

$\text{Co}_{3-x}\text{Zn}_x\text{O}_4$ ($0 \leq x \leq 1$) spinel oxides

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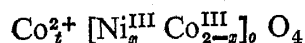
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Abstract. A series of solid solutions of composition $\text{Zn}_x\text{Co}_{3-x}\text{O}_4$ with $0 \leq x \leq 1$, crystallising in spinel structure have been characterised by measurements of unit cell parameter, electrical conductivity and magnetic susceptibility. The results have been rationalised on the basis of cation distribution. A comparison with the solid solutions of composition $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ is also made.

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

1. Introduction

Spinel oxide systems constitute an interesting class of compounds because of interesting possibilities of cation distribution at the two crystallographic environments and the attendant electrical and magnetic properties (Gorter 1954; Goodenough and Loeb 1955). In a recent paper (Gopalakrishnan and Appandairajan 1978) we have reported studies on $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$ system with the cation distribution



where the subscripts t and o refer to tetrahedral and octahedral site ions respectively. In this context, it was considered interesting to study the corresponding zinc system in view of the preponderant tendency of Zn^{2+} to occupy tetrahedral sites in contrast to Ni^{2+} and low spin Ni^{3+} in spinel oxides. The present paper reports preparation and study of crystallographic magnetic and electrical behaviour of solid solutions of the system $\text{Co}_{3-x}\text{Zn}_x\text{O}_4$ ($0 \leq x \leq 1$).

2. Experimental

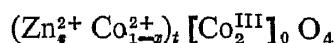
High purity hydrated cobalt nitrate and zinc nitrates were made use of in the preparation of $\text{Co}_{3-x}\text{Zn}_x\text{O}_4$ solid solutions. Compositions corresponding to different values of x were made by mixing requisite volumes of aqueous solutions (1 M) of the nitrates, evaporating them to almost dryness on a waterbath and decomposing the dried mass in air at higher temperatures. Co_3O_4 was obtained

by firing at 600° C whereas for other samples containing zinc, a lower temperature (400° C) was employed. Determination of the oxidising power and hence the average oxidation state of cobalt was carried out by standard analytical procedures (Gopalakrishnan and Appandairajan 1978). The results are given in table 1 together with the values of the unit cell parameter of the system determined from x-ray powder patterns using CoK_α radiation. Electrical conductivity and Seebeck coefficient measurements on sintered pellets were carried out by the methods described elsewhere (Palanisamy 1974). The magnetic susceptibilities of the samples were determined by the Faraday method using a Cahn balance and Brucker electromagnet.

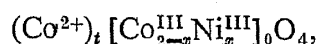
3. Results and discussion

3.1. Crystallographic studies

The x-ray diffraction data of the $\text{Co}_{3-x}\text{Zn}_x\text{O}_4$ solid solutions (table 1) indicate that monophasic spinel type products are formed in the range ($0 \leq x \leq 1$). The variation of unit cell parameters refined by Nelson-Riely plots as a function of x is given in figure 1. The unit cell parameters of Co_3O_4 (8.08 Å) and ZnCo_2O_4 (8.101 Å) obtained agree well with those reported in literature (Knop *et al* 1968; Borekov *et al* 1968). The variation of the unit cell parameter in the region $0 \leq x \leq 1$ is almost linear following Vegard's law. The observation that ZnCo_2O_4 crystallises in a slightly larger unit cell than Co_3O_4 is understandable in terms of larger ionic radius of Zn^{2+} (0.74 Å) as compared to Co^{2+} (0.71 Å). The cation distribution in the system may be written as



which has to be contrasted with the corresponding nickel system wherein the distribution is



wherein both low spin Co^{III} and Ni^{III} occupy octahedral sites.

