JOURNAL OF MATERIALS SCIENCE 24 (1989) 163-166

X-ray, electrical conductivity and infrared studies of the system $Zn_{1-x}CO_xMn_{1-x}Fe_xCrO_4$

M. N. KHAN, ASHFAQ AHMED,
Department of Physics, University of Bahrain, Bahrain
V. S. DARSHANE
Department of Chemistry, Institute of Science, Bombay 400032, India

The system $Zn_{1-x}Co_xMn_{1-x}Fe_xCrO_4$ is tetragonal in the range $0.0 \leqslant x \leqslant 0.4$ and cubic in the range $0.5 \leqslant x \leqslant 1$. Electrical resistivity temperature behaviour obeys Wilson's law for all the compounds and thermoelectric coefficient values vary between 135 to $226\,\mu V\,K^{-1}$. All compounds exhibit P-type semiconductivity and possess low mobility values ($10^{-9}\,cm^2\,V^{-1}\,sec^{-1}$). The infrared spectra show the presence of two strong absorption bands around 500 and $600\,cm^{-1}$. The probable ionic configuration for the system is suggested to be $Zn^{2+}_{1-x}Fe^{3+}_{x-y}$-$Co^{2+}_x[Mn^{3+}_{1-x}Fe^{3+}_y CO^{2+}_{x-y}Cr^{3+}]O_4$.

1. Introduction

Spinels of (AB_2O_4) type show interesting structural, electrical and magnetic properties. These properties are controlled by the nature of the ions, their charge and site distribution amongst tetrahedral and octahedral sites. Several workers [1–10] have studied solid solutions by substituting ions at A- and B-sites. O'Keefe [7] observed that the number of Mn^{3+} ions required to produce tetragonal distortion depends on the nature of the other ions present. The compound $ZnMnCrO_4$ has been reported to be a normal spinel [11]. It contains Mn^{3+} as a distorting ion and is tetragonal ($c/a > 1$). We have attempted to replace Zn^{2+} by CO^{2+} and Mn^{3+} by Fe^{3+} in the lattice and investigated the systemic change in the oxidation state and ionic configuration for the system Zn_{1-x}-$CO_xMn_{1-x}Fe_xCrO_4$ with help of X-ray, electrical conductivity, thermoelectric coefficient and infrared (IR) measurements.

2. Experimental procedure

Different compositions of the system, $Zn_{1-x}CO_x$-$Mn_{1-x}Fe_xCrO_4$ ($x = 0.0$, 0.2, 0.4, 0.5, 0.6, 0.8 and 1.0) were prepared by mixing high-purity oxides, CoO (prepared from CO_3O_4), ZnO, Fe_2O_3, Mn_2O_3 and Cr_2O_3 in acetone using appropriate molar proportions. The pellets were prepared by compressing the powder to 10 000 p.s.i. ($\sim 68.9\,N\,mm^{-2}$) using polyvinyl acetate as a binder. Pellets were first slowly fired at 773 K for 20 h in order to remove the binder and then were heated at 1173 K for 80 h.

X-ray diffraction patterns were taken on a diffractometer (Philips machine PW 1051) using Cu*Kα* radiation with a nickel filter. The X-ray patterns of all the compositions indicate the formation of a simple spinel phase. To measure the intensity, the areas under different [*h k l*] peaks were determined and values were obtained in relation to the peak area for the 3 1 1 reflection which was taken as 100. To calculate the relative integrated intensity (I) of a given [*h k l*] reflection the following formula, suggested by Buerger [12], was used.

$$I = [F_{hkl}]^2\, P\left(\frac{1 + \cos^2 2\theta}{\sin^2\theta \cos\theta}\right) \qquad (1)$$

where F is the structure factor, P is the multiplicity factor and the term

$$\frac{1 + \cos^2 2\theta}{\sin^2\theta \cos\theta} = \mathrm{LP}$$

which is the Lorentz-Polarization factor. The atomic scattering powers were taken from the literature (International Tables, 1959)..

In the spinel lattice, the [*h k l*] reflections 2 2 0, 3 1 1, 2 2 2, 4 0 0, 4 2 2, and 4 4 0 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}, I_{440}/I_{422}) for different possible models of cation distributions were calculated and compared with the observed intensity ratios.

