

X-ray, Electrical Conductivity & Mössbauer Studies of System $\text{Zn}_{1-x}\text{Fe}_x\text{MnCrO}_4$

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The system $\text{Zn}_{1-x}\text{Fe}_x\text{MnCrO}_4$ is tetragonal in the range $0 \leq x \leq 0.25$ and cubic in the range $0.5 \leq x \leq 1.0$. Fe^{3+} ions occupy B-site and proportionate amount of manganese is displaced from B- to A-site. Displaced Mn^{3+} ions get reduced to Mn^{2+} ions which occupy A-site. All the compounds possess low mobility values (10^{-7} to 10^{-8} cm²/Vs) and conduction takes place via a hopping process. Electrical resistivity-temperature behaviour obeys Wilson's law for all the compounds and thermoelectric coefficient values vary between +60 and -120 $\mu\text{V/K}$. Mössbauer data show the presence of iron in Fe^{3+} state. The probable ionic configuration of the system is: $\text{Zn}_1^{2+} \text{Mn}_x^{2+} [\text{Fe}_x^{3+} \text{Mn}_{1-x}^{3+} \text{Cr}^{3+}] \text{O}_4^{2-}$.

Oxidic spinels, because of intrinsic theoretical and commercial importance, have been studied by several workers¹ and attempts have been made to correlate structure, bonding and magnetic properties. Ferrites have interesting structural, electrical and magnetic properties which are suited for a variety of applications. These properties depend crucially upon the nature, the valence states and distribution of the metal ions over two sites in the spinel (AB_2O_4) lattice. The compound ZnMnCrO_4 has been reported to be a normal spinel². It contains Mn^{3+} as a distorting ion and is tetragonal ($c/a > 1$), while FeMnCrO_4 containing the same concentration of manganese ions exhibits cubic³ symmetry. Belyaev *et al.*⁴ from magnetic measurements have shown that in FeMnCrO_4 , Mn^{2+} ions occupy A-sites while Cr^{3+} and Fe^{3+} are at B-sites. Therefore, with a view to investigating the systematic change in oxidation state and ionic configuration of these ions, the system $\text{Zn}_{1-x}\text{Fe}_x\text{MnCrO}_4$ has been studied using X-ray, Mössbauer and electrical conductivity measurements.

Materials and Methods

Different compositions of the system $\text{Zn}_{1-x}\text{Fe}_x\text{MnCrO}_4$ were prepared by mixing high purity oxides, ZnO , Mn_2O_3 , Cr_2O_3 , Fe_2O_3 and iron metal powder ($\text{Fe}_2\text{O}_3 + \text{Fe} \rightleftharpoons 3 \text{FeO}$) in acetone in appropriate molar proportions. The unreacted oxide mixture, after homogenising each composition was subjected to TG analysis (using MOM derivatograph) up to 1173K. The loss in mass at all compositions of the system was negligible (less than 0.03%) suggesting that the compounds were sufficiently stoichiometric. The pellets were prepared using 2% solution of poly(vinyl acetate) as a binder. To remove the binder, the pellets were slowly heated at 773K for 20 hr and then fired at 1173K for 40 hr under N_2 atmosphere.

X-ray diffraction patterns were taken on a Philips machine (PW 1051) using CuK_α radiation with Ni filter. The X-ray patterns of all the compositions did not show lines other than those belonging to spinel structure. To calculate the intensity, the areas under different hkl peaks were determined by planimeter and value obtained in relation to the peak area for 311 reflection was taken as 100. To calculate the relative integrated intensity (I) of a given hkl reflection, as seen in a diffractometer with a flat plate sample holder, the following formula suggested by Buerger⁵ was used,

$$I = [F_{hkl}]^2 P L_p \quad \dots (1)$$

where F is the structure factor, P the multiplicity factor and L_p the Lorentz polarisation factor. The atomic scattering powers were taken from literature⁶.

