Electrical conduction in γ-irradiated and unirradiated zinc–iron ferrites

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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 a 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, by a hopping mechanism. For composition $x > 0.79$ 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. 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.

1. 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 brackets. Several workers [5–10] have studied solid solution by substituting ions at A and B sites. They have obtained a gradual change in the 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 $(Fe_1^{3+})_A[Fe_1^{2+} Fe_1^{3+}]_BO_4^{2-}$. It has been found [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 considered as the reason for the higher electrical conductivity in the case of lower values of x. For higher x values other conduction mechanisms should be considered.

The effect of ionizing radiation on the electrical properties of mixed oxides has received limited attention. With a view to investigating the effect of γ-irradiation on the electrical properties of ferrites the system $(Zn_x^{2+} Fe_{1-x}^{3+})_A[Fe_{1-x}^{2+} Fe_{1+x}^{3+}]_BO_4^{2-}$ has been investigated.

2. Experimental procedure

Analar-grade zinc chloride, ferrous chloride, ferric chloride and sodium hydroxide were used to prepare the investigated samples. 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 sample was dried at 370 K, then calcined in a muffle furnace in an air atmosphere at 600 K for 6 h. The final product appeared as an extremely fine-grained solid.

The amounts of zinc and iron in each prepared spinel were 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. The 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 coincide well with those reported by Gillot *et al.* [19].

Electrical conductivity measurements were performed on pellets (diameter 7 mm and thickness 8 mm) prepared by the compression of powder under a pressure of $1400\,kg\,cm^{-2}$. The d.c. conductivity of zinc–iron ferrite was measured between 5 and 900 K with a method already reported [10]. The conductivity measurements were carried out in a nitrogen atmosphere. 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 $39\,rd\,sec^{-1}$ ($0.39\,Gy\,sec^{-1}$) for 160 h.

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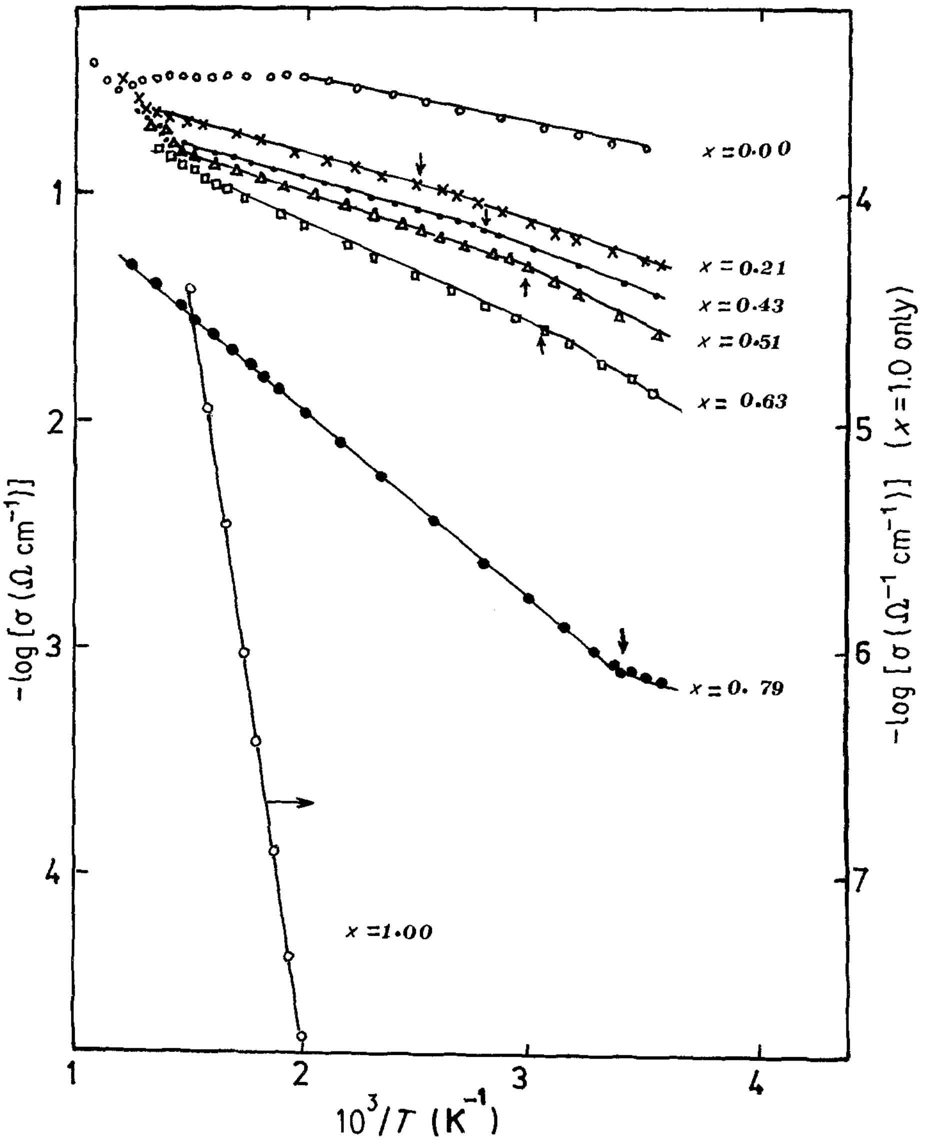

Figure 1 Effect of temperature on the electrical conductivity values of unirradiated $Zn_xFe_{3-x}O_4$ spinels.

