Structural, electrical and reflectance studies of the system $ZnMn_{2-2x}Ni_xTi_xO_4$

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Abstract. X-ray, electrical conductivity and reflectance studies of the system $ZnMn_{2-2x}Ni_xTi_xO_4$ have been carried out. The system is tetragonal in the range $0 \leqslant x \leqslant 0.25$ and cubic in the range $0.5 \leqslant x \leqslant 1$. Electrical resistivity temperature behaviour obeys Wilson's law for all the compounds and the thermoelectric coefficient values vary between 325 and $-290 \mu V/K$. The activation energy and ρ_{RT} decrease gradually with increase in concentration of charge carriers at B-site except for $ZnNiTiO_4$. Reflectance spectral studies indicate the presence of Ni^{2+} at the octahedral site.

Keywords. Spinel; x-ray; electrical conductivity; Seebeck coefficient; reflectance spectra.

1. Introduction

Compounds of AB_2O_4 type with spinel structure have been investigated by a number of workers (Blasse 1965; O'Keeffe 1961; Goodenough 1963; Ghare and Sinha 1968; Rao and Subba Rao 1970) as they show interesting structural, electrical and magnetic properties which vary with the nature of the ions, their charge and site distribution amongst tetrahedral and octahedral sites. Literature survey indicated that although considerable work has been done on zinc manganite, no work has been reported on the system $ZnMn_{2-2x}Ni_xTi_xO_4$. With a view to investigating the effect of cations of different charges and radii on structural parameter as well as mode of conduction, the above mentioned system has been studied. Similarly the cation distribution has been determined using x-ray analysis, electrical conductivity and reflectance spectroscopic studies.

2. Materials and methods

The compositions of the system $ZnMn_{2-2x}Ni_xTi_xO_4$ were prepared by mixing the component oxides (GR grade) in acetone in appropriate molar proportions. The pellets of these compositions were prepared using 2 % solution of polyvinylacetate as a binder which were first slowly heated at 773 K for 20 hr to remove the binder and then fired at 1173 K for 100 hr. The samples were cooled slowly in air at 50 K/hr. X-ray powder patterns (Philips diffractometer) were taken using Cu-K$_\alpha$ radiation with Ni-filter. The areas under different (hkl) peaks were determined by counting the squares on the cm-graph paper and their values obtained in relation to the peak for 311 reflections which was taken as 100. The $\{hkl\}$ reflections 220, 222, 400, 422 and 440 are sensitive to cation

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distribution at both the sites in the spinel lattice. To determine the cation distribution and its variation, if any, with the composition the intensity ratios 220/400, 400/422, 400/440 and 422/440 were calculated for different possible models of cation distribution and were compared with the observed ratios. The relative integrated intensity I of the given $\{hkl\}$ reflection was calculated by using a diffractometer with flat plate sample holder. The following formula suggested by Burger (1960) was used.

$$I = |F_{hkl}|^2 P \cdot L_p, \tag{1}$$

where F is the structure factor, P the multiplicity factor and L_p the Lorentz polarisation factor. The atomic scattering factors for various ions were taken from International Tables (1974).

The electrical resistivity was measured using LCR Marconi bridge. The faces of each pellet were coated with a thin layer of conducting silver paste and measured from 303 to 773 K using two-probe technique. Thermoelectric coefficient was measured from room temperature to 573 K. The thermoelectric coefficient value is considered positive if the cold end is positive, indicating p-type of semiconduction. Reflectance spectra in the range 300 to 1200 nm (33000 to 8000 cm^{-1}) were recorded (Carl Zeiss VSU-2P spectrophotometer) using $MgCO_3$ as a reference.

3. Results and disussion

3.1 *X-ray analysis*

The results of the x-ray analysis are summarised in table 1 and the lattice constant vs composition is plotted in figure 1. The system $ZnMn_{2-2x}Ni_xTi_xO_4$ is tetragonal in the range $0 \leqslant x \leqslant 0.25$ and cubic in the range $0.50 \leqslant x \leqslant 1$. The values of the lattice constants of the end members, $ZnMn_2O_4$ and $ZnNiTiO_4$ observed (table 1) are well within those reported earlier (Mason 1947; Yamaguchi 1953).

The compound $ZnMn_2O_4$ showed tetragonal symmetry ($a' = 8.06$ and $c' = 9.23$A) due to the presence of Mn^{3+} (J–T) ion at B-site. Table 1 and figure 1 show that more than 50% of Mn^{3+} ions are required at the B-site to cause tetragonal distortion in the

Table 1. Lattice parameter, resistivity, activation energy and thermo e.m.f. for the system $ZnMn_{2-2x}Ni_xTi_xO_4$.

