

Lithium-Substituted Cobalt Oxide Spinel $\text{Li}_x\text{M}_{1-x}\text{Co}_2\text{O}_4$ ($M = \text{Co}^{2+}, \text{Zn}^{2+}; 0 \leq x \leq 0.4$)

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Substitution of Li^+ into Co_3O_4 and ZnCo_2O_4 gives rise to the solid solution series $\text{Li}_x\text{M}_{1-x}\text{Co}_2\text{O}_4$ ($M = \text{Co}^{2+}$ or Zn^{2+}) having the spinel structure upto $x = 0.4$. X-Ray diffraction intensities show that the spinel solid solutions are likely to have the following cation distributions: $(\text{Co}^{2+})_t[\text{Li}_x^{2+}\text{Co}_{3-3x}^{2+}\text{Co}_{2x}^{4+}]_o\text{O}_4$ and $(\text{Zn}_{1-x}^{2+}\text{Co}_x^{2+})_t[\text{Li}_x^{2+}\text{Co}_{3-3x}^{2+}\text{Co}_{2x}^{4+}]_o\text{O}_4$. Electrical resistivity and Seebeck coefficient data indicate that the electron transport in these systems occurs by a small-polaron hopping mechanism.

1. Introduction

Substitution of lithium in several oxide spinels has been studied. For example, Li^+ substitution in Mn_3O_4 and Fe_3O_4 giving rise to LiMn_2O_4 (1) and LiFe_5O_8 (2) respectively is known. A similar substitution of Li^+ into Co_3O_4 has not to our knowledge been studied. In this paper, we report the formation and study of lithium-substituted cobalt oxides of the general formula $\text{Li}_x\text{M}_{1-x}\text{Co}_2\text{O}_4$ ($M = \text{Co}$ or Zn) having the spinel structure.

2. Experimental

AnalaR-grade lithium carbonate and metal nitrates were used in the preparation of samples. The metal nitrate solutions mixed in the required molar proportions for various values of x in $\text{Li}_x\text{M}_{1-x}\text{Co}_2\text{O}_4$ ($M =$

Co or Zn) were evaporated to near dryness on a water bath. The dried mass was then transferred to a platinum crucible and decomposed at ~ 870 K in air. The solid mass was further annealed in a stream of oxygen at the same temperature for 24 hr.

The average oxidation state of cobalt in the samples was determined by oxidimetric analysis: About 100 mg of the sample was treated with an excess of Fe^{2+} (0.1 N) solution in 4 N H_2SO_4 . After dissolution, the unreacted Fe^{2+} was titrated against standard $\text{K}_2\text{Cr}_2\text{O}_7$. A blank was performed under identical conditions. From the amount of Fe^{2+} that reacted with the sample, the average oxidation state of cobalt was calculated. The results (Table I) indicate that substitution of lithium into Co_3O_4 and ZnCo_2O_4 occurs according to the controlled-valency principle forming the solid solution series $\text{Li}_x\text{M}_{1-x}\text{Co}_2\text{O}_4$ up to $x = 0.4$. For $x > 0.4$, the experimental values of oxidation state do not agree with the calculated values. The lithium content of the

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TABLE I
AVERAGE OXIDATION STATE OF COBALT, AND UNIT CELL PARAMETER a_0 OF $\text{Li}_x\text{M}_{1-x}\text{Co}_2\text{O}_4$
($M = \text{Co}$, OR Zn)

x	$\text{Li}_x\text{Co}_{3-x}\text{O}_4$			$\text{Li}_x\text{Zn}_{1-x}\text{Co}_2\text{O}_4$		
	Average oxidation state of cobalt		a_0 (Å)	Average oxidation state of cobalt		a_0 (Å)
	Experimental	Calculated ^a		Experimental	Calculated ^b	
0.00	2.67	2.66	8.080	3.01	3.00	8.101
0.10	2.81	2.72	8.083	3.09	3.05	8.098
0.20	2.82	2.79	8.0845	3.13	3.10	8.094
0.25	2.84	2.82	8.085	3.31	3.12	8.092
0.30	2.88	2.85	8.087	3.19	3.15	8.090
0.40	2.98	2.92	8.089	3.22	3.20	8.088
0.50	2.79	3.00	8.089	2.97	3.25	8.088

^a $\text{Li}_x^+\text{Co}^{2+}\text{Co}_{3-x}^{3+}\text{Co}_{2x}^{4+}\text{O}_4$.