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

3. Results

The relation between the logarithmic value of conductivity (log σ) of $Zn_xFe_{3-x}O_4$ spinels and the reciprocal temperature ($1/T$) is shown in Fig. 1. From the plots represented in this figure three types of straight line could be distinguished. For unirradiated ferrites $(Zn^{2+}_xFe^{3+}_{1-x})_A[Fe^{2+}_{1-x}Fe^{3+}_{1+x}]_BO^{2-}_4$ 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. For $x = 0.95$ and 1.00 the plots show straight lines without any break over the entire temperature range. All breaks at higher temperatures are in the 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 I. It can be seen from Table I that as the zinc concentration increases T_c decreases. Our results show also that the activation energy values (E_a), calculated according to the Arrhenius equation, increase on increasing the concentration of zinc in the ferrites.

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 the zinc concentration (Table I).

The effect of γ-irradiation on the electrical conductivity of the ferrite samples has been well studied using a dose of 22.5 Mrd (0.225 MGy). 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 measuring temperature. The plots of log σ against $1/T$ for irradiated samples show the same behaviour as that of unirradiated ones. The results for irradiated samples are summarized and given also in Table I. From this the following can be shown:

1. T_c moves towards lower temperatures for irradiated spinels compared with the values for corresponding unirradiated samples.
2. There is a slight increase in the activation energy values, in the temperature range 380 to 630 K, of

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

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

*Temperature range 300 to 580 K.

the irradiated samples compared with unirradiated ones.

3. More negative Seebeck voltages were recorded for the γ-irradiated samples compared with 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 $\sim 450\,cm^{-1}$ and a poorly defined band at $\sim 290\,cm^{-1}$. However, for unirradiated $Zn_xFe_{3-x}O_4$ samples, where $x > 0$, the IR spectra represented in Fig. 2 show two high-frequency bands located at 560 to $540\,cm^{-1}$ (ν_1) and 450 to $400\,cm^{-1}$ (ν_2) depending on the composition of the ferrites, in addition to a low-frequency band at 350 to $330\,cm^{-1}$ (ν_3). Waldron [23] and Hafner [24] attributed the ν_1 band to the intrinsic

