

# The preparation, characterization and electrical properties of copper manganite spinels, $\text{Cu}_x\text{Mn}_{3-x}\text{O}_4$ , $0 \leq x \leq 1$

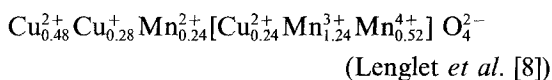
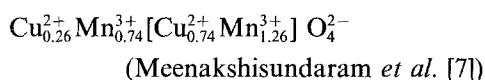
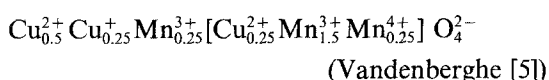
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Single-phase copper manganite spinels  $\text{Cu}_x\text{Mn}_{3-x}\text{O}_4$  with  $0 \leq x \leq 1$  were prepared by a careful thermal processing of copper-manganese co-precipitated hydroxide precursors. Powder X-ray diffraction (XRD) analysis of these spinels revealed the presence of a tetragonally distorted single spinel phase, with tetragonal distortion  $c/a > 1$  which decreases with copper content. Thermogravimetric analysis (TGA) curves, run in an oxygen atmosphere for all the compositions studied, are characterized by a stability step up to 250 to 300°C, followed by a domain of oxidation between 300 and 900°C and finally a domain of reduction that restores the initial stoichiometry of the samples. The oxidation is observed to occur in two successive steps. The phenomenon appearing at the low temperature is due to the oxidation of  $\text{Cu}^+$  ions, while that at higher temperature corresponds to the oxidation of  $\text{Mn}^{2+}$  ions in tetrahedral sites. Further, electrical resistivity measurements confirm the presence of  $\text{Cu}^+$  ions on the tetrahedral sublattice of spinel. Correlation of the results obtained by XRD, TGA and electrical resistivity measurements permits one to infer the cation distribution, given by  $\text{Cu}_x^+ \text{Mn}_{1-x}^{2+} [\text{Mn}_{2-x}^{3+} \text{Mn}_x^{4+}] \text{O}_4^{2-}$ .

## 1. Introduction

The preparation and characterization of copper manganites,  $\text{Mn}_{3-x}\text{Cu}_x\text{O}_4$  with  $0 \leq x \leq 1$ , have been studied by many workers [1-13]. Despite these studies, outstanding differences of opinion persist regarding the distribution and valency states of the cations on the tetrahedral and octahedral sublattices of the spinel structure. For example, for  $\text{CuMn}_2\text{O}_4$  alone, the distribution of cations reported in the literature varies as much as follows:



where the square brackets indicate octahedral sites.

Further, for the  $\text{Mn}_{3-x}\text{Cu}_x\text{O}_4$  system with  $0 \leq x \leq 1$ , the existence of the tetragonal distribution at room temperature was shown by Driessens and Rieck [10] and Vandenberghe *et al.* [11] while contrarily a cubic structure was reported by Kshirsagar and Biswas [12] in the range  $0.6 \leq x \leq 1$  and a tetragonal structure in the range  $0 \leq x \leq 0.6$ .

In view of such conflicting observations and also in view of the difficulties involved in synthesizing single-phase compounds which often limit the corre-

lation of structure with properties, for example in relation to their applications as NTC thermistor components [14, 15], further studies on  $\text{Mn}_{3-x}\text{Cu}_x\text{O}_4$  systems are all the more justified.

In this communication we report our results on the preparation of single-phase  $\text{Cu}_x\text{Mn}_{3-x}\text{O}_4$  spinels and their characterization by means of powder X-ray diffraction (XRD), thermogravimetry (TG) and electrical conductivity measurements. This study has permitted us to correlate their structural characteristics, chemical reactivity and electrical properties.

## 2. Experimental procedure

Co-precipitated hydroxide precursors were obtained by addition of a slight excess of sodium hydroxide solution to the mixed and well stirred copper and manganese nitrate solutions. The precipitates thus obtained were washed with distilled water and dried at 60°C.

