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# X-ray, electrical conductivity, and infrared studies of oxide spinels containing cobalt, titanium and manganese

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X-ray, electrical conductivity and infrared studies of the system $Co_{2-x}Ti_{1-x}Mn_{2x}O_4$ were carried out with a view to investigate the cation distribution. Compounds $0 \leqslant x \leqslant 0.6$ showed cubic symmetry, compounds $0.8 \leqslant x \leqslant 1$ are tetragonal. X-ray intensity calculation indicated the presence of $Co^{2+}$ and $Mn^{3+}$ at both octahedral and tetrahedral sites. A plot of activation energy against composition shows a break where crystal symmetry changes. The electrical conductivity–temperature behaviour obeys the Raschhinrichsen law. The mobility of holes calculated from infrared and conductivity data is of the order of $10^{-9}$ cm$^2$ V$^{-1}$ sec$^{-1}$. X-ray intensity calculations and conductivity measurements suggest the ionic configuration of the system to be $Co^{2+}_{1-x}Mn^{3+}_x[Co^{2+}_{2-2x}Mn^{3+}_xTi^{4+}_x]O^{2-}_4$.

## 1. Introduction

Compounds of $AB_2O_4$ type with spinel structure have been investigated by several workers [1–5], because they exhibit interesting structure, electrical and magnetic properties which vary with the nature of the ions, their charge and site distribution amongst tetrahedral and octahedral sites. We have earlier reported our results on oxidic spinel systems $ZnFeCrO_4$ and $NiFeCrO_4$ [6] and $Zn_{1-x}Co_xMn_{1-x}Fe_xCrO_4$ [7]. A literature survey indicated that although considerable work has been done on cobalt, titanite and cobalt manganite, to our knowledge no work has been reported on the system $Co_{2-x}Ti_{1-x}Mn_{2x}O_4$. The objective of this investigation was to investigate the effect of cations of different charges and radii on structural parameters as well as mode of conduction, of the system $Co_{2-x}Ti_{1-x}Mn_{2x}O_4$ using X-ray, electrical conductivity and infrared (IR) measurements.

## 2. Experimental procedure

The system $Co_{2-x}Ti_{1-x}Mn_{2x}O_4$ was prepared by mixing CoO (prepared from $Co_3O_4$), $TiO_2$ and $Mn_2O_3$ (prepared from $MnO_2$) in appropriate molar proportions in acetone. The pellets of these compositions were preapred using polyvinylacetate as a binder. Pellets were first slowly fired at 773 K for 20 h in order to remove the binder and then fired at 1173 K for 80 h. The samples were cooled slowly in air at 50 K h$^{-1}$.

X-ray diffraction patterns were taken on a Philips machine (P.W. 1051) using CuK$\alpha$ radiation with a nickel 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 [$h\,k\,l$] peaks were determined, and values obtained in relation to the peak area for the 3 1 1 reflection were taken as 100. To calculate the relative integrated intensity ($I$) of a given [$h\,k\,l$] reflection, the following formula suggested by Buerger [8] was used

$$I = [Fhkl)^2 P \frac{1 + \cos^2 2\theta}{\sin^2\theta\cos\theta} \qquad (1)$$

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 for various ions were taken from the literature [9].

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 [10]. To determine the cationic distribution and its variation with composition, the intensity ratios

$$I_{220}/I_{400},\ I_{400}/I_{422},\ I_{400}/I_{440},\ I_{422}/I_{400}$$

for different possible models of cation distribution were calculated and compared with the observed intensity ratios.

The electrical conductivity was measured using a Hewlett Packard 4140 B-PA ammeter. The end faces of each pellet were coated with a thin layer of conducting silver paste and the conductivity measured from room temperature to 773 K using a two-probe technique. The IR spectra were recorded on a Perkin–Elmer infrared spectrophotometer in the range 200 to 4600 cm$^{-1}$.

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TABLE I Lattice constant, $c/a$ ratio, and activation energy $\Delta E(ev)$ values for the system $Co_{2-x}Ti_{1-x}Mn_{2x}O_4$.

| Composition, $x$ | Lattice constant $a$ (nm) | Lattice constant $c$ (nm) | Structure* | $c/a$ | $\Delta E(ev)$ |
|---|---|---|---|---|---|
| 0.0 | 0.8385 | 0.8385 | c | 1.00 | 0.990 |
| 0.2 | 0.8396 | 0.8396 | c | 1.00 | 0.672 |
| 0.4 | 0.8389 | 0.8389 | c | 1.00 | 0.611 |
| 0.5 | 0.8375 | 0.8375 | c | 1.00 | 0.550 |
| 0.6 | 0.8380 | 0.8380 | c | 1.00 | 0.461 |
| 0.8 | 0.8254 | 0.9088 | T | 1.129 | 0.522 |
| 1.0 | 0.8090 | 0.9180 | T | 1.135 | 0.620 |

*c = cubic, T = tetragonal.