In spinel lattice the hkl reflections 220, 311, 222, 400, 422 and 440 are sensitive to cation distribution at both A- and B-sites. To determine the cation distribution and its variation with the composition, the intensity ratios (I_{220}/I_{400} , I_{220}/I_{440} and I_{400}/I_{440}) for different possible models of cation distribution were calculated and compared with the observed intensity ratios.

The DC resistivity was measured using LCR Marconi bridge. The end faces of each pellet were coated with a thin layer of conducting silver paste and the resistivity measured from room temperature to 773K using two probe technique. Thermoelectric coefficient measurements were carried out from room temperature to 573K. The sign of the thermoelectric coefficient value was designated as positive if the cold end was positive indicating p -type of semiconduction. The IR spectra were recorded in KBr on a Beckman double beam spectrophotometer from 1000 to 250 cm^{-1} .

Mössbauer spectrum for each sample (containing iron) was recorded using a constant acceleration drive in which the source could be moved with respect to a

stationary absorber operating in conjunction with a 512 channel analyzer. The spectrometer was calibrated with standard iron foil using ^{57}Co in copper matrix. About 20 mg of enriched sample was uniformly spread over 2.5 cm diameter disc. All spectra were recorded at 294K.

Results and Discussion

The results of X-ray analysis are given in Table 1 and the lattice constant versus composition is plotted in Fig. 1. The system is tetragonal in the range $0 \leq x \leq 0.25$ and cubic in the range $0.5 \leq x \leq 1.0$. The plot of $V^{1/3}$ versus composition shows a break near a critical composition region where change occurs in crystal structure. An inflection near critical composition region can be explained according to the model of Goodenough and Loeb⁷. In the cubic region the distortion of the individual octahedron is suppressed by the strain energy of the lattice d, the cations at *B*-site get ordered in alternate planes perpendicular to *C*-axis producing bulk tetragonal distortion. This causes an appreciable expansion of the lattice leading to an inflection in $V^{1/3}$ versus composition curve at the transition region. A similar break has earlier been observed by us⁸ in the oxidic spinel system $\text{ZnMn}_{2-2x}\text{Ni}_x\text{Ti}_x\text{O}_4$.

The compound ZnMnCrO_4 is tetragonal with lattice constants $a=8.27 \text{ \AA}$ and $c=8.71 \text{ \AA}$ while FeMnCrO_4 is cubic with $a=8.42 \text{ \AA}$ (Table 1). These values are in good agreement with values reported earlier^{2,3}. It is evident from Table 1 that ZnMnCrO_4 and $\text{Zn}_{0.75}\text{Fe}_{0.25}\text{MnCrO}_4$ have tetragonal symmetry because Mn^{3+} (*J-T*) ions occupy octahedral site. The cubic nature of the compounds ($x \geq 0.5$) is attributed to the fact that Mn^{3+} ion concentration decreases at *B*-site with increase in the concentration of iron in the lattice. When iron is introduced in the lattice it occupies octahedral site due to better site preference⁹ and hence proportionate amount of manganese is displaced to *A*-site. Our XRD intensity data (Table 2) show that manganese at *A*-site is in divalent state (Mn^{3+} ions are reduced to Mn^{2+} ions while going to

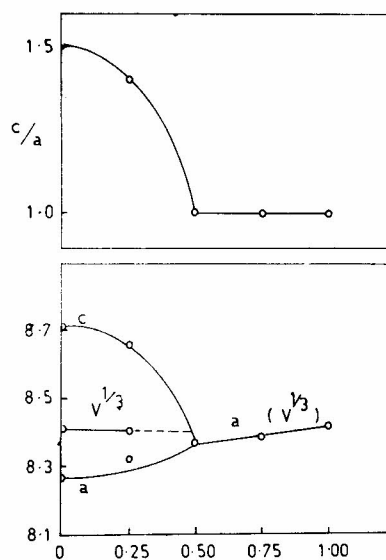


Fig. 1—Plot of lattice constant, c/a ratio versus composition for the system $\text{Zn}_{1-x}\text{Fe}_x\text{MnCrO}_4$

A-site) and hence Mn^{3+} (*J-T*) ion concentration at *B*-site decreases resulting in cubic symmetry. We have attempted to keep iron in ferrous state but our Mössbauer data (discussed later) show that iron is present in ferric state only, as a result of the equilibrium: $\text{Fe}^{2+} + \text{Mn}^{3+} \rightleftharpoons \text{Fe}^{3+} + \text{Mn}^{2+}$.

