A study of Co_{3-x}Ni_xO_4 (0 \leq x \leq 1) system

N K APPANDAIRAJAN and J GOPALAKRISHNAN*
Department of Chemistry, Indian Institute of Technology, Madras 600 036
*Present address: Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012

MS received 4 December 1977

Abstract. A series of solid solutions of composition Co_{3-x}Ni_xO_4 has been studied. For 0 < x < 1, the members crystallize in the cubic spinel structure. Measurements of dc electrical conductivity and Seebeck coefficient show that there is a transition from semiconducting state to semi-metallic state around x = 0.5 - 0.6. All compositions with x > 0.5 are semimetallic and ferrimagnetic. The results have been rationalised on the basis of the cation distribution (Co^{3+}), [Ni^{III}Co^{III}]_0O_4 for the solid solutions which permits formation of an(\epsilon_g) band through strong covalent interaction between octahedral-site low spin Co^{III}/Ni^{III} and oxide ion in the spinel structure.

Keywords. Oxide spinels; Co_{3-x}Ni_xO_4 system; structure and electrical properties.

1. Introduction

Recently many cobaltites ACo_2O_4 (A = Zn, Ni, Fe, Mn and Cu) have been investigated (Miyatani et al 1966; Holgerson and Karlson 1929; Kawano and Achieva 1966; Boucher et al 1970; Shimada et al 1975). Of these NiCo_2O_4 is an interesting case showing ferrimagnetism (\mu_B = 1.25). To account for the magnetic behaviour, Blasse (1963) suggested that the valence and site distribution of cations in this compound is (Co^{3+}), [Ni^{III}Co^{III}]_0O_4 (where the roman superscripts indicate low spin oxidation state and the arabic superscripts high spin state) while Knop et al (1968) suggested a distribution (Co^{3+}), [Ni^{II}+Co^{III}]_0O_4 that accounts equally well for the observed ferrimagnetic moment. The results of neutron diffraction study are not inconsistent with either model. A survey of the literature reveals that no systematic study of electrical transport properties of cobaltite-spinel oxides seem to have been made excepting for reports that CoO_4 is a p-type semiconductor (Rao and Subbarao 1974). It was thought that a study of the electrical behaviour of NiCo_2O_4 and Co_{3-x}Ni_xO_4 (0 \leq x \leq 1) system would shed light on the oxidation state and cation-distribution in this system. The present paper reports the results of preparation and studies of crystallographic and electrical behaviour of solid solutions of the system Co_{3-x}Ni_xO_4 (0 \leq x \leq 1).

2. Experimental

AnalAr grade hydrated cobalt and nickel nitrates were made use of in the preparation of Co_{3-x}Ni_xO_4 solid solutions. Compositions corresponding to different values of
x were made by mixing requisite volumes of aqueous solutions (1M) of the nitrates, evaporating them to almost dryness on a water bath and decomposing the dried mass in air at higher temperatures. \( \text{Co}_3\text{O}_4 \) was obtained by firing at 600°C whereas for members containing nickel, a lower temperature (300–350°C) was employed. Determination of the oxidising power and hence the average oxidation state of the transition metal ion in the samples were carried out by oximetric analysis. About 100 mg of the sample is treated with excess \( \text{Fe}^{2+} \) solution in 4N \( \text{H}_2\text{SO}_4 \). After dissolution of the sample, the excess \( \text{Fe}^{2+} \) is determined by titration with standard \( \text{K}_2\text{Cr}_2\text{O}_7 \). From the volume of \( \text{Fe}^{2+} \) consumed, the oxidising power and the average oxidation state of the transition metal ions are calculated. The results are given in table 1.

The analytical results (table 1) indicate that in the \( \text{Co}_{3-x}\text{Ni}_x\text{O}_4 \) solid solutions for \( 0 \leq x \leq 1 \), two of the three transition metal ions exist in the trivalent state as in \( \text{Co}_3\text{O}_4 \).

The samples were further characterised by x-ray powder diffraction using \( \text{CoK} \alpha \) radiation. Electrical conductivity and Seebeck coefficient measurements on sintered cylindrical pellets were made by the methods described elsewhere (Palanisamy 1974).