Table 1. Crystallographic and analytical data of $\text{Zn}_x\text{Co}_{3-x}\text{O}_4$ system.

x	a_0 (Å)	Average oxidation state of T.M. ion
0.00	8.080	2.67
0.10	8.082	2.68
0.25	8.086	2.68
0.4	8.089	2.68
0.5	8.090	2.68
0.6	8.092	2.67
0.75	8.096	2.67
0.9	8.098	2.66
1.0	8.101	2.67

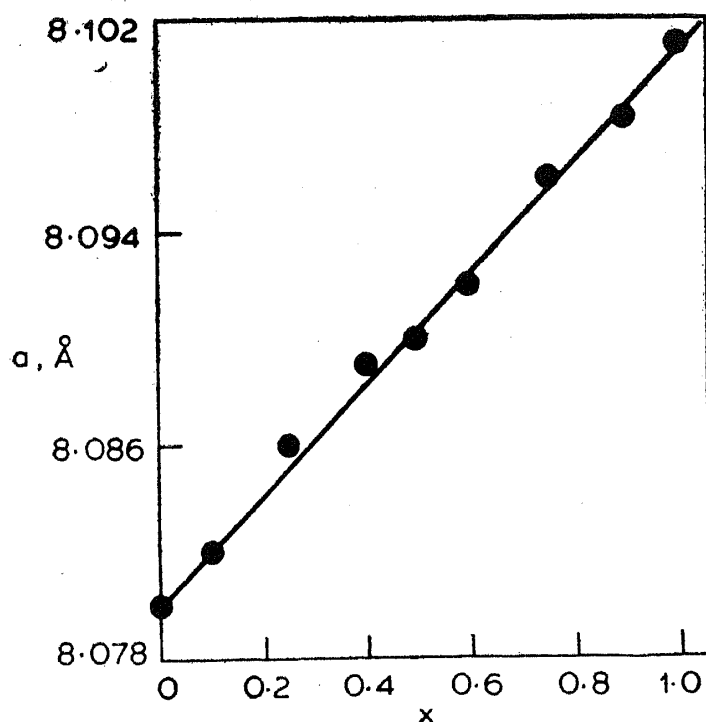


Figure 1. Variation of lattice parameter in Co_{3-x}Zn_xO₄ system.

3.2. Electrical and magnetic behaviour of Co_{3-x}Zn_xO₄ system

The variation of room temperature resistivity, Seebeck coefficient and activation energy for electrical conduction with composition are given in figures 2-4. Though substitution by zinc brings about a gradual decrease in both resistivity and Seebeck coefficient upto $x = 1$, all the solid solutions behave as semiconductors as against the nickel system wherein a semi-metallic behaviour is exhibited by samples with $x > 0.5$. The electrical transport property of nickel system has been explained by us on the basis that σ^* (eg) band is populated by substitution of Co^{III} by low spin Ni^{III} ($t_{2g}^6 eg^1$) at the octahedral sites. But when only Co^{III} ($t_{2g}^6 eg^0$) ions occupy octahedral sites, the σ^* (eg) band is empty and hence Co₃O₄ and solid solutions of Co_{3-x}Zn_xO₄ system remain semiconducting throughout. The general decrease in resistivity and its activation energy with increasing zinc substitution (figures 2 and 4) seems to suggest that the ions at the tetrahedral sites in the spinel solid solutions do play a role, albeit minor, in deciding the electrical transport behaviour.

The variation of magnetic susceptibility with temperature for various values of x is given in figure 5 as a function $1/\chi$ vs T . All members of the solid solutions series show only paramagnetic behaviour in contrast to the observation that in the Co_{3-x}Ni_xO₄ system, members with $x > 0.5$ are ferrimagnetic. The residual magnetic susceptibility of Zn_xCo_{3-x}O₄ system is mainly due to the presence of Co²⁺ ions (high spin with configuration: $3d^7 : eg^4 t_{2g}^3$) at the tetrahedral sites. In general, $1/\chi$ vs T plots for all Co_{3-x}Zn_xO₄ samples show two linear regions with a break around 100-180° K, the temperature of break decreases with increasing

