (hopping mechanism). For compositions $x > 0.79$ it was found that the transition of the charge carriers through cation vacancies is the predominant mechanism. Some breaks in the conductivity–temperature curves were found near the Curie points. The Seebeck voltage measurements showed that γ-irradiated and unirradiated spinels behave as *n*-type semiconductors. The effect of γ-irradiation on the conductivity, activation energy, charge carriers and the conduction mechanism is discussed.

INTRODUCTION

Recently several mixed metal oxides having the general formula XY_2O_4 [1–11] have been investigated as they exhibit interesting structural, electrical, magnetic and catalytic properties. In these oxidic spinels the physical properties were found to be dependent on the nature of the ions involved, their charges and their site distribution amongst 8-tetrahedral (A) and 16-octahedral (B) sites. For these oxidic spinels two extreme distributions of cations are possible: the "normal" $(X)_A[Y_2]_BO_4$ and the "inverse" $(Y)_A[XY]_BO_4$ distribution [11], where the ions in the octahedral sites are in square brakets. Several workers [5–10] have studied the solid solution by substituting ions at (A) and (B) sites. A gradual change was found in the

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solid state chemistry and in the physical properties of these oxidic spinels by varying the composition of the solution.

Magnetite Fe_3O_4 is one of these oxidic spinels. It possesses an inverse spinel structure [12] with the cation distribution $(Fe_1^{3+})_A[Fe^{2+}F_1^{3+}]_B O_4^{2-}$. It has been proposed [13–19] that for substituted magnetite $M_xFe_{3-x}O_4$ a fast electron exchange between ions of different valencies lying on equivalent sites is the reason for the higher electrical conductivity in case of lower values of x, while for higher x-values other conduction mechanisms should be considered.

The effect of ionizing radiation on the electrical properties of mixed oxides has recieved limited attention. With a view to investigate the effect of γ-irradiation on the electrical properties of ferrites, the system $(Zn_x^{2+} Fe_{1-x}^{3+})_A[Fe_{1-x}^{2+}Fe_{1+x}^{3+}]_B O_4^{2-}$ has been investigated.

EXPERIMENTAL

AnalaR grade zinc chloride, ferrous chloride, ferric chloride and sodium hydroxide were used to prepare the samples investigated. The hydroxide co-precipitation technique was used in the preparation of $Zn_xFe_{3-x}O_4$ spinels, where x lies in the range $0 \leqslant x \leqslant 1$. Each of the co-precipitated samples was dried at 370 K, then calcined in a muffle furnace in air atmosphere at 600 K for 6 h. The final product appeared as extremely fine grained solids.

The amount of zinc and iron in each prepared spinel was analysed using the atomic absorption technique. The Fe^{2+} ion content in each spinel was determined by volumetric analysis [20].

X-ray analysis confirmed the spinel phase formation in both γ-irradiated and unirradiated samples. Synthesized materials are mixed spinels (Fe^{2+} ions are on octahedral sites and Zn^{2+} ions on tetrahedral sites) and the lattice parameter varies linearly with x. The lattice parameters recorded in this work were in good agreement with those reported by Gillot et al. [19].

Electrical conductivity measurements were performed on pellets (diameter 7 mm and thickness 8 mm) prepared by compression of powder under pressure of 1400 kg cm^{-2}. The dc-conductivity of zinc–iron ferrite was measured between 5 and 900 K using a method already reported [10]. The conductivity measurements were carried out in nitrogen atmosphere. The Seebeck coefficient measurements were made at temperature intervals of $\Delta T \approx 50$ K (against platinum).

The investigated spinels were irradiated with γ-rays using a ^{60}Co-cell with a dose rate of 39 rad s^{-1} for 160 h.

IR-spectra for unirradiated and γ-irradiated ferrites were recorded using a Perkin–Elmer 325 spectrophotometer, KBr disks and Nujol oil mulls.

RESULTS

The relation between the logarithmic values of conductivity (log σ) of $Zn_xFe_{3-x}O_4$ spinels and the reciprocal values of temperature ($1/T$) is shown in Fig. 1. From the plots presented in this figure three types of straight lines could be distinguished. For unirradiated ferrites $(Zn_x^{2+}Fe_{1-x}^{3+})_A[Fe_{1-x}^{2+}Fe_{1+x}^{3+}]_BO_4^{2-}$ with composition $x = 0.00$, 0.21, 0.43, 0.51 and 0.63 straight lines with two breaks were observed, whereas for $x = 0.79$ only one break could be detected. On the other hand, for $x = 0.95$ and $x = 1.00$ the above plots in Fig. 1 show straight lines without any break over the entire temperature range. All breaks at higher temperatures are in the