The d.c. resistivity was investigated using an LCR Marconi bridge. The end faces of each pellet were coated with a thin layer of conducting silver paste and resistivity was measured from 400 to 800 K using a two-probe technique. Thermoelectric coefficient was measured from room temperature to 440 K. The sign of thermoelectric coefficient value was designated as positive if the cold end was positive indicating p-type semiconduction.

The IR spectra were recorded on a Perkin–Elmer Infrared Spectrophotometer in the range 200 to $4000\,cm^{-1}$.

3. Results and discussion

The results of X-ray analysis are given in Table I. Plots of lattice constant against composition and c/a ratio against composition are shown in Figs 1 and 2. The

0022–2461/89 $03.00 + .12 © *1989 Chapman and Hall Ltd.*

TABLE I Lattice constants, c/a ratio, activation energy (ΔE) and thermoelectric coefficient (α) values for the system $Zn_{1-x}CO_xMn_{1-x}Fe_xCrO_4$

Sample no.	Composition x	Lattice constant		Structure type	c/a	ΔE (eV)	(μV K^{-1})
		a (nm)	c (nm)				
1.	0.0	0.830	0.868	T	1.046	0.48	135
2.	0.2	0.827	0.863	T	1.044	0.54	140
3.	0.4	0.828	0.856	T	1.034	0.59	165
4.	0.5	0.842	0.842	C	1.000	0.61	200
5.	0.6	0.841	0.841	C	1.000	0.67	210
6.	0.8	0.839	0.839	C	1.000	0.68	220
7.	1.0	0.837	0.837	C	1.000	0.74	226

C = cubic, T = tetragonal.

system is tetragonal in the range $0 \leqslant x \leqslant 0.4$ and cubic in the range $0.5 \leqslant x \leqslant 1$. The plot of $V^{1/3}$ against composition shows a break near a critical composition region where change occurs in the crystal structure. Such an inflexion can be explained according to the model of Goodenough and Loeb [9]. In the cubic region the distortion of the individual octahedron is suppressed by the strain energy of the lattice d cation at B-site, yet was ordered producing bulk tetragonal distortion. This causes an appreciable expansion of the lattice leading to an inflexion in the $V^{1/3}$ against composition curve at the transition region. Similar studies were reported in the system, $ZnMn_{2-2x}Ni_xTi_xO_4$ by Mulla and Darshane [13].

The compound $ZnMnCrO_4$ is tetragonal (a = 0.830 nm and c = 0.868 nm). These values are in good agreement with values reported by Baltzer *et al.* [11] and Gorter [1]. The compound $COFeCrO_4$ is cubic (a = 0.838 nm) as shown in Table I. It is evident from Table I that $ZnMnCrO_4$ and $Zn_{0.6}Fe_{0.4}Mn_{0.6}CO_{0.4}CrO_4$ have tetragonal symmetry because Mn^{3+} (J–T) ions occupy an octahedral site. The cubic nature of the compound ($x \geqslant 0 5$) is attributed to the fact that the Mn^{3+} concentration decreases at the B-site with increase of Fe^{3+} in the lattice; it occupies an octahedral site due to better site preference [14] and a small amount of Fe^{3+} is displaced to an A-site in order to preserve the cubic symmetry.

The cationic distribution at two sites in the system has been concluded from X-ray intensity calculation taking into consideration the structure factor for the planes 220, 400, 422, and 440 which are quite sensitive to cation distribution. The observed and calculated intensity ratios for the compound $COFeCrO_4$ and $Zn^{2+}_{0.5}Fe^{3+}_{0.5}Mn^{3+}_{0.5}CO^{2+}_{0.5}Cr^{3+}O_4$ using different models are summarized in Table II and III. It is seen that the models in which $Fe^{3+}_{0.20}CO^{2+}_{0.80}$ in $COFeCrO_4$ and $Zn^{2+}_{0.50}Fe^{3+}_{0.30}CO^{2+}_{0.20}$ in $Zn_{0.50}Fe_{0.50}Mn_{0.50}CO_{0.50}CrO_4$ are present at A-sites, while $Mn^{3+}_{0.50}CO^{2+}_{0.30}Fe^{3+}_{0.20}CrO_4^{3+}$ are at B-sites, show better agreement. This site occupancy is in agreement with the site preference energy data [14].