Composition	Colour	Structure type	Lattice parameters (A)	ρ at RT (ohm-cm)	ΔE (eV)	α (μV/°C)
$ZnMn_2O_4$	Brownish black	T	$a' = 8.06$ $c' = 9.23$	1.20×10^9	0.67	325
$ZnMn_{1.5}Ni_{0.25}Ti_{0.25}O_4$	Brownish black	T	$a' = 8.047$ $c' = 9.15$	1.01×10^9	0.61	77
$ZnMn_{1.0}Ni_{0.5}Ti_{0.5}O_4$	Brownish black	C	$a = 8.36$	9.81×10^8	0.53	40
$ZnMn_{0.5}Ni_{0.75}Ti_{0.75}O_4$	Brown	C	$a = 8.40$	8.15×10^8	0.46	−19
$ZnNiTiO_4$	Yellowish green	C	$a = 8.45$	$> 10^{12}$	1.08	−290

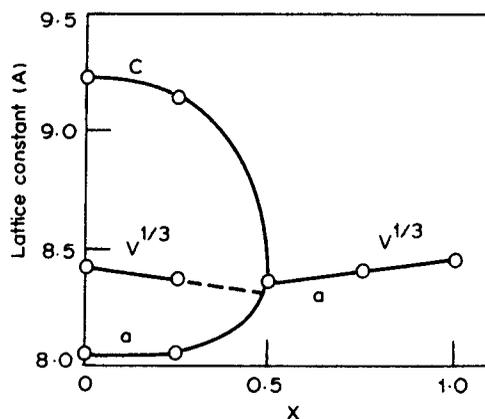C = cubic, T = tetragonal.

Figure 1. Plot of lattice constant and $V^{1/3}$ *vs* composition for the system $ZnMn_{2-2x}Ni_xTi_xO_4$.

lattice. This higher value (62·5 %) of critical fraction suggests the presence of ions with different charges and/or radii at B-site (Jain and Darshane 1981). Figure 1 also shows that the plot of $V^{1/3}$ *vs* composition shows a break at the transition region, similar to the studies reported in Zn-Ge-Co-Mn (Wickham and Croft 1958) and $ZnMnFeO_4$-$GaCoMnO_4$ (Jain and Darshane 1981) oxide spinel systems. The sudden change in the volume at the critical composition can be attributed to the change in the elastic energy of the crystal (Goodenough and Loeb 1955).

The cation distribution in oxidic type compounds can be obtained by x-ray diffraction intensity calculations. The observed and calculated intensities were computed for the composition taking into consideration the structure factors for the planes 220, 400, 422 and 440 which are quite sensitive to cation distribution. Intensity was calculated for different models in which (i) Ni^{2+}, Ti^{4+} and Mn^{3+} (ii) Ni^{3+}, Ti^{4+}, Ti^{2+} and Mn^{3+} (iii) Ni^{3+}, Ti^{3+} and Mn^{3+} and (iv) Ni^{2+}, Ti^{4+}, Mn^{2+} and Mn^{4+} are present at B-site. Intensity ratios for the compound $ZnNi_{0.5}Ti_{0.5}MnO_4$ are given in table 2. The calculated intensity ratios show better agreement with the observed intensity ratios in which Zn^{2+} occupy A site and Ni^{2+}, Ti^{4+} and Mn^{3+} are at B site. This model is also supported by site preference energy values (Miller 1959). Hence the ionic configuration of the system can be written as $Zn^{2+}[Mn^{3+}_{2-2x}Ni^{2+}_x Ti^{4+}_x]O_4^{2-}$

Table 2. Comparison of intensity ratios for $Zn[Ni_{0.5}Ti_{0.5}Mn]O_4$.