## 3. Results and discussion

The results of the X-ray analysis are summarized in Table I and the lattice constant is plotted against composition in Fig. 1. The system $Co_{2-x}Ti_{1-x}Mn_{2x}O_4$ is cubic in the range of $0.0 \leqslant x \leqslant 0.6$ and tetragonal in the range of $0.8 \leqslant x \leqslant 1$. The compound $Co_2TiO_4$ crystallized in cubic symmetry with lattice constant ($a = 0.8385$ nm). This value is slightly lower than the values reported by Hubsch and Giavoille [11] ($a = 0.845$ nm) and Srivastava *et al.* [12] ($a = 0.841$ nm). The compound $CoMn_2O_4$ is tetragonal ($a = 0.809$ nm, $c = 0.918$ nm), the tetragonal distortion is observed when $\geqslant 75\%$ of the B-sites are occupied by $Mn^{3+}$ (J-T, Jahn Teller) ions. This higher value of the critical fraction suggests the presence of ions with different charges and/or radii at the B-site [13].

Fig. 2 shows the X-ray diffractogram of one of the samples, the calculated parameters of which are given in Table I. It is clear from Fig. 1 that the plot of $V^{1/3}$ against composition shows a break at the transition region where a change occurs in the crystal structure. An inflection near the critical composition region can be explained by the model of Goodenough and Loeb [14]; similar results have been reported in Zn–Ge–CoMn by Wickham and Croft [15].

The cationic distribution at two sites in the system has been deduced by X-ray intensity calculations, 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 $Co_{1.5}Ti_{0.5}MnO_4$ using different models are summarized in Table II. It is seen that in the model with $Co^{2+}_{0.75}$, $Mn^{3+}_{0.25}$ are present at the A-site and $Co^{2+}_{0.25}$ $Mn^{3+}_{0.75}$ and $Ti^{4+}$ are present at the B-site, which shows better agreement with the observed and calculated intensity ratios. This site occupancy is in agreement with the site preference energy data [16].

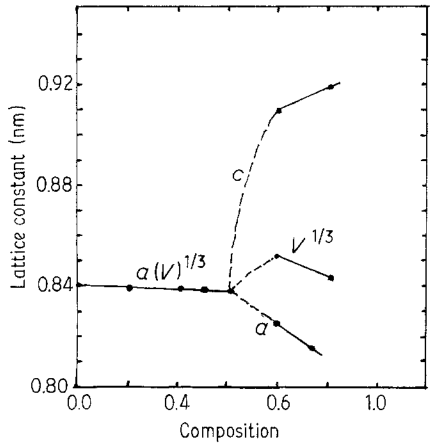

*Figure 1* Plot of lattice constant against composition for the system $Co_{2-x}Ti_{1-x}Mn_{2x}O_4$.

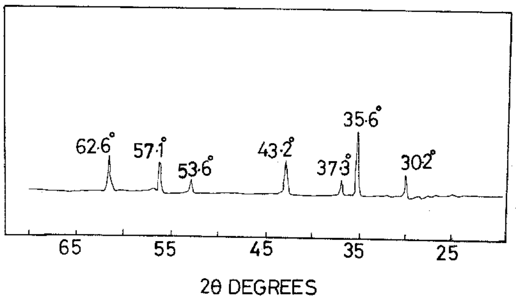

*Figure 2* X-ray diffractograms for a typical composition for the system $Co_{2-x}Ti_{1-x}Mn_{2x}O_4$.

Fig. 3 shows the plot of log conductivity of all different compositions of the system. All the conductivity data obeyed the Raschhinrichsen law, i.e. $\sigma = \sigma_0 \exp(-\Delta E_a/KT)$. All conductivity graphs shown contain straight lines. Table I gives the derived values of activation energy and relates them to composition. It has been reported by Verwey *et al.* [17] that the electrical conductivity in the transition metal oxide is high if the material contains cations of the same element and their valency differs by unity, and they are situated at similar sites in the crystal, e.g.

$$Fe^{3+}[Fe^{2+}Fe^{3+}]O_4^{2-}\ (PRT \simeq 10^{-2}\,\Omega\,cm)$$

The electrical conductivity, $\sigma$, is related to the number of charge carriers, $P$, and their mobility, $\mu$, at room temperature by the relation

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

where $l$ is the electrical charge, $P$ is the number of holes per unit volume, and $\mu$ is the mobility of holes. Taking the average unit cell volume as $(0.834\,nm)^3$ the value of hole concentration would be

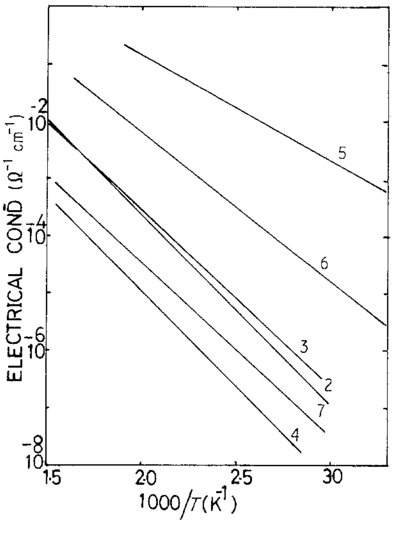

*Figure 3* Plot of logarithm of conductivity against $1/T$ for the system $Co_{2-x}Ti_{1-x}Mn_{2x}O_4$.

