Thermochimica Acta, 93 (1985) 473-476
Elsevier Science Publishers B.V., Amsterdam

# EFFECT OF HIGH TEMPERATURES ON CATION DISTRIBUTION: $NiMn_2O_4$-$FeMn_2O_4$ SYSTEM

J.A. Kulkarni and V.S. Darshane*
The Institute of Science, Bombay 400 032, INDIA

## ABSTRACT

The paper describes an investigation of the relation between cation distribution and variables such as temperature and composition for the system $NiMn_2O_4$ - $FeMn_2O_4$. A comparative study of the variation in the structural parameters, activation energy and thermoelectric coefficient with reference to cation distribution has been carried out.

## INTRODUCTION

The compositions of the system $Ni_{1-x}Fe_xMn_2O_4$ belong to spinels. In the present studies, the compounds $NiMn_2O_4$ and $FeMn_2O_4$ with their intermediate solid solutions are selected as they represent the ideal candidature for exploring the relative stabilities of various cations like $Mn^{2+}$, $Mn^{3+}$, $Mn^{4+}$, $Fe^{2+}$ and $Fe^{3+}$ among the octahedral and/or tetrahedral interstices depending on the equilibrium temperature from which the compounds were annealed or quenched. The annealed compositions represent the cation distribution at the room temperature since, they get enough time to equilibrate themselves with the slowly decreasing temperature. Whereas, quenching retains the cation distribution at the firing temperature from which it is cooled.

## MATERIALS AND METHODS

The compositions of the system $Ni_{1-x}Fe_xMn_2O_4$ were prepared by conventional ceramic technique. The nominal compositions in $Ni_{1-x}Fe_xMn_2O_4$ represent the Ni and Fe in divalent state whereas Mn in trivalent form. The compounds were fired seperately at 1173 K (A), 1323 K (B) and 1473 K (C). The cooling rate was 50 K per hour. The fourth batch was heated at 1473 K (D) and was water quenched.

X-ray powder diffraction analysis was carried out using Ni filtered $CuK_\alpha$ radiation. DC resistivity and thermoelectric power measurements were carried out on the samples in a hard circular pellet form. Details of the set up and measurements are given elsewhere[1].

## RESULTS AND DISCUSSION

The results of X-ray analysis are shown in Fig. 1. The observed peaks were well defined and could be indexed in terms of single phase cubic spinel

---

Proceedings of ICTA 85, Bratislava

structure. The observations showed that the lattice parameter slowly increases on going from $x = 0.0$ to $x = 1.0$. Further, for the same value of x, there is no appreciable change in the lattice constant with increasing sintering temperature.

DC electrical resistivity measurements up to 900K showed the semiconducting nature of all the compositions (annealed and quenched). The values of activation energy (Q) are plotted against composition (x)-Fig.2. The values slowly increase in the series but remain nearly same for the x with increase in sintering temperature. The values are higher for the quenched series. A temperature independent thermoelectric coefficient ($\alpha$) is observed for all the compositions in the temperature range from 300 to 650K. This behaviour has been attributed to the polaron hopping conductivity in these compounds[2]. The mobility was found to be very low ($\mu = 10^{-9} - 10^{-10}$ $cm^2/V\text{-}sec$). The hopping mechanism is confined to the valence distribution of the manganese ions which occupy octahedral sites[3]. The compounds showed n-type behaviour in the case of $x = 0.0$, 0.2, 0.8 and 1.0 irrespective of the firing temperatures.

In the case of $NiMn_2O_4$ which is n-type semiconductor, many attempts have been made to establish its ionic configuration[4] and the configuration $Mn^{3+}/Ni^{2+}Mn^{3+}_{1-x}Mn^{2+}_{x}/\ O_4$ fits well with our experimental results. The presence of small amount of $Mn^{2+}$ explains satisfactorily the observed low room temperature resistivity ($\simeq$ 1000 ohm - cm). Hopping of electron between $Mn^{2+}$ - $Mn^{3+}$ ion pairs gives rise to n-type conductivity in the compound. Eventhough $Mn^{2+}$ is believed to be present in the compound, the amount is too small to be detected by chemical means. With the increase in the firing temperature, the physical constants viz. lattice parameter, activation energy and thermoelectric coefficient remained almost unchanged, implying only the unaltered cation distribution with changed synthetic conditions.

In the case of $FeMn_2O_4$ and substituted solid solutions the situation was found to be different. The cation distribution for $FeMn_2O_4$ has also been discussed in the literature[5].

It is accepted that no iron is present in the compound in 2+ state but gets converted to 3+ state following the reaction

$$Fe^{2+} + Mn^{3+} \rightleftharpoons Mn^{2+} + Fe^{3+} \qquad (1)$$

Thus it is believed that all Fe in $FeMn_2O_4$ is present in the 3+ state and Mn in two different oxidation states, 2+ and 3+. Our thermoelectric power measurements revealed an another possible process

$$Mn^{3+} + Mn^{3+} \rightleftharpoons Mn^{2+} + Mn^{4+} \qquad (2)$$

through which some $Mn^{4+}$ ions are formed in the compound. Room temperature resistivity of $FeMn_2O_4$ (A) is $10^4$ ohm-cm which increased to $10^5$ for $FeMn_2O_4$(C).