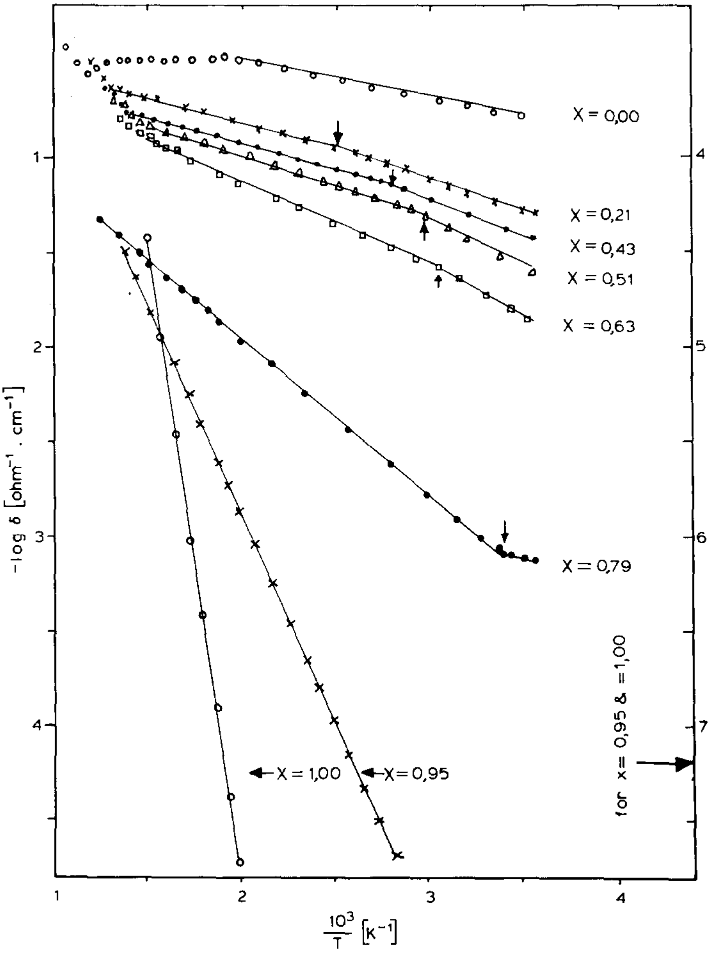

Fig. 1. Effect of temperature on the electrical conductivity values of unirradiated $Zn_xFe_{3-x}O_4$ spinels.

TABLE 1

Electrical conductivity data of γ-irradiated and unirradiated spinels $Zn_xFe_{3-x}O_4$

Sample compos. x	σ (ohm^{-1}cm^{-1}) at 500 K		E_a (eV) 380–630 K		T_c (K)		θ (μV K^{-1})	
	Unirrad.	Irrad.	Unirrad.	Irrad.	Unirrad.	Irrad.	Unirrad.	Irrad.
$x = 0.00$	3.2×10^{-1}	1.3×10^{-1}	0.038 [a]	0.048 [a]	850	800	−53	−63
$x = 0.21$	1.5×10^{-1}	1.1×10^{-1}	0.047	0.053	780	750	−74	−80
$x = 0.43$	1.1×10^{-1}	9.5×10^{-2}	0.056	0.060	719	700	−119	−126
$x = 0.51$	9.5×10^{-2}	8.6×10^{-2}	0.059	0.062	695	680	−134	−140
$x = 0.63$	7.2×10^{-2}	6.4×10^{-2}	0.083	0.086	638	628	−192	−208
$x = 0.79$	1.1×10^{-2}	8.4×10^{-3}	0.161	0.168	288	281	−324	−352
$x = 0.95$	1.3×10^{-6}	1.1×10^{-6}	1.121	1.134	–	–	−490	−506
$x = 1.00$	1.8×10^{-8}	1.6×10^{-8}	1.321	1.330	–	–	−526	−537

[a] At a temperature range of 300–580 K.

vicinity of the Curie points (T_c) of the respective spinels [21,22]. These breaks in the conductivity values at higher temperatures and the conductivity data of all the different compositions of the investigated ferrites are given in Table 1. It can be seen from Table 1 that as the zinc concentration increases T_c decreases. Our results also show that the activation energy values (E_a), calculated according to the Arrhenius equation, increase with increasing concentration of zinc in the ferrites (Table 1).

The Seebeck coefficient measurements show that all the investigated compositions of $Zn_xFe_{3-x}O_4$ spinels are n-type semiconductors and the Seebeck voltage (θ) of the spinel becomes less negative with increasing zinc concentration (Table 1).