TABLE II Comparison of intensity ratios for $Co_{1.5}Ti_{0.5}MnO_4$

| Site of cations | | $I_{220}/I_{400}$ | | $I_{400}/I_{422}$ | | $I_{400}/I_{440}$ | | $I_{422}/I_{400}$ | |
|---|---|---|---|---|---|---|---|---|---|
| A-site | B-site | Obs. | Calc. | Obs. | Calc. | Obs. | Calc. | Obs. | Calc. |
| $Co^{2+}_{0.5}Ti^{4+}_{0.5}$ | $Mn^{3+}$ | 1.8165 | 1.0672 | 1.4741 | 2.5015 | 0.3844 | 0.5007 | 0.2608 | 0.2001 |
| $Co^{2+}_{0.55}Ti^{4+}_{0.25}Mn^{3+}_{0.20}$ | $Co^{2+}_{1.25}Ti^{4+}_{0.25}Mn^{3+}_{0.50}$ | | 1.1440 | | 2.3333 | | 0.4842 | | 0.2075 |
| $Co^{2+}_{0.50}Mn^{3+}_{0.50}$ | $Co^{2+}_{1.0}Mn^{3+}_{0.50}Ti^{4+}_{0.50}$ | | 1.3713 | | 1.9524 | | 0.4439 | | 0.2274 |
| $Co^{2+}_{0.50}Ti^{4+}_{0.50}$ | $Co^{2+}_{1.5}Mn^{3+}_{0.50}Ti^{4+}_{0.50}$ | | 0.9242 | | 2.8886 | | 0.5347 | | 0.1851 |
| $Co^{2+}_{0.50}Mn^{3+}_{0.50}$ | $Co^{2+}_{0.50}Mn^{3+}_{0.50}Ti^{4+}_{1.0}$ | | 1.5964 | | 1.6771 | | 0.4116 | | 0.2454 |
| $Co^{2+}_{0.75}Mn^{3+}_{0.25}$ | $Co^{2+}_{0.25}Mn^{3+}_{0.75}Ti^{4+}_{1.0}$ | | 1.8166 | | 1.4743 | | 0.3846 | | 0.2608 |

$10^{22}\,cm^{-3}$ and the mobility value is of the order of $10^{-9}\,cm^2\,V^{-1}\,sec^{-1}$. The mobility ($\mu$) can be calculated using the Heikes and Johnston equation [18]

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

where $\Delta E$ is the average activation energy, $K$ the Boltzman constant, $d$ the jump length and $v$, the lattice frequency. The mobility value is of the order of $10^{-9}\,cm^2\,V^{-1}\,sec^{-1}$.

Infrared studies indicated the presence of two strong absorption bands at around 500 and $600\,cm^{-1}$ as shown in Fig. 4. However, the band at $600\,cm^{-1}$ being stronger than $500\,cm^{-1}$ was considered for calculating the lattice frequency in Equation 3.

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

$$\mu = \mu_0 \exp(-\Delta E/KT) \tag{4}$$

where $\mu_0$ is a constant representing the mobility at $T = \infty$. In the case of low-mobility semiconductors and its exponential temperature dependence, the charge carriers are localized to a particular site and electrical conduction involves the hopping of charge carriers from one site to another during lattice vibrations. Thus mobility shows exponential temperature dependence.

It is seen from Table I that as the value of $x$ decreases from $x = 1.0$ to $x = 0.6$, the value of activation energy also decreases from 0.620*ev* to 0.461*ev* and at the transition region it suddenly increases, suggesting the close similarity between the conduction mechanism and crystal symmetry. Increase in the activation energy (0.550*ev* at $x = 0.5$ as compared to $x = 0.6$ (0.461*ev*)) is due to the fact that a cooperative distortion force has broadened the band gap and hence more energy is required.

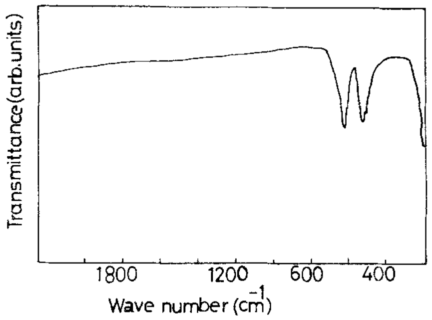

*Figure 4* The infrared transmittance spectra for a typical composition for the system $Co_{2-x}Ti_{1-x}Mn_{2x}O_4$.