Thermal decomposition in air of the precursors does not lead directly to single spinel phase formation. Instead, the decomposition at 700°C results in a mixture of phase comprising  $\text{Mn}_2\text{O}_3$  and  $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4$ , as shown by XRD analyses and thermogravimetry. After 700°C, a weight loss due to the reduction of these oxides was observed. Then in the range 900 to 1200°C the solid solution  $\text{Cu}_x\text{Mn}_{3-x}\text{O}_4$  appeared with a slight presence of  $\text{Mn}_3\text{O}_4$  phase. For all compositions the magnitude and temperature of the reduction decrease with copper content (Figs 1 and 2). These features can be explained according to the

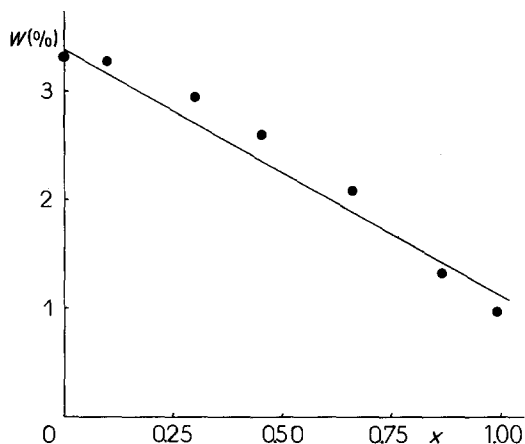
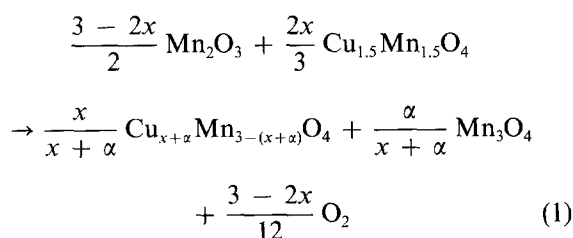


Figure 1 Weight loss  $W$  against copper content  $x$  in  $\text{Cu}_x\text{Mn}_{3-x}\text{O}_4$ . (—) Weight loss as calculated from Reaction 1 (see text) with  $\alpha \ll x$ ; (●) experimental weight loss obtained through TG analysis of  $\text{Cu}_x\text{Mn}_{3-x}\text{O}_4$  samples in the temperature range 830 to 980°C.

equation



with  $\alpha \ll x$ . The experimental weight loss as a function of copper content agrees with the weight loss calculated from Reaction 1 as shown in Fig. 1.

To obtain single-phase spinels with  $\text{Cu}_x\text{Mn}_{3-x}\text{O}_4$  with  $0 \leq x \leq 1$  the Mn-Cu co-precipitated hydroxide precursors were decomposed at 700°C to yield powders which were pressed into disc form (6 mm diameter and 2 mm thickness) under 7 kbar. These pressed discs were submitted to heat treatments in air, with different profiles, as depicted in Table I, to yield the single-phase spinels.

### 2.1. Physical measurements

On the above-mentioned single-phase  $\text{Cu}_x\text{Mn}_{3-x}\text{O}_4$  spinels, powder XRD patterns were recorded at room temperature using an automatic Siemens diffractometer D501 using  $\text{CoK}\alpha$  radiation.

Thermogravimetric measurements on these samples were performed in air or in an oxygen atmosphere

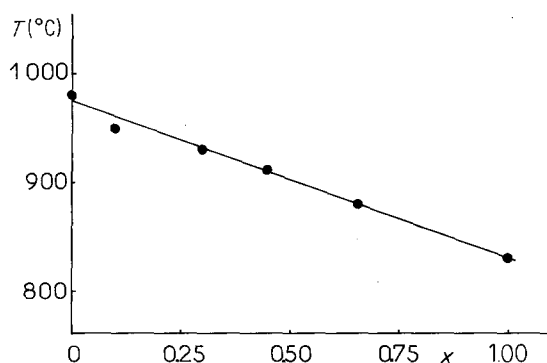


Figure 2 The temperature of reduction occurring about 700°C, as a function of copper content during thermal decomposition of hydroxide precursors.

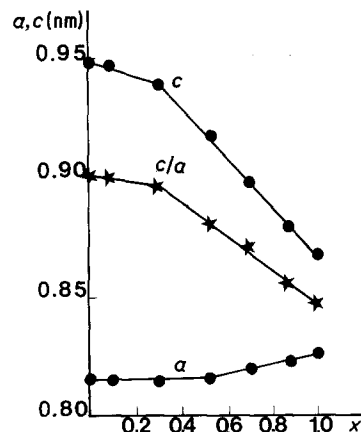


Figure 3 The lattice parameters  $a$  and  $c$  and the ratio  $c/a$  (no scale given) of  $\text{Cu}_x\text{Mn}_{3-x}\text{O}_4$  spinels determined as a function of copper content  $x$ .

using a Netzsch 409E analyser at a rate of heating of  $2^\circ\text{C min}^{-1}$ .