The cation distribution at two sites in the system has been arrived at by XRD intensity calculations carried out at an interval of $Y=0.05$ (whereby Y is the inversion parameter) for all the compositions. The various permutations and combinations for the cationic arrangements between two sites have been taken using the site preference energy data⁹. However, the observed and calculated intensity ratios which are comparatively closer are summarised in Table 2 for the following models in which (i) Zn^{2+} , Mn^{2+} ; (ii) Zn^{2+} , Mn^{2+} , Fe^{3+} ; (iii) Zn^{2+} , Fe^{3+} ; (iv) Zn^{2+} , Fe^{2+} ; and (v)

Table 1—Lattice Constant, c/a Ratio, Activation Energy (ΔE) and Thermoelectric Coefficient (α) values for the System $\text{Zn}_{1-x}\text{Fe}_x\text{MnCrO}_4$

Composition	Lattice constant (Å)	Structure type	c/a	Activation Energy ΔE (eV)	α ($\mu\text{V/K}$)
ZnMnCrO_4	$a=8.27$ $c=8.71$	T	1.05	0.53	60
$\text{Zn}_{0.75}\text{Fe}_{0.25}\text{MnCrO}_4$	$a=8.30$ $c=8.66$	T	1.04	0.55	40
$\text{Zn}_{0.5}\text{Fe}_{0.5}\text{MnCrO}_4$	$a=8.37$	C	1.00	0.59	33
$\text{Zn}_{0.25}\text{Fe}_{0.75}\text{MnCrO}_4$	$a=8.39$	C	1.00	0.62	-60
FeMnCrO_4	$a=8.42$	C	1.00	0.65	-120

Table 2—Comparison of Intensity Ratios for FeMnCrO_4

Cations at		I_{220}/I_{400}		I_{220}/I_{440}		I_{400}/I_{440}	
A-Site	B-Site	Obs	Calc	Obs	Calc	Obs	Calc
FeMnCrO_4							
Mn^{2+}	$\text{Fe}^{3+}\text{Cr}^{3+}$	1.28	1.30	0.60	0.60	0.47	0.46
$\text{Fe}^{3+}\text{Mn}^{2+}$	$\text{Mn}^{2+}\text{Fe}^{3+}\text{Cr}^{3+}$		1.38		0.62		0.44
Fe^{3+}	$\text{Mn}^{2+}\text{Cr}^{3+}$		1.47		0.63		0.43
Fe^{2+}	$\text{Mn}^{3+}\text{Cr}^{3+}$		1.60		0.67		0.41
$\text{Mn}^{3+}\text{Fe}^{2+}$	$\text{Mn}^{2+}\text{Fe}^{3+}\text{Cr}^{3+}$		1.38		0.62		0.44
$\text{Zn}_{0.5}\text{Fe}_{0.5}\text{MnCrO}_4$							
$\text{Zn}^{2+}\text{Fe}^{3+}\text{Mn}^{2+}$	$\text{Mn}^{2+}\text{Fe}^{3+}\text{Cr}^{3+}$		2.12		0.70		0.30
$\text{Zn}^{2+}\text{Fe}^{3+}$	$\text{Mn}^{2+}\text{Mn}^{3+}\text{Cr}^{3+}$		2.16		0.71		0.29
$\text{Zn}^{2+}\text{Fe}^{2+}$	$\text{Mn}^{3+}\text{Cr}^{3+}$		2.20		0.78		0.28
$\text{Zn}^{2+}\text{Mn}^{3+}\text{Fe}^{2+}$	$\text{Mn}^{2+}\text{Fe}^{3+}\text{Cr}^{3+}$		2.11		0.71		0.30
$\text{Zn}^{2+}\text{Mn}^{2+}$	$\text{Fe}^{3+}\text{Cr}^{3+}$	2.05	2.04	0.68	0.68	0.33	0.34