The effect of γ-irradiation on the electrical conductivity of the ferrite samples was thoroughly studied using a dose of 22.5 Mrad. The results obtained show that the electrical conductivity values of irradiated spinels $Zn_xFe_{3-x}O_4$ are less than the values of the corresponding unirradiated ones at the same temperature, while the plots of log σ vs. $1/T$ for irradiated samples show the same behaviour as those of unirradiated ones. The results of irradiated samples are summarized in Table 1, from which the following can be shown: (1) T_c moves towards lower temperatures for irradiated spinels compared with that of the corresponding unirradiated samples. (2) A slight increase in the activation energy values, in the temperature range 380–630 K, of the irradiated samples compared with those of unirradiated ones. (3) More-negative values of Seebeck voltage were recorded for the γ-irradiated samples compared with those of the corresponding unirradiated spinels.

The IR-spectra of γ-irradiated and unirradiated $Zn_xFe_{3-x}O_4$ systems are shown in Fig. 2, from which it can be seen that for unirradiated Fe_3O_4, where $x = 0$, there are two frequency bands at ~ 550 and ~ 450 cm^{-1} and a poorly defined band at ~ 290 cm^{-1}. However, for unirradiated $Zn_xFe_{3-x}O_4$

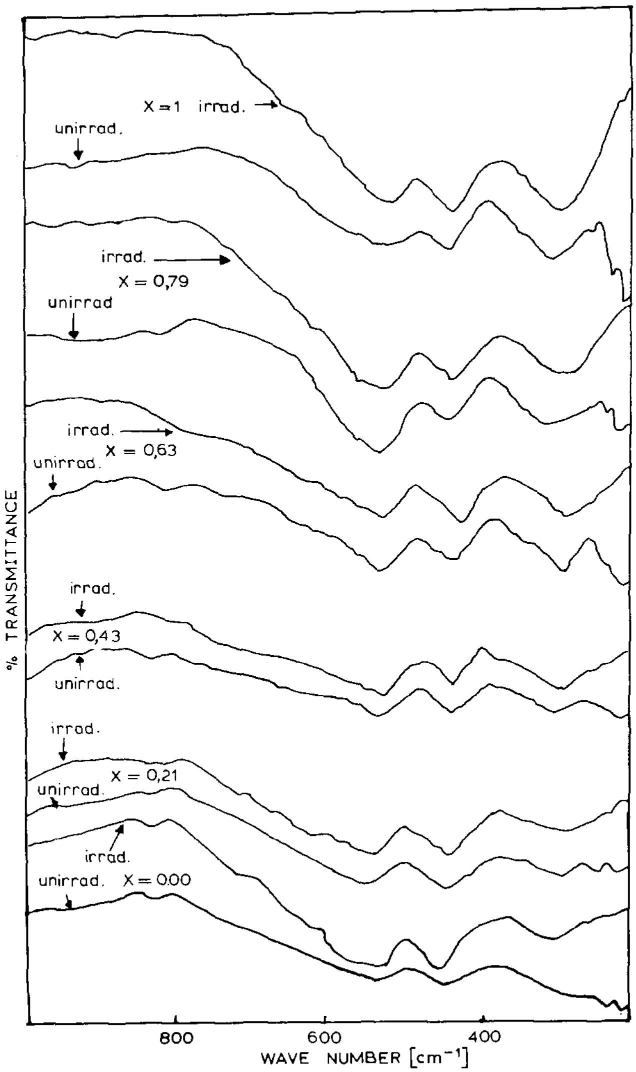

Fig. 2. IR-spectra of γ-irradiated and unirradiated $Zn_xFe_{3-x}O_4$ spinels.

samples, where $x > 0$, the IR-spectra presented in Fig. 2 show two high frequency bands located at 560–540 (ν_1) and 450–400 cm^{-1} (ν_2) depending on the composition of the ferrites in addition to a low frequency band at 350–330 cm^{-1} (ν_3). Waldron [23] and Hafner [24] attributed the ν_1 band to the intrinsic vibration of the tetrahedral groups, and the ν_2 band to the octahedral groups. The ν_3 band, which appears in the samples containing Zn^{2+} ions, could be assigned to Zn^{2+} tetrahedral vibration. Gamma-irradiation of the ferrite samples causes shifts in the ν_1 and ν_2 bands to higher frequencies, in addition to increasing the development of the 290 cm^{-1} band appearing in the spectra of the pure Fe_3O_4 sample.

DISCUSSION

From the above results, one can see that the conductivity values of irradiated and non-irradiated $Zn_xFe_{3-x}O_4$ lie in the semiconductor range. The negative values of the Seebeck coefficient show that the investigated spinels are n-type semiconductors. An appearance of magnetic order is observed by the break in the conductance–temperature curves and by the changes in the activation energies of semiconductions. The breaks in σ-values at higher temperatures are in the vicinity of Curie temperatures of the spinels investigated [21,22]. The γ-irradiation effect does not change the sign of the Seebeck voltage and leads to very slight change in the activation energy of the electrical conduction. This means that the conduction mechanism in the investigated spinels is not changed by the irradiation process. The downward displacement in T_c by decreasing the content of Fe^{2+} ions in the spinels as well as by the irradiation process could be related, as will be shown in the following discussion.