^b $\text{Li}_x^+\text{Zn}_{1-x}^{2+}\text{Co}_x^{2+}\text{Co}_{3-x}^{3+}\text{Co}_{2x}^{4+}\text{O}_4$.

samples were analyzed by flame photometry and were found to agree ($\pm 2\%$) with the theoretically expected values.

Experimental procedures for the study of structure and electrical properties were the same as described in an earlier paper (3).

3. Results and Discussion

3.1 Crystal Chemistry

The X-ray powder diffraction patterns of $\text{Li}_x\text{M}_{1-x}\text{Co}_2\text{O}_4$ ($M = \text{Co}$ or Zn) are characteristic of the spinel structure. The cubic unit cell parameter a_0 varies almost linearly with x up to 0.4 (Fig. 1). Although the patterns for samples with $x > 0.4$ are spinel-like and there is no additional phase detectable by X-ray diffraction, the unit cell parameter does not vary significantly from the value for $x = 0.4$. This together with the chemical analysis result seem to indicate that the solid solution series exists only up to ~ 0.4 .

Co_3O_4 and ZnCo_2O_4 are normal spinels having the cation distribution $(M)_t[\text{Co}_2]_o\text{O}_4$ ($M = \text{Co}$ or Zn), where the subscripts t and o denote tetrahedral- and octahedral-site

ions, respectively. Substitution of lithium can occur either at the tetrahedral sites replacing M ions or at the octahedral sites replacing Co^{3+} ions. Lithium is known to occupy tetrahedral (e.g., LiV_2O_4) as well as octahedral sites (e.g., LiFe_5O_8) in oxide spinels (2, 4). Keeping these facts in view we can write the following cation distributions for $\text{Li}_x\text{Co}_{1-x}\text{Co}_2\text{O}_4$ spinels:

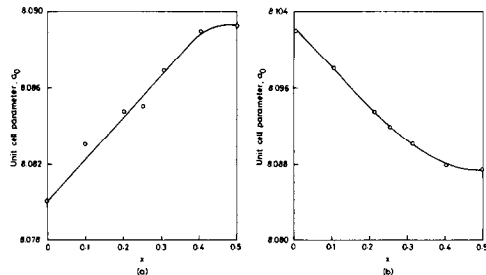
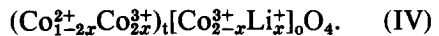
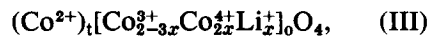
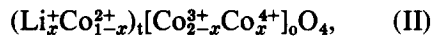


FIG. 1. Variation of unit cell parameter a_0 with x of (a) $\text{Li}_x\text{Co}_{1-x}\text{Co}_2\text{O}_4$ and (b) $\text{Li}_x\text{Zn}_{1-x}\text{Co}_2\text{O}_4$.

TABLE II
CALCULATED AND OBSERVED X-RAY POWDER
DIFFRACTION INTENSITIES FOR $\text{Li}_{0.25}\text{Co}_{2.75}\text{O}_4$

<i>hkl</i>	Calculated relative intensity for cation distributions				Observed intensity (<i>I</i> / <i>I</i> ₀)
	I ^a	II ^b	III ^c	IV ^d	
111	14.2	14.4	1.4	1.9	6
220	20.0	21.4	32.0	31.0	27
311	100.0	100.0	100.0	100.0	100
222	9.7	9.6	5.0	5.1	6
400	29.4	29.1	17.2	17.5	15
422	7.1	7.2	11.4	11.3	10
333	7.7	7.7	7.7	7.70	25
511	23.1	23.1	23.1	23.10	35
440	47.0	47.0	44.2	44.3	9
533	11.3	11.3	11.3	11.3	

^a $(\text{Li}_{0.25}\text{Co}_{0.5}^{2+}\text{Co}_{0.25}^{3+})_t[\text{Co}_{1.0}^{3+}]_o\text{O}_4$.