The d.c. resistivities of all different compositions of the system, when measured as a function of temperature, vary between 106 and 102 Ω cm^{-1} and activation energies vary between 0.48 and 0.74 eV (Table I). Electrical resistivity temperature behaviour as shown in Fig. 3, obeys Wilson's law $\varrho = \varrho_0 \exp [\Delta E/KT]$, indicating the semiconducting nature of all the compounds. In transition metal oxides, electrical resistivity is low, if the compound contains cations of the same element situated at similar sites but with their valency differing by unity [15]. High resistivity values indicate that the elements with only one stable oxidation state are present at the B-site. Similar results have been reported by Mulla and Darshane [16].

The plot of thermo e.m.f. (μV) developed across the compounds against temperature differences (ΔT) is given in Fig. 4. From Table I it is observed that all compounds of the system are p-type semiconductors. The reason can be attributed to the loss of some zinc oxide during the firing process creating vacancies at the A-site. As a result a small amount of Fe^{3+} may move from the B-site to the A-site. Such a possibility has been suggested by Blase [17] and Lotgering [18]. The cation valancies at the B-site will trap holes giving rise to p-type conduction.

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

$$\sigma = ne\mu \qquad (2)$$

where e is the electronic charge. Taking the average unit cell volume (0.835 nm), the value of hole concentration

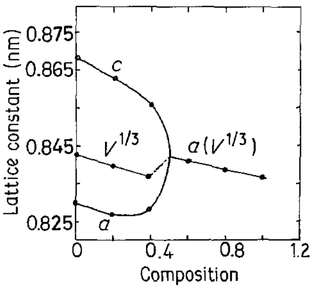

Figure 1 Plot of lattice constant against composition for the system $Zn_{1-x}CO_xMn_{1-x}Fe_xCrO_4$.

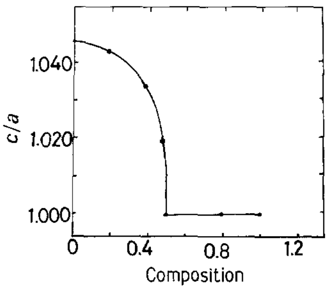

Figure 2 Plot of c/a ratio against composition.

TABLE II Comparison of intensity ratios for $COFeCrO_4$

Cations at		I_{220}/I_{440}		I_{220}/I_{400}		I_{440}/I_{422}	
A-site	B-site	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
Fe^{3+}	CO^{2+}, Cr^{3+}		0.61		1.33		1.97
Fe^{2+}	CO^{3+}, Cr^{3+}		0.69		1.58		1.92
CO^{2+}	Fe^{3+}, Cr^{3+}		0.70		1.82		1.47
Cr^{3+}	Fe^{3+}, CO^{2+}	0.68	0.50	1.71	0.89	1.60	3.04
$Fe^{2+}_{0.5}$, $Fe^{3+}_{0.5}$	$CO^{2+}_{0.5}$, $CO^{3+}_{0.5}$, Cr^{3+}		0.65		1.42		1.98
$Fe^{3+}_{0.2}$, $CO^{2+}_{0.8}$	$Fe^{3+}_{0.8}$, $Fe^{2+}_{0.2}$, Cr^{3+}		0.68		1.71		1.56

TABLE III Comparison of intensity ratios for $Zn_{0.5}CO_{0.5}Mn_{0.5}Fe_{0.5}CrO_4$