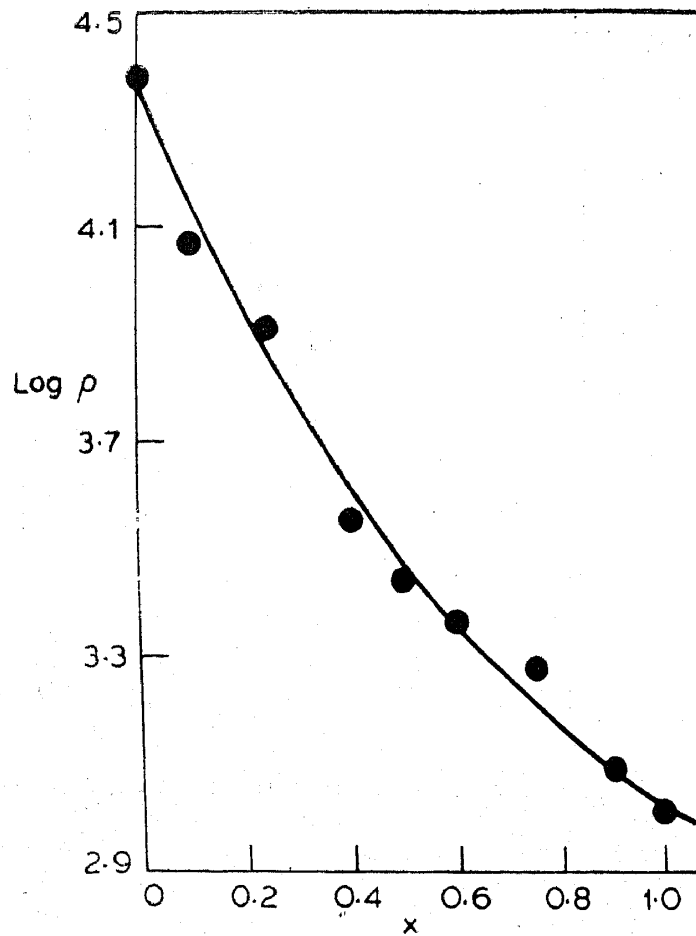


Figure 2. Room temperature resistivity in $\text{Co}_{3-x}\text{Zn}_x\text{O}_4$ system.

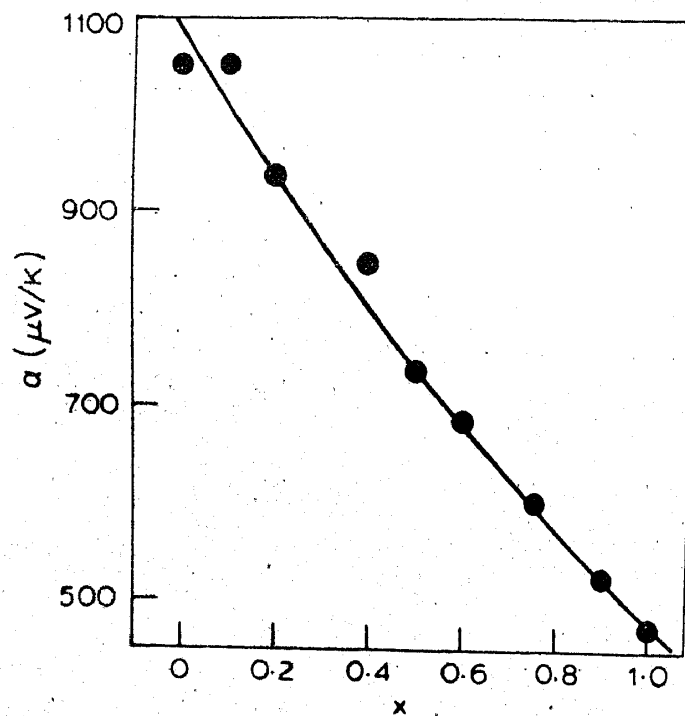


Figure 3. Variation of Seebeck coefficient at room temperature.