Electrical conductivity measurements were carried out at  $25 \pm 0.05^\circ\text{C}$  using an AOIPMN 5122 multimeter. Samples were prepared by depositing the silver electrodes on opposite faces of the disc samples, followed by their thermal treatment at 850°C.

## 3. Results and discussion

### 3.1. XRD Analyses

Fig. 3 depicts the evolution of lattice parameters for  $\text{Cu}_x\text{Mn}_{3-x}\text{O}_4$  specimens as a function of copper content  $x$ . All solid solutions  $\text{Cu}_x\text{Mn}_{3-x}\text{O}_4$  ( $0 \leq x \leq 1$ ) were found to be tetragonally distorted from cubic symmetry ( $c/a > 1$ ). Dunitz and Orgel [16, 17] have ascribed such distortion to the Jahn-Teller effect [18] on the octahedrally coordinated  $\text{Mn}^{3+}$  ions which stabilize the distortion with  $c/a > 1$ . The decrease of tetragonal distortion observed for our samples can be explained by taking into account the decreasing number of distorting ions like  $\text{Mn}^{3+}$  ions present both at the A and B sites, four limiting ionic configurations can be proposed as follows:

- (i)  $\text{Cu}_x^+ \text{Mn}_{1-x}^{2+} [\text{Mn}_{1-x}^{3+} \text{Mn}_x^{4+}] \text{O}_4^{2-}$
- (ii)  $\text{Cu}_x^{2+} \text{Mn}_{1-x}^{2+} [\text{Mn}_{2-x}^{3+}] \text{O}_4^{2-}$
- (iii)  $\text{Mn}^{2+} [\text{Cu}_x^+ \text{Mn}_{2-3x}^{3+} \text{Mn}_{2x}^{4+}] \text{O}_4^{2-}$
- (iv)  $\text{Mn}^{2+} [\text{Cu}_x^{2+} \text{Mn}_{2-2x}^{3+} \text{Mn}_x^{4+}] \text{O}_4^{2-}$

These four formulae can explain the decrease of tetragonal distortion as a function of copper content either by diminishing the  $\text{Mn}^{3+}$  ion content in B sites

TABLE I The conditions of preparation of single-phase spinels,  $\text{Cu}_x\text{Mn}_{3-x}\text{O}_4$  with  $0 \leq x \leq 1$

$x$	Heat treatment temperature ( $^\circ\text{C}$ )	Time (h)	Structure of spinel
0.00	1250	4	Tetragonal
0.09	1200	48	Tetragonal
0.15	1200	48	Tetragonal
0.30	1200	48	Tetragonal
0.45	1150	48	Tetragonal
0.60	980	48	Tetragonal
0.90	910	48	Tetragonal
0.99	900	48	Tetragonal

