

A study of $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$ ($0 \leq x \leq 1$) 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

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Abstract. A series of solid solutions of composition $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$ has been studied. For $0 \leq x \leq 1.1$, 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 $(\text{Co}^{2+})_t [\text{Ni}^{\text{III}}\text{Co}^{\text{III}}]_0\text{O}_4$ for the solid solutions which permits formation of $\sigma^*(e_g)$ band through strong covalent interaction between octahedral-site low spin $\text{Co}^{\text{III}}/\text{Ni}^{\text{III}}$ and oxide ion in the spinel structure.

Keywords. Oxide spinels; $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$ system; structure and electrical properties.

1. Introduction

Recently many cobaltites ACo_2O_4 ($\text{A} = \text{Zn}, \text{Ni}, \text{Fe}, \text{Mn}$ 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 $(\text{Co}^{2+})_t [\text{Ni}^{\text{III}}\text{Co}^{\text{III}}]_0\text{O}_4$ (where the roman superscripts indicate low spin oxidation state and the arabic superscripts high spin state) while Knop *et al* (1968) suggested a distribution $(\text{Co}^{3+})_t [\text{Ni}^{2+}\text{Co}^{\text{III}}]_0\text{O}_4$ 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 Co_3O_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 $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$ ($0 \leq x \leq 1$) 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 $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$ ($0 \leq x \leq 1$).

2. Experimental

AnalaR grade hydrated cobalt and nickel nitrates were made use of in the preparation of $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$ 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. Co_3O_4 was obtained by firing at 600°C whereas for members containing nickel, a lower temperature ($300\text{--}350^\circ\text{C}$) 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 oxidimetric analysis. About 100 mg of the sample is treated with excess Fe^{2+} solution in $4\text{N H}_2\text{SO}_4$. After dissolution of the sample, the excess Fe^{2+} is determined by titration with standard $\text{K}_2\text{Cr}_2\text{O}_7$. From the volume of 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 Co_3O_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 1. Crystallographic and analytical data of $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$ samples.

x	$a_0, \text{\AA}$	Average oxidation state of T.M. ion
0.00	8.080	2.66
0.10	8.083	2.70
0.25	8.087	2.69
0.40	8.093	2.68
0.50	8.099	2.67
0.60	8.106	2.70
0.75	8.114	2.66
0.90	8.116	2.68
1.00	8.119	2.70

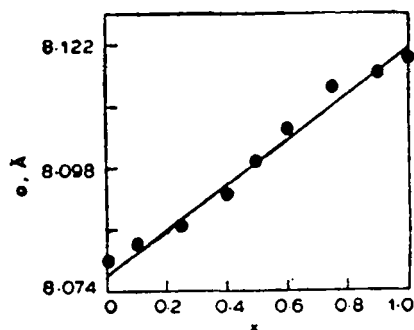


Figure 1. Variation of lattice parameter in $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$ system.

mostly of NiO , appear in the x-ray pattern, indicating that monophasic spinel solid solutions can be obtained for the system $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$ only in the composition range $0 \leq x \leq 1.0$. 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_3O_4 (8.08\AA) and NiCo_2O_4 (8.119\AA) 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 $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$ is almost linear following Vegard's law in the region $0 \leq x \leq 1$ (figure 1). Co_3O_4 , a normal spinel has the cation distribution $(\text{Co}^{2+})_t [\text{Co}^{\text{III}}\text{Co}^{\text{III}}]_o \text{O}_4$. Assuming that the substitution of nickel takes place in the octahedral site as low spin Ni^{III} , one can write the cation-distribution for NiCo_2O_4 as $(\text{Co}^{2+})_t [\text{Ni}^{\text{III}}\text{Co}^{\text{III}}]_o \text{O}_4$ as suggested by Blasse (1963). The fact that NiCo_2O_4 crystallizes in a slightly larger unit cell than Co_3O_4 is understandable in terms of the larger ionic radius of low spin Ni^{III} (0.56\AA) as compared to low spin Co^{III} (0.525\AA) in the octahedral oxygen coordination. The general cation distribution for the solid solution series may then be written as $(\text{Co}^{2+})_t [\text{Ni}_x^{\text{III}}\text{Co}_{2-x}^{\text{III}}]_o \text{O}_4$. The alternative distribution suggested by Knop *et al* (1968), $(\text{Co}^{3+})_t [\text{Ni}^{2+}\text{Co}^{\text{III}}]_o \text{O}_4$ is not consistent with the electrical properties as seen below.