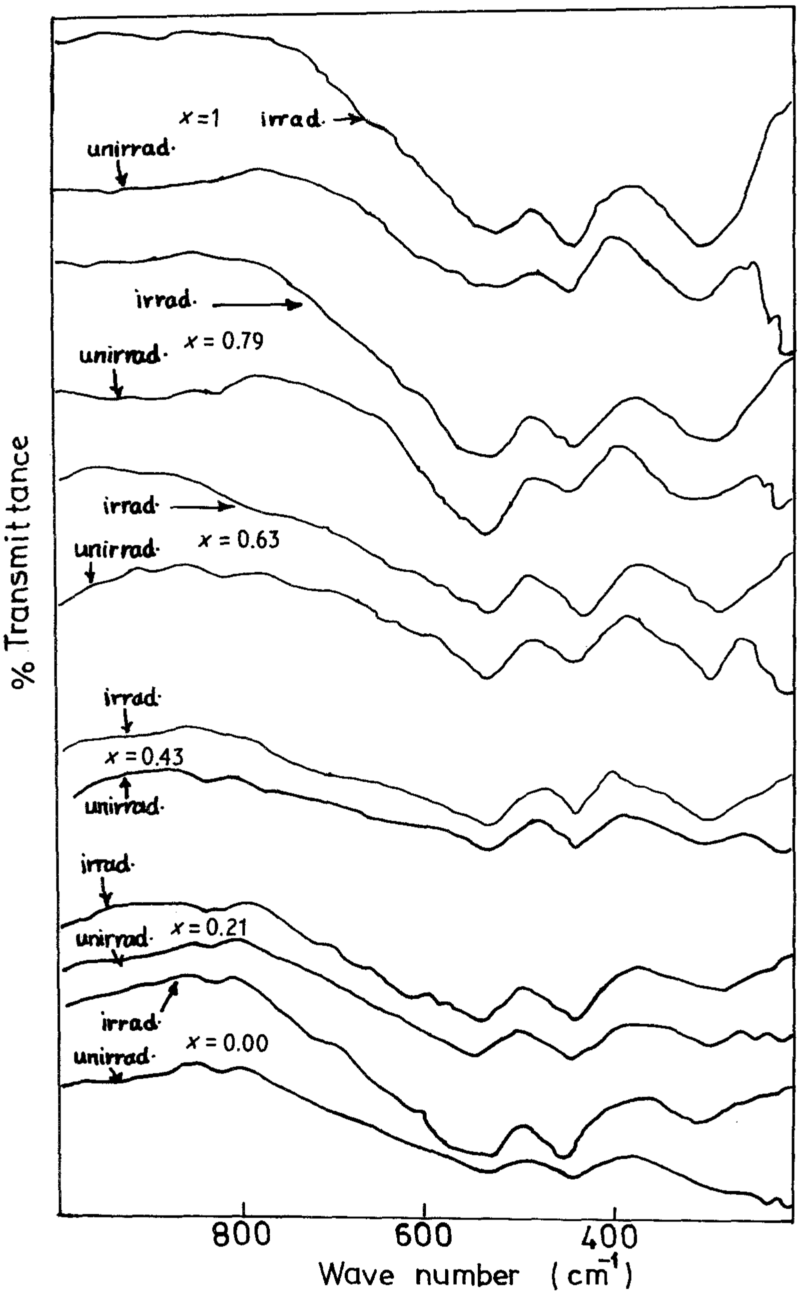

Figure 2 IR spectra of γ-irradiated and unirradiated $Zn_xFe_{3-x}O_4$ spinels.

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. The effect of γ-irradiation on the ferrite samples causes a shift 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 spectrum of the pure Fe_3O_4 sample.

4. 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 semiconduction. The breaks in σ values at higher temperatures are in the vicinity of the Curie temperatures of the investigated spinels [21, 22]. γ-irradiation does not change the sign of the Seeback voltage and leads to a very slight change in the activation energy of electrical conduction. This means that the conduction mechanism in the investigated spinels is not changed by the irradiation process. The displacements of T_c to lower temperatures by decreasing the content of Fe^{2+} ions in the spinels, as well as by the irradiation process, could be related to each other 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 difference in E_a values for $x \leqslant 0.79$ and $x > 0.79$ (Table I). This could be interpreted on a basis of the presence of two conduction mechanism 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 slightly increasing E_a values, with increasing concentration of Zn^{2+} ions can be attributed to a decrease in Fe^{2+} ions lying on octahedral sites. This leads to a decrease in the Fe^{2+}/Fe^{3+} ratios on the octahedral sites and in turn a decrease in 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 some formation of Fe^{2+} ions on tetrahedral sites and at the same time causes a decrease in the Fe^{2+}/Fe^{3+} ratios on octahedral sites. At the same time, the possibility of the formation of zinc atoms and Zn^+ ions on tetrahedral positions in irradiated $Zn_xFe_{3-x}O_4$ is not excluded here. This is due to the addition of electrons released from Fe^{2+} ions during the irradiation process, onto Zn^{2+} ions. However, the IR spectra of $Zn_xFe_{3-x}O_4$, where $x > 0$, show that the position of the ν_3-band ($\sim 340\,cm^{-1}$), which is assigned to the tetrahedral vibration of Zn^{2+} ions, does not change by irradiation. This means that, if zinc or Zn^+ defects are formed during the irradiation process, then they should be present in lower concentrations. However, the formation of lower concentrations of zinc defects in irradiated $Zn_xFe_{3-x}O_4$ should lead to an increase in the δ values by irradiation, but this is not observed in our results (Table I). Therefore, the formation of zinc defects in the irradiated samples can be 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. However, they do not contribute much to conduction by the hopping mechanism, due to the larger distance between tetrahedral sites compared with that between octahedral sites.

(ii) The decrease in the Fe^{2+}/Fe^{3+} ratios on octahedral sites by the irradiation process. This causes a decrease in the rate of electron exchange between Fe^{2+} and Fe^{3+} by the hopping mechanism, which also causes a decrease in the conductivity.

(iii) The presence of Zn^+ defects on tetrahedral positions. However, the contribution of this defect to the electrical conduction is very low. This is due to its presence in lower concentrations and due to the lower rate of the electron exchange between the different ions lying on tetrahedral positions by hopping mechanism, as mentioned in (i) above.

Generally, all these points cause a decrease in the σ values of irradiated samples compared with non-irradiated ones, as shown in our results (Table I).

Second, for $x > 0.79$ our results show that the σ values become very low and E_a values become very high as compared with those values where $x < 0.79$. This may be attributed to the higher decrease in the concentration of Fe^{2+} ions lying on octahedral sites, which upsets the electron exchange between Fe^{2+} and Fe^{3+} ions by other conduction mechanisms. This 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 (Equation 1) on tetrahedral sites. The accumulation 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.

5. Conclusion

The electrical conductivity of γ-irradiated and unirradiated $Zn_xFe_{3-x}O_4$ spinels for $0 \leqslant x \leqslant 0.79$ can be interpreted as due to an electron exchange between Fe^{2+} and 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 a decrease in the Fe^{2+}/Fe^{3+} ratios on octahedral sites. All the investigated irraidated and unirradiated ferrites behave as *n*-donor semiconductors.

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