Zn^{2+} , Mn^{3+} , Fe^{2+} are present at tetrahedral A-sites. It is seen that models in which Mn^{2+} in FeMnCrO_4 and Zn^{2+} and Mn^{2+} in $\text{Zn}_{0.5}\text{Fe}_{0.5}\text{MnCrO}_4$ are present at A-sites show better agreement with the observed and calculated intensity ratios. These models are also further supported by site preference energy values⁹ (Zn^{2+} , -31.6; Mn^{2+} , -14.7; Mn^{3+} , +3.1; Fe^{3+} , -13.3 and Cr^{3+} , +16.6 kcal/g at wt). Hence following ionic configuration is proposed for the present system: $\text{Zn}_{1-x}^{2+}\text{Mn}_x^{2+}[\text{Mn}_{1-x}^{3+}\text{Fe}_x^{3+}\text{Cr}^{3+}]\text{O}_4^{2-}$.

The DC resistivities of all the different compositions of the system, when measured as a function of temperature vary between 10^6 and 10^2 ohm cm^{-1} and the activation energies between 0.53 and 0.65 eV (Table 1). Electrical resistivity temperature behaviour obeys Wilson's law indicating semiconducting nature of different compositions (Fig. 2). High resistivity values indicate that the elements with only one stable oxidation state are present at B-sites. In transition metal oxides, electrical resistivity is low, if the compound contains the cations of the same element situated at similar sites but with their valency differing by unity¹⁰. Similar results have been observed by us in nickel manganite and copper manganese chromite¹¹.

The plot of thermo e.m.f. (ΔV) developed across the compounds against temperature difference (ΔT) is given in Fig. 3. From Table 1, is observed that the compounds ZnMnCrO_4 , $\text{Zn}_{0.75}\text{Fe}_{0.25}\text{MnCrO}_4$ and $\text{Zn}_{0.5}\text{Fe}_{0.5}\text{MnCrO}_4$ are *p*-type semiconductors while other compounds show *n*-type behaviour. Thermoelectric coefficient values are listed in Table 1.

The electrical conductivity (σ) is related to the number of charge carriers (n) and their mobility (μ) at room temperature by the relation:

$$\sigma = ne\mu \quad \dots (2)$$

where e is the electronic charge. Taking the average unit cell volume (8.38 Å³), the value of hole

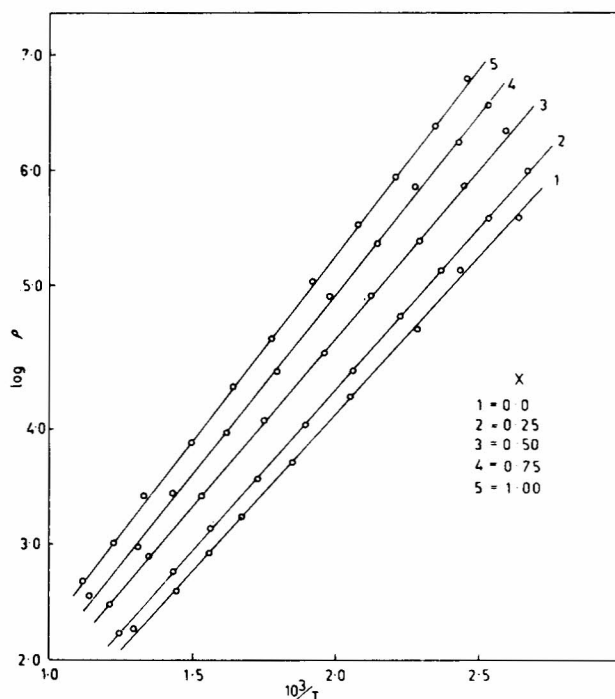


Fig. 2—Plot of $\log \rho$ versus $10^3/T$ for the system $\text{Zn}_{1-x}\text{Fe}_x\text{MnCrO}_4$

concentration would be $10^{22}/\text{cc}$ and mobility values vary between 10^{-7} and 10^{-8} cm^2/Vs . The mobility (μ) can be calculated using Heikes and Johnston equation¹².