Our conductivity results of γ-irradiated and unirradiated $(Zn_x^{2+}Fe_{1-x}^{3+})_A[Fe_{1-x}^{2+}Fe_{1+x}^{3+}]_BO_4^{2-}$ spinels show large differences in E_a-values for $x \leqslant 0.79$ and $x > 0.79$ (Table 1). This could be interpreted on the basis of the presence of two conduction mechanisms in the whole range of x, $0 \leqslant x \leqslant 1$.

First, for $x \leqslant 0.79$ an electron hopping mechanism between Fe^{2+} and Fe^{3+} ions, which lie on octahedral sites, could explain our results as shown from the following points: (1) The decrease in σ-values, which is accompanied by slight increase in E_a-values, with increasing concentration of Zn^{2+} ions can be attributed to the decrease in Fe^{2+} ions lying on octahedral sites. This leads to decrease in the Fe^{2+}/Fe^{3+} ratios present on the octahedral sites and in turn decreases the rate of electron exchange between Fe^{2+} and Fe^{3+} ions. These results were also observed for other ferrite spinels [19,25]. (2) The decrease in the σ-values by γ-irradiation can be interpreted as follows:

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

This reversible interaction leads to the formation of some Fe^{2+} ions on tetrahedral sites and at the same time causes a decrease in Fe^{2+}/Fe^{3+} ratios present on octahedral sites. At the same time, the possibility of the formation of Zn and Zn^+ ions on tetrahedral positions in irradiated $Zn_xFe_{3-x}O_4$ is not excluded here. This is due to transfer of the electron released from Fe^{2+} ions during the irradiation process, onto Zn^{2+} ions. But the IR-spectra of $Zn_xFe_{3-x}O_4$, where $x > 0$, shows that the position of the ν_3 band (~ 340 cm^{-1}), which is assigned to the tetrahedral vibration of Zn^{2+} ions, is not changed by irradiation. This means that, if Zn or Zn^+ defects are formed during the irradiation process, then their presence is in low concentration. However, the formation of low concentrations of Zn defect in irradiated $Zn_xFe_{3-x}O_4$ should lead to an increase in the σ-values by irradiation: this is not observed in our results (Table 1). Therefore, the probability of the formation of Zn-defect in the irradiated samples is excluded here. Now, according to the above mechanism the conduction in irradiated samples will be attributed to the following: (i) The presence of Fe^{2+} and Fe^{3+} ions on tetrahedral positions: but, they do not contribute much to conduction (by the hopping mechanism), due to the large distance between tetrahedral sites compared with that between octahedral sites. (ii) The decrease in the Fe^{2+}/Fe^{3+} ratios present on octahedral sites due to the irradiation process. This causes a decrease in the rate of the electron exchange between Fe^{2+}/Fe^{3+} by the hopping mechanism, which also causes a decrease in the conductivity. (iii) The presence of Zn^+ defects on tetrahedral positions, but the contribution of this defect in the electrical conduction is very low. This is due to its presence in low concentrations and due to the lower rate of electron exchange between the different ions lying on tetrahedral positions by the hopping mechanism, as mentioned in (i). Generally, all these points cause a decrease in the σ-values of irradiated samples compared with those of non-irradiated ones, as shown in Table 1.

Secondly, for $x > 0.79$ our results show that the σ-values become very low and E_a-values become very high compared with those values where $x < 0.79$. This may be attributed to the greater decrease in the concentration of Fe^{2+} ions lying on octahedral sites which leads to disturbance of the electron exchange between Fe^{2+} and Fe^{3+} ions by other conduction mechanisms. The behaviour was also observed for other divalent substituted ferrites [26–29], at higher values of x, and the conduction could be explained on the basis of the transport of the charge carriers through cation vacancies.

The results of IR-spectra supported our assumption of the formation of Fe^{2+} ions induced by γ-irradiation, (eqn. (1)) on tetrahedral sites. The building of Fe^{2+} ions, which have a larger ionic radius than Fe^{3+} ions, on tetrahedral sites causes a shift in the ν_1 band to higher frequencies, as shown in Fig. 1.

CONCLUSION

The electrical conductivity of γ-irradiated and unirradiated $Zn_xFe_{3-x}O_4$ spinels for $O \leqslant x \leqslant 0.79$ can be interpreted as due to an electron exchange between Fe^{2+}/Fe^{3+} ions lying on octahedral sites (hopping mechanism). Whereas for $x > 0.79$ the conduction may proceed through cation vacancies. The γ-irradiation process causes a decrease in the electrical conduction due to the decrease in the ratios of Fe^{2+}/Fe^{3+} present on octahedral sites. All the investigated irradiated and unirradiated ferrites behave as n-donor semiconductors.

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