^b $(\text{Li}_{0.25}\text{Co}_{0.75}^{2+})_t[\text{Co}_{0.75}^{3+}\text{Co}_{0.25}^{4+}]_o\text{O}_4$.

^c $(\text{Co}^{2+})_t[\text{Co}_{1.25}^{3+}\text{Co}_{0.5}^{4+}\text{Li}_{0.25}^{+}]_o\text{O}_4$.

^d $(\text{Co}_{0.5}^{3+}\text{Co}_{0.5}^{4+})_t[\text{Co}_{1.75}^{3+}\text{Li}_{0.25}^{+}]_o\text{O}_4$.

We can write similar cation distributions for the $\text{Li}_x\text{Zn}_{1-x}\text{Co}_2\text{O}_4$ system also.

Of the four cation distributions, (I) and (IV), which place trivalent cobalt in tetrahedral sites, may be regarded as impossible considering the fact that this ion existing in the low-spin state has a predominant tendency to occupy octahedral sites in oxides. Cation distributions (I) and (IV), which create no charge carriers at the octahedral sites, may also be ruled out on the basis of electrical properties (see Section 3.2). Hence (II) or (III) is the likely cation distribution for the series. A small increase of the unit cell parameter with increasing *x* in $\text{Li}_x\text{Co}_{1-x}\text{Co}_2\text{O}_4$ can be accounted for by both the distributions (II) and (III). In (II), tetrahedral site Co^{2+} ($r = 0.57 \text{ \AA}$) is replaced by Li^+ at the same site ($r = 0.594 \text{ \AA}$). Simultaneously an equivalent amount of octahedral site low-spin Co^{3+} ($r = 0.525 \text{ \AA}$) is oxidized to Co^{4+} (which is also likely to exist in the low-spin state, $r \sim 0.51 \text{ \AA}$). In (III), low-spin Co^{3+} at octahedral sites is

replaced by Li^+ at the same site ($r = 0.74 \text{ \AA}$); an equivalent amount of Co^{4+} is formed at this site. We cannot therefore distinguish between the cation distributions on the basis of unit-cell-parameter variations alone.

Probable cation distribution in spinels can be arrived at by comparing the observed and calculated X-ray diffraction intensity ratios of a certain pairs of (*hkl*) reflections such as $I(400)/I(220)$ and $I(220)/I(440)$ after making due corrections for the Lorentz polarization factors (5). The calculated intensities for cation distribution (I)–(IV) together with the experimental values for $\text{Li}_{0.25}\text{Co}_{2.75}\text{O}_4$ are given in Table II, while the calculated intensity ratios $I(220)/I(440)$, $I(400)/I(220)$, and $I(220)/I(311)$ are compared with the experimental values in Table III. It is seen that the calculated intensities of distributions (I) and (II) are similar and those of (III) and (IV) are likewise similar; experimental values of intensities are close to the latter distributions. However, since distribution (IV) is ruled out on the basis of electrical properties, we feel that cation distribution (III) is the most likely one for $\text{Li}_x\text{Co}_{3-x}\text{O}_4$ spinels. Similarly intensity calculations indicate that the probable cation distribution for the zinc spinels is $(\text{Zn}_{1-x}^{2+}\text{Co}_x^{2+})_t[\text{Co}_{2-3x}^{3+}\text{Co}_{2x}^{4+}\text{Li}_{1-x}^{+}]_o\text{O}_4$.

TABLE III
CALCULATED AND OBSERVED X-RAY DIFFRACTION
INTENSITY RATIOS OF SELECTED (*hkl*) REFLECTIONS
FOR $\text{Li}_{0.25}\text{Co}_{2.75}\text{O}_4$

Cation distribution	$I(220)/I(440)$	$I(400)/I(220)$	$I(220)/I(311)$
I ^a	0.43	1.47	0.20
II ^b	0.46	1.36	0.21
III ^c	0.72	0.54	0.32
IV ^d	0.70	0.56	0.31
Observed ratio	0.77	0.56	0.27

^{a,b,c,d} See footnote to Table 2.