$$\mu = \frac{ed^2v \exp. (-\Delta E/kT)}{kT} \quad \dots (3)$$

where ΔE is the activation energy, k the Boltzman constant, d the jump length and v the lattice frequency. The μ -value thus calculated is 10^{-9} cm^2/Vs . Infrared spectra of different compositions of the system exhibit two strong absorption bands at 450 and 600 cm^{-1} .

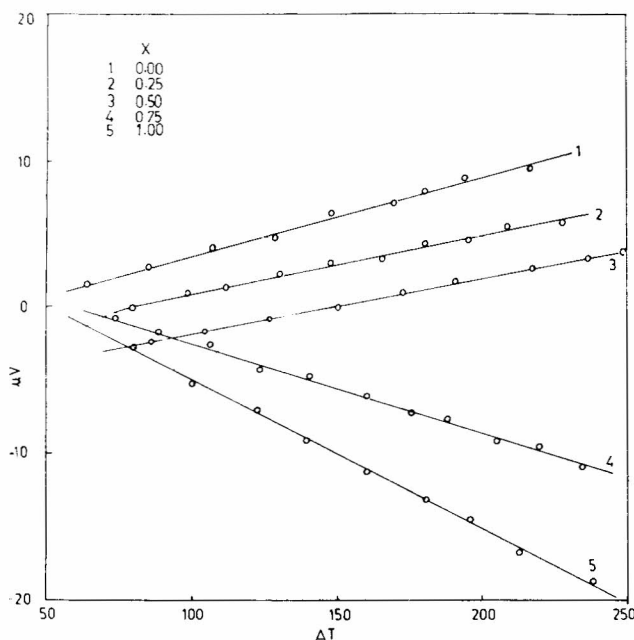


Fig. 3—Plot of μV versus ΔT for the system $Zn_{1-x}Fe_xMnCrO_4$

These bands are due to the intrinsic vibration of octahedral cations¹³. However, the band at 600 cm^{-1} , which is stronger of the two, has been taken into consideration while using Eq. (3) for the calculation of mobility (μ).

The different compositions of the system $Zn_{1-x}Fe_xMnCrO_4$ possess low mobility values. In the case of low mobility semiconductors such as ferrites, the activation energy is often associated with the mobility of charge carriers rather than their concentration. The charge carriers are considered as localised at the ions or vacant sites and the conduction occurs via a hopping type process which implies a thermally activated electronic mobility. As a result the carrier mobility shows an exponential $\Delta E/T$ dependence

$$\mu = \mu_0 \exp. (-\Delta E/kT) \quad \dots (4)$$

This type of behaviour arises due to the presence of significantly large energy separations between oxygen 3d, 4s and 2p band in transition metal oxides. Owing to this large separation, unlike metals, there is less hybridisation of 3d, 4s and oxygen 2p orbitals which inhibit itinerant conduction behaviour¹⁴. On substituting Fe^{3+} in the lattice, ΔE increases (Table 1) due to the fact that completely filled Zn^{2+} d-orbitals have much lower energy and are more contracted than the Fe^{3+} orbitals.

It is well known that the electrical conductivity in solids is highly sensitive to the slight variation in stoichiometry or defect formation. In the present system wherein octahedral sites are occupied by Mn^{3+} , Fe^{3+} and Cr^{3+} ions, first three compounds are p-type

semiconductors and this is attributed to $Mn^{3+} + Mn^{4+}$ pair formation. Very small concentration of Mn^{4+} must be present in the lattice otherwise compounds would have shown insulating nature. The p-type behaviour in zinc-rich compounds can also be attributed to the loss of zinc in firing process and as a result cation vacancies are created at A-site and hence compounds show p-type conduction. Such a mechanism has been observed by Blasse¹⁵ and Lotgering¹⁶ in the case of zinc-rich compounds.