Cations at		220/400		400/422		400/440		422/440	
A-Site	B-Site	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
Zn^{2+}	$Ni^{2+}_{0.5}Ti^{4+}_{0.5}Mn^{3+}$		2·90		0·90		0·36		0·40
Zn^{2+}	$Ni^{3+}_{0.5}Ti^{2+}_{0.25}Ti^{4+}_{0.25}Mn^{3+}$	2·88	2·95	0·94	0·87	0·37	0·40	0·39	0·44
Zn^{2+}	$Ni^{3+}_{0.5}Ti^{3+}_{0.5}Mn^{3+}$		2·95		0·88		0·42		0·44
Zn^{2+}	$Ni^{2+}_{0.5}Ti^{4+}_{0.5}Mn^{4+}_{0.5}Mn^{2+}_{0.5}$		2·96		0·88		0·43		0·46

3.2 *Electrical properties*

The room temperature dc resistivity in all the compounds varied between 10^8 and 10^{12} ohm-cm and the activation energy between 0·49 and 1·08 eV. Electrical resistivity-temperature behaviour obeyed Wilson's law ($\rho = \rho_0 \exp \Delta E/kT$) indicating the semiconducting nature of the compounds (figure 2). High resistivity values of the compounds indicate that the elements with only one stable oxidation state are present at B-site. In transition metal oxides, electrical resistivity is low if the compound contains the cations of the same element situated at the similar site but with their valency differing by unity *e.g.* $Fe^{3+}[Fe^{2+}Fe^{3+}]O_4^{2-}$ ($\rho_{RT} \simeq 10^{-2}$ ohm-cm) (Verwey *et al* 1951).

The plot of thermoelectric voltage (μV) *vs* temperature (ΔT) is given in figure 3. A positive sign indicates that the sample is of p-type and the negative shows n-type. It is seen that the compounds where $x \leqslant 0.5$ are p-type and for $x > 0.5$ they are n-type semiconductors. Thermoelectric power of $ZnNiTiO_4$ is negative and decreases with temperature in the range 30 to 120°C and increases with temperature in the range 120 to 300°C. This is due to the fact that the mobility of n-type carriers is higher than that of p-type (up to 120°C) and as temperature increases the mobility of p-type carriers rises rapidly compensating for n-type carriers.

The conduction mechanism in the present system can be explained as follows. In the first three compounds ($x \leqslant 0.5$) p-type semiconduction was observed. This is attributed
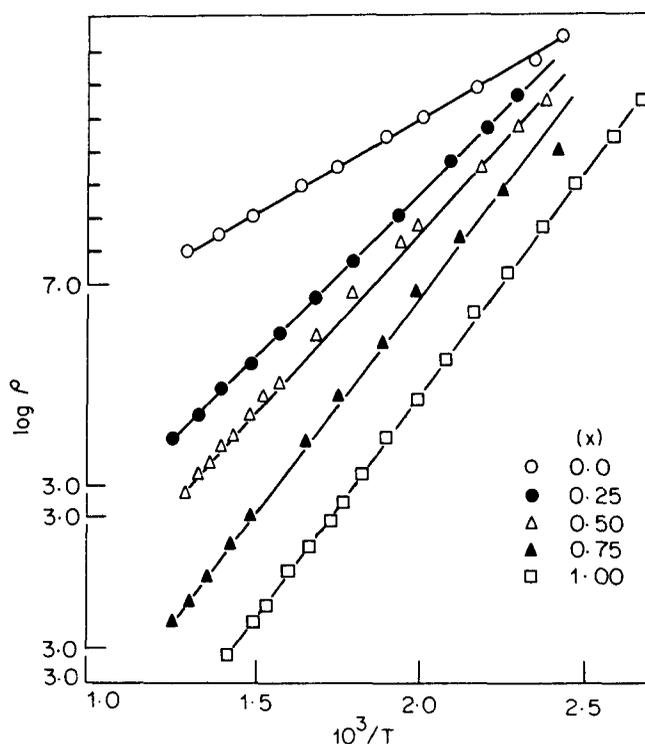

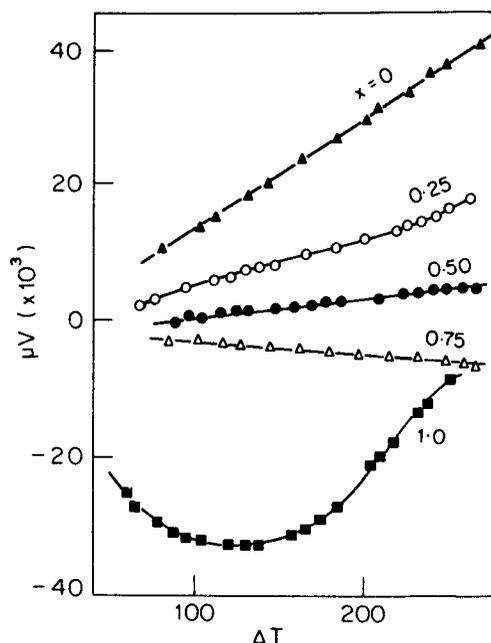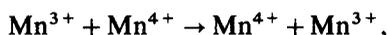**Figure 2.** Plot of log ρ *vs* $10^3/T$ for the system $ZnMn_{2-2x}Ni_xTi_xO_4$.