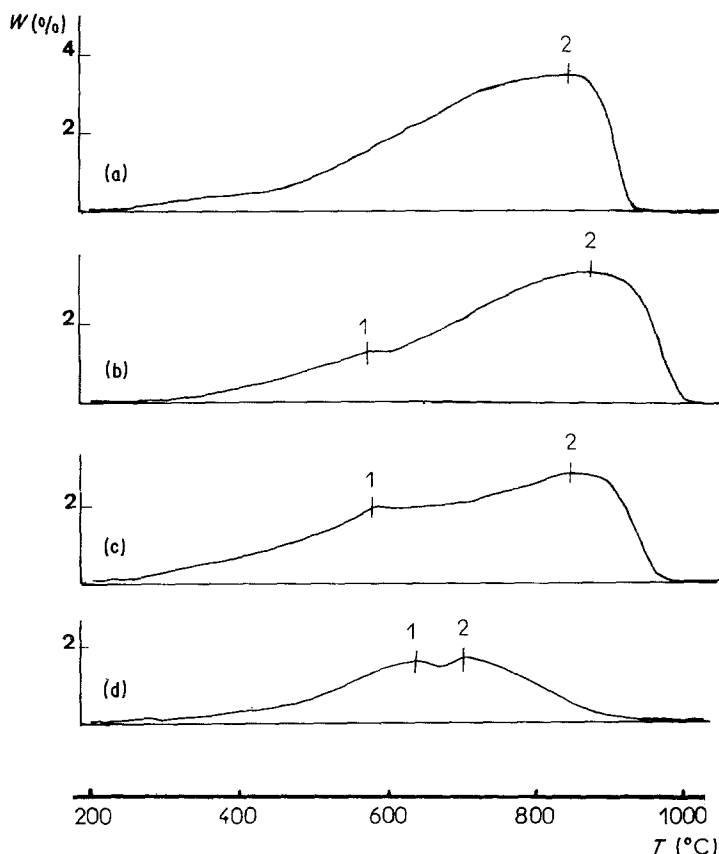


Figure 4 Thermogravimetric curves of  $\text{Cu}_x \text{Mn}_{3-x} \text{O}_4$  spinels up to  $1000^\circ \text{C}$ , under an oxygen atmosphere: (a)  $x = 0.00$ , (b)  $x = 0.10$ , (c)  $x = 0.30$ , (d)  $x = 0.86$ .

(Formulae (i), (iii) and (iv)) or because of the presence of  $\text{Cu}^{2+}$  in A sites (Formulae (ii)). Thus  $\text{Mn}^{3+}$  ions at the B sites produce tetragonal distortion with  $c/a > 1$  which is compensated in the opposite sense  $c/a < 1$  by  $\text{Cu}^{2+}$  at the A sites [19].

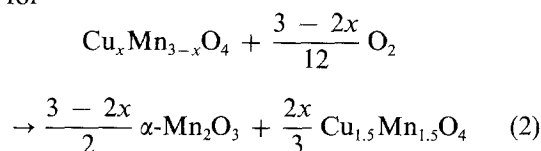
Baffier and Huber [20] have pointed out that the existence of the tetragonal distortion in ferromanganite spinels depends on the concentrations of  $\text{Mn}^{3+}$  ions. That means that they should be on about 50% of all the octahedral sites for giving rise to a tetragonal distortion. For  $\text{Mn}^{3+}$  ions under this concentration value, no tetragonal distortion did appear. Accordingly, it follows that out of the four configurations postulated above for our samples the last two, i.e. (iii) and (iv) are ruled out as the  $\text{Mn}^{3+}$  content is too low to give a tetragonal distortion corresponding to the compositions with  $x > 0.33$  and  $x > 0.50$ , respectively, in the case of Formulae (iii) and (iv). Only the configurations (i) and (ii) (copper ions at the A sites) may explain the observation of tetragonality throughout the range  $0 \leq x \leq 1$ .

### 3.2. Thermogravimetric studies

TGA on the copper manganites under an oxygen atmosphere up to  $1000^\circ \text{C}$  gave clues to the reactivity and stability of these systems with oxygen as a function of temperature. TGA curves (Fig. 4) for all the compositions studied are characterized by a stability step up to 250 to  $300^\circ \text{C}$  followed by a domain of oxidation between 300 and  $900^\circ \text{C}$ , and finally a domain of reduction that restores the initial stoichiometry of the samples.

Powder XRD analyses of the oxidation products indicate the existence of  $\alpha\text{-Mn}_2\text{O}_3$  and a cubic spinel phase. The determination of the total weight gain

during oxidation (Fig. 5) is found to follow the Reaction 2 below, as shown by a good correlation between the experimental points and the calculated curve for



After this oxidation in two steps, the samples are subjected to a decomposition such that the mixture of  $\alpha\text{-Mn}_2\text{O}_3 + \text{Cu}_{1.5} \text{Mn}_{1.5} \text{O}_4$  loses its excess oxygen and the stoichiometry of the manganites is restored, as confirmed by the presence of a single spinel phase by XRD analysis.

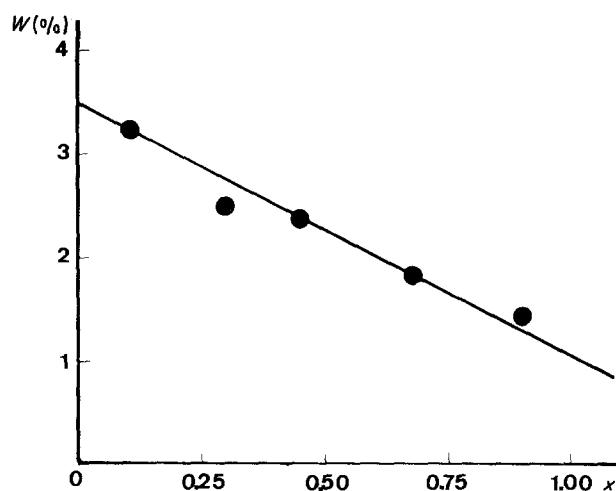


Figure 5 The variation of the total weight gain during the oxidation of  $\text{Cu}_x \text{Mn}_{3-x} \text{O}_4$  spinels as a function of copper content  $x$ . (—) Weight gain calculated from Reaction 2 (see text); (●) experimental weight gain discerned through TGA.