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

The variations of room temperature electrical resistivity and Seebeck coefficient with composition x in $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$ are given in figures 2 and 3. Co_3O_4 is a *p*-type semiconductor ($\rho \sim 10^4$ ohms cm) with a large positive Seebeck coefficient ($+600 \mu\text{V}/^\circ\text{K}$). Substitution of nickel up to $x \sim 0.5$ 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 $\rho \sim 10$ ohm cm and $a \sim 30 \mu\text{V}/^\circ\text{K}$. These values of resistivity were obtained by two-probe measurements. For compositions with $x > 0.5$ showing low resistivity,

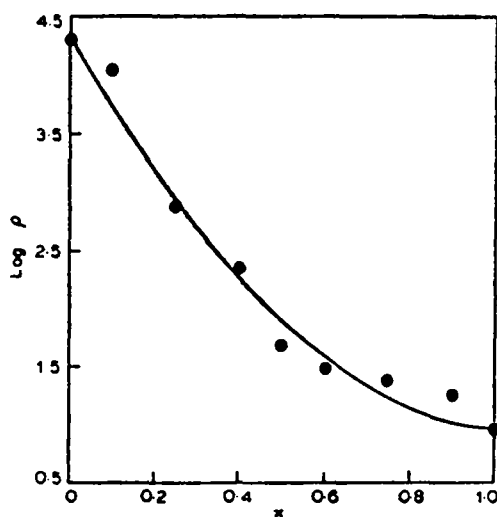


Figure 2. Room temperature resistivity in $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$ system.

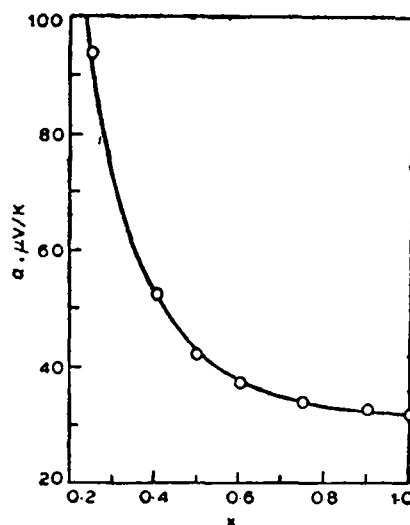


Figure 3. Variation of Seebeck coefficient at room temperature.

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 $x \leq 0.5$, 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 $\log \rho$ 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 $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$ is very similar to that of $\text{LaCo}_{1-x}\text{Ni}_x\text{O}_3$ (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 semi-metallic nature in $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$ system for $x > 0.5$ is understandable in terms of the cation distribution suggested by Blasse (1963) for NiCo_2O_4 ; $(\text{Co}^{2+})_t[\text{Ni}^{\text{III}}\text{Co}^{\text{III}}]_0\text{O}_4$. The solid solutions would then have the distribution $(\text{Co}^{2+})_t[\text{Ni}_x^{\text{III}}\text{Co}_{2-x}^{\text{III}}]_0\text{O}_4$. 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_3O_4 , Goodenough (1965) has suggested that a $\sigma^*(e_g)$ 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

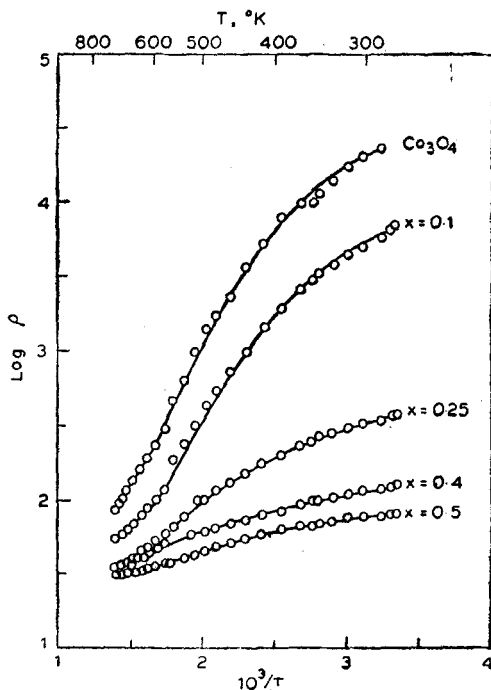


Figure 4. Electrical resistivity in $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$ system.

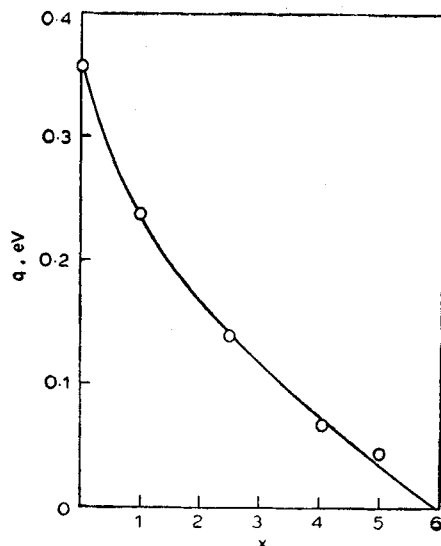


Figure 5. Activation energy for resistivity in $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$ system.

nature ($T_N=40^\circ\text{K}$). However Co_3O_4 is only a semiconductor because the σ^* (e_g) band is empty (Co^{III} has the electronic configuration $t_{2g}^6 e_g^0$). In $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$ system, if the nickel ions substitute for Co^{III} in the octahedral site as low spin Ni^{III} ($t_{2g}^6 e_g^1$) 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 still only semiconducting behaviour, perhaps because the charge carriers are 'Anderson-localised' (Mott 1972), since the donor centres (Ni^{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 ferrimagnetic for values $x > 0.5$. NiCo_2O_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.

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