The compounds $Zn_{0.25}Fe_{0.75}MnCrO_4$ and $FeMnCrO_4$ show n-type behaviour. In these compositions a little oxygen deficiency is suspected owing to the ability of Fe_2O_3 to lose oxygen when heated at elevated temperatures. This oxygen non-stoichiometry will give rise to some Cr^{2+} ions so as to maintain the electrical neutrality. The n-type behaviour in these compounds can also be attributed to the following hopping mechanism: $Mn^{2+} + Mn^{3+} \rightleftharpoons Mn^{3+} + Mn^{2+}$. Thus we have both types of charge carriers in these compounds and the observed thermoelectric coefficient (α) results from the compensating effect of p-type and n-type charge carriers.

In $Zn_{1-x}Fe_xMnCrO_4$ the observed thermoelectric coefficient is temperature-independent and charge carriers show phonon-assisted hopping with low mobility values. These results probably characterise the presence of small polaron hopping charge carriers¹⁷⁻¹⁹.

The room temperature Mössbauer spectra for the compounds $x=0.5$ and 1 are shown in Fig. 4. The spectra of all the compounds show quadrupole splitting varying from 0.58 to 0.38 mm/s (In the system $Zn_{1-x}Fe_xMnCrO_4$ for $x=0.25, 0.5, 0.75$ and 1.0 the quadrupole splitting values are 0.58, 0.46, 0.42 and 0.38 respectively). The quadrupole splitting decreases with decrease in concentration of Mn^{3+} (J-T) and increase in concentration of Fe^{3+} ions at B-sites. Further there is sudden decrease in the quadrupole splitting for the composition $Zn_{0.5}Fe_{0.5}MnCrO_4$ where change in crystal structure from tetragonal to cubic occurs. Similar observation has also been reported by Jain and Darshane²⁰ for the system $Zn_{1-x}Co_xFeMnO_4$.

In fact all the compounds of the system should have shown zero quadrupole splitting since Fe^{3+} ion at B-sites is S state ion (σ_s ground state) with spherically symmetric electronic configuration. Consequently, there should not have been any electric field gradient (EFG). However, in all the compounds quadrupole splitting is observed. This behaviour is explained as follows. It is possible that the original trigonal field at the octahedral site may lift the degeneracy of the t_{2g} orbitals thereby causing EFG at the Fe^{3+} nucleus, leading to quadrupole splitting²¹.

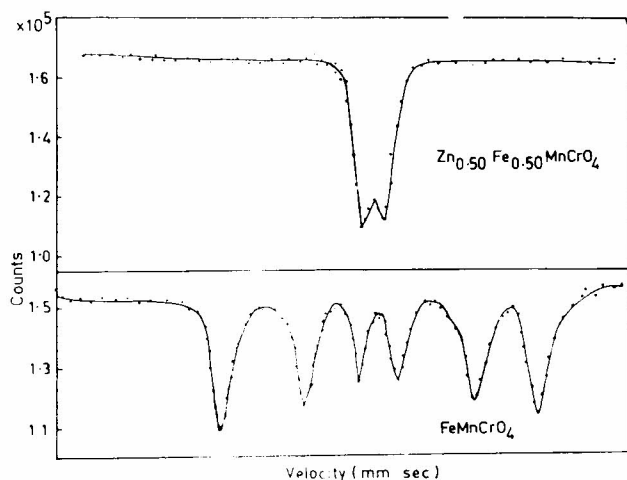


Fig. 4 —Mössbauer spectra at 294 K

Isomer shift value for tetragonally distorted $\text{Zn}_{0.75}\text{Fe}_{0.25}\text{MnCrO}_4$ is 0.38 ± 0.02 mm/s while for cubic compounds the values are 0.26, 0.24 and 0.23 ± 0.02 mm/s with respect to iron. The present isomer shift values are typical of high spin Fe^{3+} ions (0.20 to 0.50 mm/s) at *B*-site as reported by a number of workers²¹⁻²³.

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