3. Results and discussion

X-ray diffraction data of the \( \text{Co}_{3-x}\text{Ni}_x\text{O}_4 \) solid solutions (table 1) clearly indicate that monophasic spinel type products are formed up to \( x = 1.0 \). For values of \( x \geq 1.1 \), apart from the diffraction lines characteristic of the spinel structure, additional lines,

<table>
<thead>
<tr>
<th>( x )</th>
<th>( a_0, \text{Å} )</th>
<th>Average oxidation state of T.M. ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>8.080</td>
<td>2.66</td>
</tr>
<tr>
<td>0.10</td>
<td>8.083</td>
<td>2.70</td>
</tr>
<tr>
<td>0.25</td>
<td>8.087</td>
<td>2.69</td>
</tr>
<tr>
<td>0.40</td>
<td>8.093</td>
<td>2.65</td>
</tr>
<tr>
<td>0.50</td>
<td>8.099</td>
<td>2.67</td>
</tr>
<tr>
<td>0.60</td>
<td>8.106</td>
<td>2.70</td>
</tr>
<tr>
<td>0.75</td>
<td>8.114</td>
<td>2.66</td>
</tr>
<tr>
<td>0.90</td>
<td>8.116</td>
<td>2.68</td>
</tr>
<tr>
<td>1.00</td>
<td>8.119</td>
<td>2.70</td>
</tr>
</tbody>
</table>

![Figure 1](image.png)

Figure 1. Variation of lattice parameter in \( \text{Co}_{3-x}\text{Ni}_x\text{O}_4 \) system.
A study of Co$_{3-x}$Ni$_x$O$_4$ (0 ≤ x ≤ 1) system

mostly of NiO, appear in the x-ray pattern, indicating that monophasic spinel solid solutions can be obtained for the system Co$_3$O$_4$ only in the composition range 0 ≤ x ≤ 1. The variation of unit cell parameters refined by Nelson-Riely plots, as a function of composition x, is given in figure 1. The unit cell parameters of Co$_3$O$_4$ (8.08Å) and NiCo$_2$O$_4$ (8.119Å) obtained in this work compare well with those reported in the literature (Knop et al. 1968). The variation of unit cell parameters across the series Co$_3$-$_x$Ni$_x$O$_4$ is almost linear following Vegard's law in the region 0 ≤ x ≤ 1 (figure 1). Co$_3$O$_4$, a normal spinel has the cation distribution (Co$^{2+}$)$_4$[Co$^{III}$Co$^{III}$]$_6$O$_4$. Assuming that the substitution of nickel takes place in the octahedral site as low spin Ni$^{II}$, one can write the cation-distribution for NiCo$_2$O$_4$ as (Co$^{2+}$)$_x$[Ni$^{III}$Co$^{III}$]$_{6-x}$O$_4$ as suggested by Blase (1963). The fact that NiCo$_2$O$_4$ crystallizes in a slightly larger unit cell than Co$_3$O$_4$ is understandable in terms of the larger ionic radius of low spin Ni$^{III}$ (0.56Å) as compared to low spin Co$^{III}$ (0.525 Å) in the octahedral oxygen coordination. The general cation distribution for the solid solution series may then be written as (Co$^{2+}$)$_x$[Ni$^{III}$Co$^{III}$]$_{6-x}$O$_4$. The alternative distribution suggested by Knop et al. (1968), (Co$^{2+}$)$_x$[Ni$^{III}$Co$^{III}$]$_{6-x}$O$_4$ is not consistent with the electrical properties as seen below.

3.1. Electrical behaviour of Co$_{3-x}$Ni$_x$O$_4$ system

The variations of room temperature electrical resistivity and Seebeck coefficient with composition x in Co$_{3-x}$Ni$_x$O$_4$ are given in figures 2 and 3. Co$_3$O$_4$ is a p-type semiconductor (ρ ~ 10$^4$ ohms cm) with a large positive Seebeck coefficient (+600 μV/$^\circ$K). Substitution of nickel up to x ~ 0.5 brings about a drastic decrease of both the resistivity and Seebeck coefficient. In the composition range 0.5 ≤ x ≤ 1.0, there is no significant variation, the values remaining almost constant around ρ ~ 10 ohm cm and α ~ 30 μV/$^\circ$K. These values of resistivity were obtained by two-probe measurements. For compositions with x > 0.5 showing low resistivity,

Figure 2. Room temperature resistivity in Co$_{3-x}$Ni$_x$O$_4$ system.