Cations at		I_{220}/I_{440}		I_{220}/I_{400}		I_{440}/I_{422}	
A-site	B-site	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
$Zn^{2+}_{0.5}$, $Fe^{3+}_{0.5}$	$Mn^{3+}_{0.5}$, $CO^{2+}_{0.5}$, Cr^{3+}		0.69		2.00		1.28
$Zn^{2+}_{0.5}$, $CO^{2+}_{0.5}$	$Fe^{3+}_{0.5}$, $Mn^{3+}_{0.5}$, Cr^{3+}		0.74		2.32		1.12
$Zn^{2+}_{0.5}$, $Fe^{2+}_{0.5}$	$CO^{2+}_{0.5}$, $Mn^{3+}_{0.5}$, Cr^{3+}		0.74		2.08		1.26
$Zn^{2+}_{0.5}$, $Fe^{2+}_{0.5}$	$CO^{2+}_{0.5}$, $Mn^{+4}_{0.5}$, Cr^{3+}	0.71	0.72	2.14	2.04	1.20	1.28
$Zn^{2+}_{0.5}$, $Fe^{3+}_{0.5}$	$CO^{2+}_{0.25}$, $CO^{3+}_{0.25}$, $Mn^{2+}_{0.25}$, $Mn^{3+}_{0.25}$, Cr^{3+}		0.72		1.99		1.29
$Zn^{2+}_{0.5}$, $Fe^{3+}_{0.3}$, $CO^{2+}_{0.2}$	$Mn^{3+}_{0.5}$, $CO^{2+}_{0.3}$, $Fe^{3+}_{0.2}$, Cr^{3+}		0.71		2.13		1.21

is found to be $5.82 \times 10^{22}\,cm^{-3}$ and mobility value is $10^{-9}\,cm^2\,V^{-1}\,sec^{-1}$.

The mobility (μ) can be calculated using Heikes and Johnston's equation [19]

$$\mu = \frac{ed^2\gamma \exp(-\Delta E/KT)}{KT} \qquad (3)$$

where e is electronic charge, d is the jump length, γ is lattice frequency, K is Boltzmann's constant, ΔE is the activation energy and T is the temperature in K. The mobility value is found to be $10^{-9}\,cm^2\,V^{-1}\,sec^{-1}$. Infrared spectra of different compositions of the system exhibit two strong absorption bands at 500 and $600\,cm^{-1}$. However, the band at $600\,cm^{-1}$, which is the stronger of the two, has been taken into consideration for calculating the lattice frequency in Equation 3.

All the compounds of the system possess low mobility which increases exponentially with increasing temperature following the relationship

$$\mu = \mu_0 \exp(-\Delta E/KT)$$

where μ_0 is a constant representing the mobility at $T = \infty$. In the case of low-mobility semiconductors and their exponential temperature dependence, the charge carriers are located at a particular site and electrical conduction involves the hopping of charge carriers from one site to another, driving lattice variations. The mobility shows exponential temperature dependence.

From Table I, it is seen that the activation energy increases due to the fact that the concentration of Fe^{3+} increases in the lattice which substitutes Mn^{3+} in the lattice. It may be also possible that the Zn^{2+} d^{10} orbitals have a much lower energy and are more contracted that CO^{2+} d^7 orbitals.

Torte and co-worker [20, 21] have observed that in normal ferrites both the absorption bands depend on the nature of octahedral cations and do not significantly depend upon the nature of the tetrahedral ions. However, Waldron [22] and Hafner [23], who were amongst the first to study the vibrational spectra of ferrites, attribute the band around $600\,cm^{-1}$ to the intrinsic vibrations of tetrahedral complexes and that around $450\,cm^{-1}$ to the intrinsic vibrations of octahedral complexes. The IR spectrum of $ZnMnCrO_4$ obtained here reveals that the absorption band around $600\,cm^{-1}$ does not show any splitting or shoulder. However, there is evidence of weak splitting in the absorption band around $500\,cm^{-1}$ which may be due

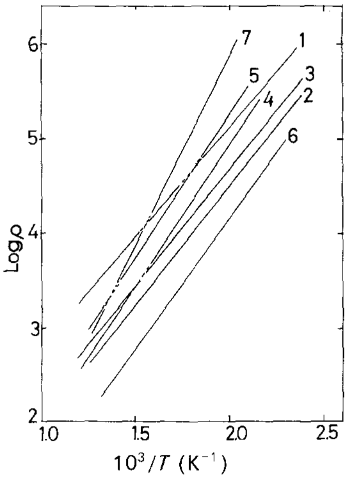

Figure 3 Plot of log ϱ against $10^3/T$ for the system $Zn_{1-x}CO_xMn_{1-x}Fe_xCrO_4$.