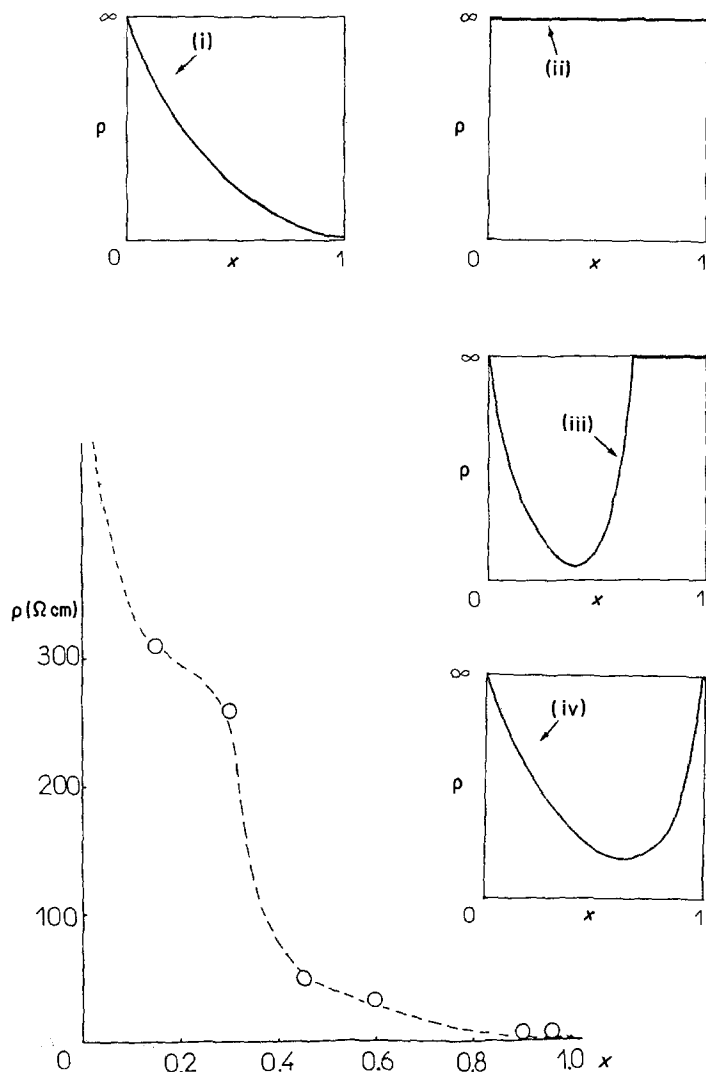
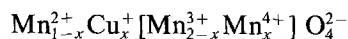


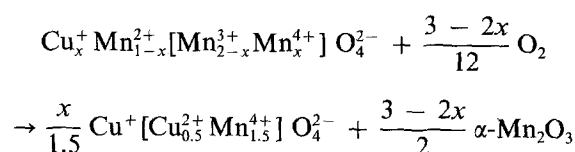
Figure 6 The electrical resistivity at 25°C against  $x$ . Curves (i) to (iv) show the theoretical variation of the electrical resistivity as a function of  $x$ , taking into account the variation of the number of  $\text{Mn}^{3+}\text{Mn}^{4+}$  pairs, for the four hypothetical distributions of Formulae (i) to (iv) (see text). Experimental points (O) show the observed variation of electrical resistivity with  $x$ .

The oxidation is observed to occur in two steps whose intensities vary as a function of copper content. A comparison of the thermal curves for samples with  $x = 0$  and  $x \neq 0$  permits us to attribute the phenomenon appearing at the higher temperatures to the oxidation of the tetrahedral  $\text{Mn}^{2+}$  ions to  $\text{Mn}^{3+}$  ions. The low-temperature oxidation step is due to the oxidation of  $\text{Cu}^+$  ions, and as expected it increases with  $x$  while the latter oxidation step diminishes with increasing  $x$  in accord with the increasing substitution of tetrahedral  $\text{Mn}^{2+}$  ions by  $\text{Cu}^+$  ions. These observations support for the following cation distribution:



which gives for  $x = 1$ ,  $\text{Cu}^+[\text{Mn}^{3+}\text{Mn}^{4+}]\text{O}_4^{2-}$  and the mechanism of oxidation may then be depicted by the

following:



It is of interest to note that the phases obtained during the oxidation of samples are identical to those existing in the same temperature region for products obtained by the thermal decomposition of co-precipitated hydroxide precursors. This explains why it is not possible to prepare the single-phase copper manganites in air below 900°C.