Figure 3. Variation of Seebeck coefficient at room temperature.
measurements by four-probe technique have been carried out. The results show that for these samples the resistivity is much lower (∼0.2 ohm cm) and its variation with temperature from 30 – 100°C is almost constant indicating semi-metallic nature.

For samples with x =< 0.5, the variation of electrical resistivity with temperature in the range 30–400°C is shown in figure 4. Activation energies for conduction obtained from these plots of log ρ vs 1/T are given in figure 5. The data show that the activation energy steadily decreases with x and disappears almost completely between x = 0.5 and 0.6.

The electrical transport behaviour of Co_{3–x}Ni_{x}O_{4} is very similar to that of LaCo_{1–x}Ni_{x}O_{3} (Rao et al 1975; Gopalakrishnan et al 1976) wherein a semiconductor-to-metal transition is observed. Recently a large number of such extrinsic semiconductor systems showing a transition to metallic or semimetallic-state has been discussed (Mott 1972; Rao et al 1975; Rao and Om Prakash 1977). The transition to semimetallic nature in Co_{3–x}Ni_{x}O_{4} system for x > 0.5 is understandable in terms of the cation distribution suggested by Blasse (1963) for NiCo_{2}O_{4}; (Co^{2+})_{y}[Ni^{III}Co^{II}]_{1–y}O_{4}. The solid solutions would then have the distribution (Co^{2+})_{y}[Ni^{III}Co^{II}]_{1–y}O_{4}. Goodenough (1965, 1969) has discussed the electrical transport properties of spinels in terms of qualitative one-electron energy band schemes. It has been suggested that the electrical behaviour in oxide spinels result mainly from the octahedral B-site cations and interactions thereof. In the spinel structure the B-site octahedra share their edges so that both direct B-B interaction as well as 90°B-O-B interaction are important in deciding the electronic behaviour. For Co_{3}O_{4}, Goodenough (1965) has suggested that a σ*(ε) band is formed by strong covalent B-O-B type interaction between the octahedral site low-spin Co^{III} ions to account for its anti-ferromagnetic

![Figure 4. Electrical resistivity in Co_{3–x}Ni_{x}O_{4} system.](image_url)
A study of $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$ ($0 \leq x \leq 1$) system

![Graph showing activation energy for resistivity in $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$ system.](image)

Figure 5. Activation energy for resistivity in $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$ system.

nature ($T_N = 40^\circ\text{K}$). However $\text{Co}_3\text{O}_4$ is only a semiconductor because the $\sigma^*$ ($e_g$) band is empty ($\text{Co}^{\text{III}}$ has the electronic configuration $t^6_2e^0_6$). In $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$ system, if the nickel ions substitute for $\text{Co}^{\text{III}}$ in the octahedral site as low spin $\text{Ni}^{\text{III}}$ ($t^6_2e^1_6$) then it would result in placing charge carriers in the $\sigma^*$($e_g$) band. However, for small values of x, and at low temperatures (below about 450°K) the samples of $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$ system show only semiconducting behaviour, perhaps because the charge carriers are "Anderson-localised" (Mott 1972), since the donor centres ($\text{Ni}^{\text{III}}$) would be randomly distributed. Plots of $\ln \rho$ vs $T^{-1/4}$ for samples with $x<0.5$ show approximately linear behaviour below $\sim 450^\circ\text{K}$.

Qualitative magnetic measurements have shown that the samples become ferromagnetic for values $x>0.5$. $\text{NiCo}_2\text{O}_4$ has already been reported to be ferrimagnetic with magnetization 1.25 $\mu_B$. Further work on the magnetic behaviour of this system is in progress.

Acknowledgements

The authors thank Professor M V C Sastri for his keen interest and encouragement throughout this work. Special thanks of the authors are due to Professor C N R Rao, for helpful suggestions and comments on this work. Acknowledgement is made to the Department of Science and Technology, New Delhi for the financial support of this work.

References

Holgerston S and Karlson A 1929 Z. anorg. allg. Chem. 183 384
Mott N F 1972 Adv. Phys. 21 785
Rao C N R, Bhide V G and Mott N F 1975 Phil. Mag. 32 1277
Rao C N R and Om Parkash 1977 Phil. Mag. 35 1111
Rao C N R, Om Prakash and Ganguly P 1975 J. Solid State Chem. 15 186