Figure 3. Plot of μV *vs* ΔT for the system $ZnMn_{2-2x}Ni_xTi_xO_4$.

to the following process:

$$Mn^{3+} + Mn^{4+} \rightarrow Mn^{4+} + Mn^{3+},$$

where the motion of Mn^{4+} ion acts as a hole. However in the last two compounds $x \geqslant 0.75$.

Slight departure from stoichiometry produces Ti^{3+} ion in the lattice which acts as donor with respect to Ti^{4+} ion and donor levels are introduced near $3d$ bands. These Ti^{3+} ions (donors) produce conduction electrons near $3d$ levels and are ultimately responsible for n-type conduction in $ZnNiTiO_4$ and $ZnNi_{0.75}Ti_{0.75}Mn_{0.5}O_4$. Increasing concentration of Ti^{4+} ions in the lattice ($x \geqslant 0.75$) indicates that $Ti^{3+} \rightarrow Ti^{4+}$ mechanism becomes more predominant as compared to $Mn^{3+} \rightarrow Mn^{4+}$ and, therefore, shows n-type behaviour in the last two cases. This is also one of the reasons for the decrease in ΔE and ρ_{RT} in our compounds (table 1). The high values of ΔE and ρ_{RT} in $ZnNiTiO_4$ are attributed to the presence of nickel and titanium in $2+$ and $4+$ oxidation states only.

3.3 *Reflectance spectra*

Reflectance spectra can conveniently detect octahedrally and tetrahedrally co-ordinated nickel ions in solids. Three bands were observed in the region 8,000 to $33000\ cm^{-1}$ for all the compounds while for $ZnNiTiO_4$ the bands were observed at (i) 9750 (ii) 15250 and (iii) $27500\ cm^{-1}$ (figure 4). The positions of bands of the spectra closely agree with those of Porta *et al* (1974) and Schmidz-Du Mont *et al* (1965) who have investigated zinc-nickel-aluminate and zinc-magnesium-aluminate spinels. Besides the above bands Schmidz-Du Mont *et al* (1965) observed a band around
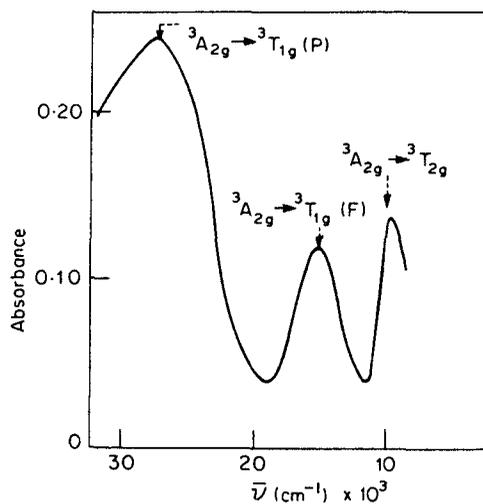
Figure 4. Reflectance spectrum for $ZnNiTiO_4$.

17000 cm^{-1} which is due to tetrahedrally co-ordinated nickel. The above band is not observed in our compositions since nickel is present at octahedral site only, which is supported by x-ray investigation and site preference energy values (Miller 1959). As pointed out by Schmidz Du Mont *et al* (1965) the bands (i), (ii) and (iii) are due to

$$^3A_{2g} \rightarrow {}^3T_{2g}, \, {}^3A_{2g} \rightarrow {}^3T_{1g} \, (F) \text{ and } {}^3A_{2y} \rightarrow {}^3T_{1g} \, (P)$$

transitions respectively. The assignment of the above bands to octahedrally co-ordinated nickel is also supported by the study of transition metal complexes (Drago 1965).

4. Conclusions

(i) The system $ZnMn_{2-2x}Ni_xTi_xO_4$ is tetragonal in the range $0 \leqslant x \leqslant 0.25$ and cubic in the range $0.5 \leqslant x \leqslant 1$. (ii) X-ray analysis and electrical conductivity data suggest the ionic configuration as $Zn^{2+}[Mn_{2-2x}^{3+}Ni_x^{2+}Ti_x^{4+}]O_4$. (iii) The compounds for $x \leqslant 0.5$ are p-type while for $x > 0.5$ are n-type semiconductors. (iv) Reflectance measurements suggest the presence of Ni^{2+} at octahedral site only.

Acknowledgements

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