### 3.3. Electrical conductivity studies

Fig. 6 displays the variation of the d.c. resistivity at 25°C as a function of the copper content  $x$ , while Table II summarizes the electrical resistivity data. In all solid solutions  $\text{Cu}_x\text{Mn}_{3-x}\text{O}_4$  throughout the range  $0 \leq x \leq 1$  the resistivity decreases very rapidly with increasing  $x$ . A minimum resistivity is observed for  $x = 1$  and it corresponds to a value of 1.5 Ω cm, in agreement with the published data on  $\text{CuMn}_2\text{O}_4$  [6].

The substitution of copper ions for manganese ions in insulating spinel material  $\text{Mn}_3\text{O}_4$  gives rise to a semiconductor. The resistivity of these semiconducting phases can reach as much as  $\sim 1$  Ω cm. Both  $\text{Mn}^{3+}$  and

TABLE II Electrical resistivity against composition for the system  $\text{Cu}_x\text{Mn}_{3-x}\text{O}_4$ , recorded at 25°C

$x$	$\rho$ (Ω cm)
0.00	$\infty$
0.15	310
0.30	261
0.45	50
0.60	33
0.90	7
0.99	1.5

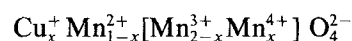
Mn<sup>4+</sup> ions are present in octahedral sites and the electronic exchange between Mn<sup>3+</sup> and Mn<sup>4+</sup> ions promotes the conductivity in this type of semiconductor. Thus the shape of the resistivity curves as a function of copper content ( $x$ ) will be different according to the sites and the oxidation states of copper ions in the spinel lattice. Taking into account the variation of the number of Mn<sup>3+</sup>-Mn<sup>4+</sup> pairs, the theoretical variation of resistivity can be plotted against copper content for the various distributions. In Fig. 6 the different variations of experimental and theoretical resistivities with copper content are presented.

An inspection of the experimental curve for the variation of resistivity with  $x$  along with calculated curves for the four hypothetical configurations showed an insulating character for Formula (ii) and a maximum number of Mn<sup>3+</sup>-Mn<sup>4+</sup> ion pairs corresponding to a minimum resistivity at  $x = 0.4$  for Formula (iii) and at  $x = 0.66$  for Formula (iv). This therefore rules out the cation distribution given by Formulae (ii), (iii) and (iv) and supports the configuration of Formula (i). The number of Mn<sup>3+</sup>-Mn<sup>4+</sup> ion pairs which contribute to the conduction through a hopping mechanism, calculated as a function of  $x$  for Formula (i),  $\text{Cu}_x^+ \text{Mn}_{1-x}^{2+} [\text{Mn}_{2-x}^{3+} \text{Mn}_x^{4+}] \text{O}_4^{2-}$ , is maximum for  $x = 1$ . This is in conformity with the observation that at  $x = 1$  the observed resistivity is minimum and this, along with the mutual overall agreement shown by the experimental curve and theoretical curve for Formula (i), lends strong support to Formula (i) as representing cation distribution.

#### 4. Conclusion

Copper-manganese co-precipitated hydroxides have been employed to prepare single-phase copper manganese spinels,  $\text{Cu}_x \text{Mn}_{3-x} \text{O}_4$  with  $0 \leq x \leq 1$ . Powder XRD analysis of these spinels revealed the presence of a single phase having a tetragonally distorted spinel structure, the tetragonal distortion ( $c/a < 1$ ) decreasing with copper content. Oxidation process and electrical resistivity behaviour indicates the presence of Cu<sup>+</sup> ions on the tetrahedral sublattice of the spinels. The XRD evidence, thermal characteristics and the comparison of experimental curves with the calculated ones for electric resistivity measurements indicated that the cation distribution in these spinels was close

to



#### Acknowledgements

The authors are grateful to Dr A. C. Vajpei for critical reading and help with the manuscript.

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Received 9 November 1987  
and accepted 1 March 1988