The average order of activation energy remained the same. The total conductivity of spinel compounds is given by the relation

$\sigma = ne\mu + pe\mu$. (3) n in the equation is associated with the $Mn^{2+}$ ions and hopping of electrons between $Mn^{2+}$ and $Mn^{3+}$ occurs, whereas, p the electron holes are associated with $Mn^{4+}$ ions and hop between adjacent $Mn^{3+}$ sites. In order to prove the presence of both the types of charge carriers in the compound, we have some of the compositions with positive values of $\alpha$ and some with the negative as can be seen from Fig. 3. $\alpha$ in any given case is again related to the positive and negative charge carriers and conductivity by the equation

$$\alpha = \frac{\alpha_h \sigma_h + \alpha_e \sigma_e}{\sigma_h + \sigma_e} \qquad (4)$$

where, h and e are p and n type charge carriers respectively. $\alpha$ for the $FeMn_2O_4$ (A) is observed to be only -50 µV/K which increased to -150 µV/K for $FeMn_2O_4$ (C) indicating decrease in $\alpha_h$ and increase in $\alpha_e$ i.e. $Mn^{2+}$ concentration increases and that of $Mn^{4+}$ decreases. The observed peak at $x = 0.4$ which seems to be a critical composition,can easily be explained by equation (4).

Slow increase in the activation energy values and order of resistivity in a series can be understood as iron is substituted in the lattice which along with nickel ions helps in interrupting the chain of manganese hopping sites. Further, lack of compensating tetrahedral $Mn^{3+}$ ions for octahedral $Mn^{3+}$ (J-T ions) is another reason to consider.

In the case of 1473K quenched series, eventhough the values of lattice constant remain nearly the same as that of 1473K annealed, the values of activation energy are quite higher and thermoelectric coefficient shows less negative and more positive values as seen in Fig. 3. This may be due to ionic migration between the sublattices[6]. During conductivity measurements, the cations try to rearrange themselves needing more activation energy for the conduction. Further, the cations $Mn^{2+}$ and $Fe^{3+}$, possessing nearly the same site preference energy can easily migrate through the lattice, will reduce number of n-type hopping pairs at the octahedral sites for conduction. Under this situation p-type charge carriers would dominate the process and consequently the compounds with $0.2 \lesssim x \lesssim 0.6$ show large positive and others smaller negative value of thermoelectric coefficient.

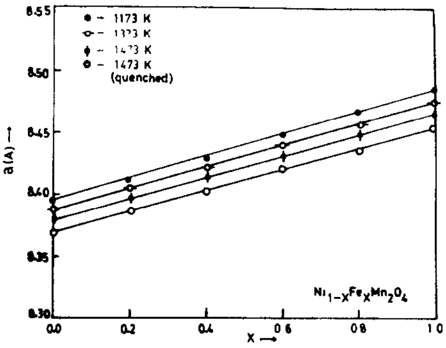

Fig-1 Plot of lattice constant vs composition

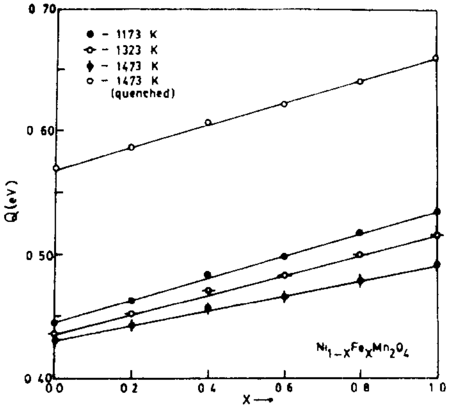

Fig-2 Plot of activation energy vs composition

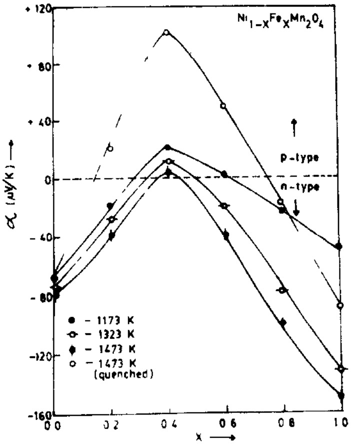

Fig-3 Plot of thermoelectric coefficient vs composition

*Mössbauer investigation of $FeMn_2O_4$ has shown the equal distribution of $Fe^{3+}$ ions between tetrahedral and octahedral sites and absence of any $Fe^{2+}$ ions in the lattice. Our conductivity and thermopower measurements of the entire system synthesized at different temperatures suggest the presence of $Mn^{4+}$ ions in the compounds and the configuration of $FeMn_2O_4$ can conveniently be expressed by the formula*

$$Fe^{3+}_{0.5}\,Mn^{2+}_{0.5}\,\Big|\,Fe^{3+}_{0.5}\,Mn^{2+}_{0.5}\,Mn^{3+}_{1-y}\,Mn^{2+}_{y/2}\,Mn^{4+}_{y/2}\Big|\,O_4.$$

## *REFERENCES*

1. *J.A. Kulkarni, Ph.D.Thesis, University of Bombay, 1985.*
2. *J.A. Kulkarni, K. Muraleedharan, J.K. Srivastava, V.R. Marathe, V.S. Darshane. C.R.K. Murty and R. Vijayaraghavan, J. Phys. C:Solid State Phys., (In Press).*
3. *P.S. Jain and V.S. Darshane, Pramana, 20 (1983) 7.*
4. *G.T. Bhandge and H.V. Keer; J. Phys. C: Solid State Phys., 9 (1976) 1325.*
5. *Landolt-Bornstein, Series III, 4a (1970) and 12b (1980).*
6. *M. Rosenberg and P. Nicolau, Phys. Stat. Sol., 6 (1964) 101.*