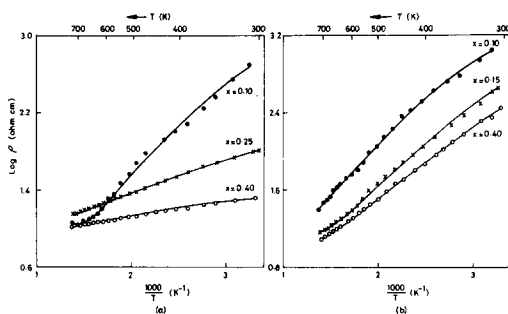


FIG. 2. Variation of logarithm of electrical resistivity with reciprocal temperature of (a) $\text{Li}_x\text{Co}_{1-x}\text{Co}_2\text{O}_4$ and (b) $\text{Li}_x\text{Zn}_{1-x}\text{Co}_2\text{O}_4$.

3.2. Electrical Properties

The spinel solid solutions show p-type semiconducting behavior. The variation of logarithm of electrical resistivity with reciprocal temperature of some of the members is shown in Fig. 2. The values of resistivity and Seebeck coefficient at 300 K and activation energies for electrical conduction are collected in Table IV. It is seen that in both the series these quantities decrease with increase of x . These results, together with the observation that the Seebeck coefficient of the individual members roughly remains constant over the temperature region 300–500 K, may be taken to indicate that the electrical transport in these systems occurs by a small-polaron hopping mechanism (6). Assuming that the majority of charge carriers are the holes associated with Co^{4+} ions at octahedral sites, the decrease of activation energy with

increasing x may signal that the charge transport tends toward narrowband conduction with increasing x may signal that the charge transport tends towards narrowband conduction with increasing Co^{4+} ion concentration; increasing Co^{4+} ion concentration at octahedral sites is expected to increase the cobalt–oxygen covalent interaction.

That the electron transport in these materials occurs by a hopping mechanism is further supported by the Seebeck coefficient data. Seebeck coefficient of oxide semiconductors exhibiting hopping semiconduction is given by (6)

$$\alpha = \frac{k}{e} \left[\ln \frac{N - P}{p_i} + \frac{S_R^*}{k} \right] \\ \approx 198 \log \frac{N - P}{P} + A(\mu\text{V}.\text{deg}^{-1}),$$

where N and P are respectively the number of polaron sites and the number of polarons available per formula unit. For the cobalt spinels studied in this work, N may be identified as the sum of Co^{3+} and Co^{4+} at the octahedral sites and P the Co^{4+} ions. Hence, according to the above equation, a plot of α against $\log [\text{Co}^{3+}/\text{Co}^{4+}]$ is expected to be linear with a slope around 198. It is gratifying that the plots are indeed linear with the expected slopes indicating that the electrical transport in these systems approximates to small-polaron hopping model.

TABLE IV
ELECTRICAL TRANSPORT PROPERTIES OF $\text{Li}_x\text{M}_{1-x}\text{Co}_2\text{O}_4$ ($M = \text{CO}$ OR Zn)

x	$\text{Li}_x\text{Co}_{1-x}\text{Co}_2\text{O}_4$			$\text{Li}_x\text{Zn}_{1-x}\text{Co}_2\text{O}_4$		
	ρ (ohm.cm) at 300 K)	E_a (eV)	α ($\mu\text{V}.\text{K}^{-1}$) at 300 K	ρ (ohm.cm) at 300 K	E_a (eV)	α ($\mu\text{V}.\text{K}^{-1}$) at 300 K
0.00	2×10^4	0.36	+600	1.1×10^5	0.20	+470
0.10	3.6×10^2	0.20	+450	6.9×10^2	0.18	+350
0.25	1.8×10^{-1}	0.07	+320	5.1×10^2	0.16	+250
0.40	1.4×10^{-1}	0.03	+260	3.5×10^2	0.15	+170

It should, however, be remarked that the exact polaron geometry in these systems is difficult to arrive at from the limited data presented here. In oxide spinels containing Li^+ together with highly charged cations at octahedral sites, it is known (7) that cation clusters are formed which, make it difficult to estimate the values of N and p in the above equation. A more extensive study is needed for a complete understanding of electron transport in these systems.

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