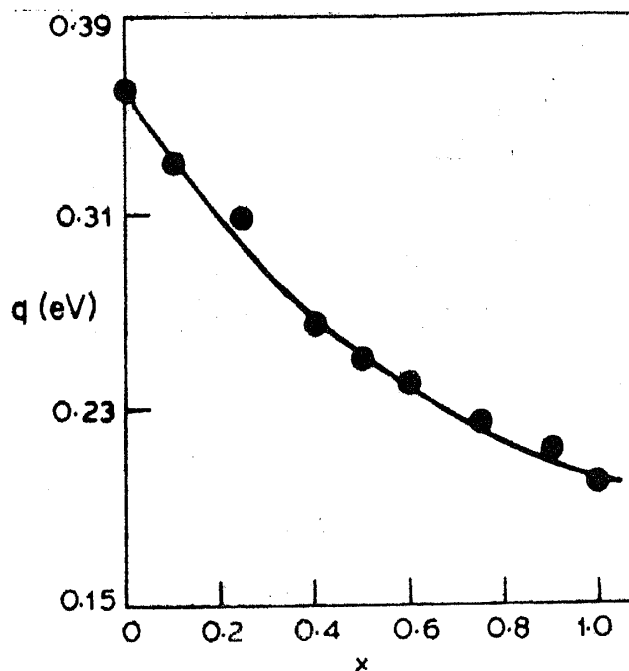


Figure 4. Activation energy for electrical conduction in $\text{Co}_{3-x}\text{Zn}_x\text{O}_4$.

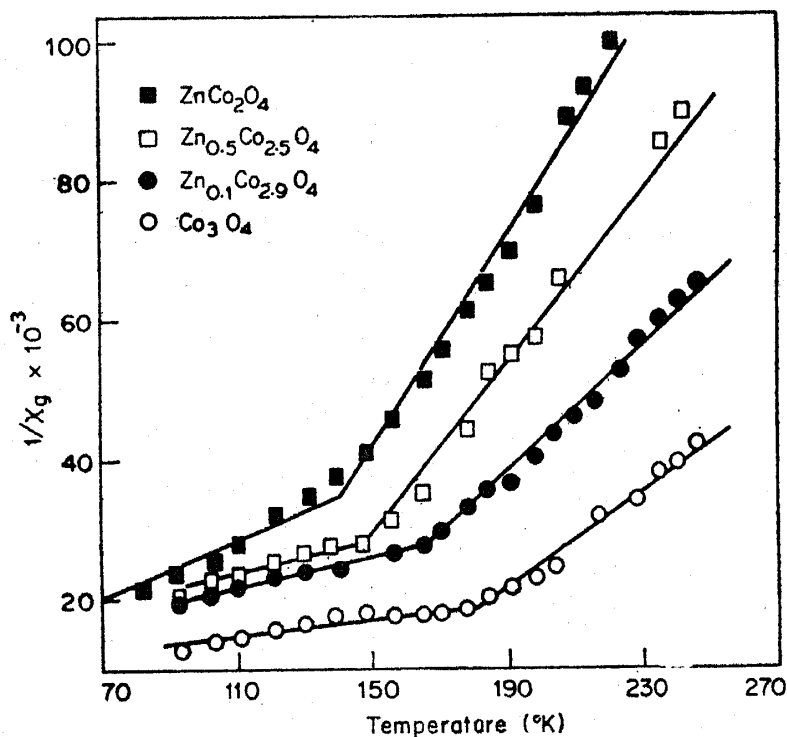


Figure 5. Variation of $1/X_g$ vs temperature for $\text{Co}_{3-x}\text{Zn}_x\text{O}_4$ system.

zinc substitution. In the plot of X vs T , a plateau is observed around the same temperature region. This may be due to change of spin state of Co^{3+} in this temperature region. In general, substitution of Zn^{2+} in Co_3O_4 decreases the suscep-

tibility—a result which is understandable in terms of diamagnetic Zn^{2+} replacing paramagnetic Co^{3+} . The fact that $(Zn)(Co_2^{III})_0O_4$ is paramagnetic (Bonnenberg and Wijn 1970) seems to suggest that trivalent cobalt ions at octahedral sites have non-zero high spin population even at low temperatures. Similar behaviour of trivalent cobalt in perovskite oxides is reported in the literature (Rao *et al* 1976).

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