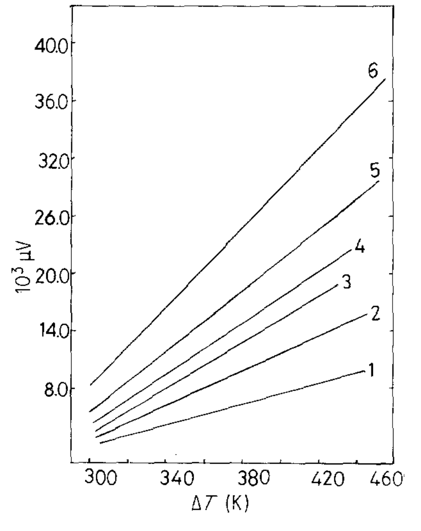

Figure 4 Plot of thermo e.m.f. against temperature.

to the presence of the Mn^{3+} (J–T) ion at the B-site. It is well known that the vibration frequencies depend on the cation mass, cation oxygen bonding force, distance and unit-cell parameter. Thus from X-ray, electrical and IR studies, we suggest the probable cation distribution for the system to be

$$Zn^{2+}_{1-x}Fe^{3+}_{x-y}CO^{2+}_{x}[Mn^{3+}_{1-x}Fe^{3+}_{y}CO^{2+}_{x-y}Cr^{3+}]O^{2-}_{4}$$

Acknowledgements

M. N. Khan acknowledges the laboratory assistance of Evelyn Holt, Brunel University in the area of X-ray diffraction work. The support and encouragement given by Dr Marwan Kamal, President of the University of Bahrain is gratefully acknowledged.

References

1. E. W. GORTER, *Philips Res. Rept.* **9** (1954) 295.
2. T. M. HASTINGS and L. M. CORLESS, *Rev. Mod. Phys.* **25** (1953) 114.
3. S. T. KSHIRSAGAR and A. B. BISWAS, *J. Phys. Chem. Solids* **28** (1967) 1493.
4. D. G. VICKHAM and W. J. CROFT, *ibid.* **7** (1958) 351.
5. H. BLASE, *Philips. Res. Rept.* **20** (1965) 528.
6. A. BHADURI, H. V. KEER and A. B. BISWAS, *Ind. J. Pure Appl. Phys.* **12** (1974) 745.
7. M. O'KEEFE, *J. Phys. Chem. Solids* **21** (1961) 172.
8. P. D. DESHPANDE, D. K. KULKARNI and P. V. KHANDEKAR, *Curr. Sci.* **43** (1974) 474.
9. J. B. GOODENOUGH and A. L. LOEB, *Phys. Rev.* **98** (1955) 391.
10. P. S. JAIN and V. S. DARSHANE, *Ind. J. Chem.* **19A** (1980) 153.
11. P. K. BALTZER, P. J. WOJTWICZ, M. ROBBINS and E. LOPATIN, *Phys. Rev.* **151** (1966) 367.
12. M. BUERGER, *J. Crystal Struct. Anal.* (Wiley, New York, 1960).
13. B. A. MULLA and V. S. DARSHANE, *Proc. Ind. Acad. Sci. (Chem. Sci)* **92** (1983) 139.
14. A. MILLER, *J. Appl. Phys.* **30** (1959) 245.
15. E. J. W. VERWEY, P. B. BRAWN, E. W. GORTER, F. C. ROMEIJN and J. H. Z. VAN SANTHEN, *Phys. Chem.* **198** (1951) 6.
16. B. A. MULLA and V. S. DARSHANE, *Ind. J. Chem.* **22A** (1983) 143.
17. G. BLASE, *J. Phys. Chem. Solids* **27** (1966) 383.
18. F. K. LOTGERING, *ibid.* **27** (1966) 139.
19. R. R. HEIKES and W. D. JOHNSTON, *J. Chem. Phys.* **26** (1957) 582.
20. P. TORTE, *Spectrochim. Acta* **19** (1965) 49.
21. J. PREUDHOMME and P. TORTE, *ibid.* **27A** (1971) 961.
22. R. D. WALDRON, *Phys. Rev.* **99** (1955) 1727.
23. S. Z. HAFNER, *Kristallogr.* **115** (1961) 331.

Received 14 October 1987
and accepted 11 February 1988