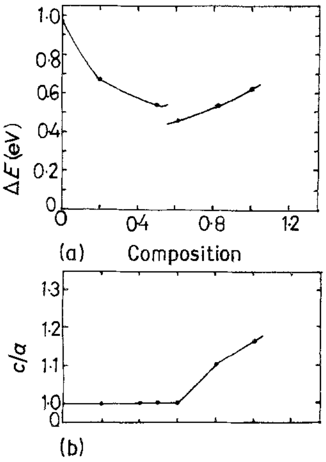

*Figure 5* Plots of (a) activation energy and (b) $c/a$ ratio, against composition for the system $Co_{2-x}Ti_{1-x}Mn_{2x}O_4$.

From Fig. 5. it is clear that a break in activation energy is noted where crystal symmetry changes; such a break has also been reported by Kshirsagar and Sabane [19] in the system $Co_xCu_{1-x}Mn_2O_4$. This shows that the effect of crystal symmetry is reflected in the mechanism of the conduction process in this system.

Waldron [20] and Hafner [21], who were amongst the earliest workers to study the vibrational spectra of ferrites, attribute the band around $600\,cm^{-1}$ to the intrinsic vibrations of tetrahedral complexes. The IR spectrum of the system $Co_{2-x}Ti_{1-x}Mn_{2x}O_4$ obtained 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 to the presence of the $Mn^{3+}$ (J-T) ion at the B-site. Thus from X-ray, electrical conductivity and IR studies, we suggest the probable cationic distribution for the system $Co_{2-x}Ti_{1-x}Mn_{2x}O_4$ to be $Co^{2+}_{1-x}Mn^{3+}_x$-$[Co^{2+}_{2-2x}Mn^{3+}_x Ti^{4+}_x]O^{2-}_4$.

## References

1. G. BLASSE, *Philips Res. Rept* **20** (1965) 528.
2. M. O'. KEEFFE, *J. Phys. Chem. Solids* **21** (1961) 172.
3. J. B. GOODENOUGH, "Magnetism and Chemical Bond" (Wiley, New York, London, 1963) p. 120.

4. D. B. GHARE AND A. P. B. SINHA, *J. Phys. Chem. Solids* **29** (1968) 865.
5. C. N. R. RAO and G. V. SUBBA RAO, *Phys. Status Solidi* **A1** (1970) 597.
6. M. N. KHAN, S. AL-DALLAL and A. AHMED, Proceedings of the International Conference on "Effects of modes of formation on the structure of glass" Vanderbilt University, Nashville, Tennessee, USA, 16–20 June (1987).
7. M. N. KHAN, A. AHMED and V. S. DARSHANE, *J. Mater. Sci.* in press (1989).
8. M. J. BUERGER, "Crystal, structure analysis" (Wiley, New York, 1960) p. 46.
9. "International Tables for X-ray crystallography", Vol. 4 (Kynoch, Birmingham, 1959).
10. E. F. BERTAUT, *Compt. Rend.* **230** (1950) 213.
11. J. HUBSCH and G. GAVOILLE, *Phys. Rev. B* **17** (1982) 4384.
12. J. K. SRIVASTRAVA, J. A. KULKARNI, S. RAMAKRISHNAN, S. SINGH, V. R. MARATHE, G. CHANDRA, V. S. DARSHANE and R. VIJAYARAGHAVAN, *J. Phys C. Solid State Phys.* **20** (1987) 2139.
13. P. S. JAIN and V. S. DARSHANE, *Nucl. Phys. Solid State Phys. Symp.* (*silver jubilee*) *B.A.R.C. Bombay* **24c** (1981) 529.
14. J. B. GOODENOUGH and A. L. LOEB, *Phys. Res.* **98** (1955) 391.
15. D. G. WICKHAM and W. J. CROFT, *J. Phys. Chem Solids* **7** (1958) 361.
16. A. MILLER, *J. Appl. Phys.* **30** (suppl) (1959) 245.
17. E. J. W. VERWEY, P. B. BRAUN, E. W. GORTER, F. C. ROINEIGN and J. H. VAN SAUTEN, *Z. Phys. Chem.* **198** (1951) 6.
18. R. R. HEIKES and W. D. JOHNSTON, *J. Chem. Phys.* **26** (1957) 582.
19. S. T. KSHIRSAGAR and C. D. SABANE, *J. Appl. Phys* **10** (1971) 794.
20. R. D. WALDRON, *Phys. Rev.* **99** (1955) 1727.
21. S. Z. HAFNER, *Kristallogr.* **115** (1961) 331.

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