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LITHIUM DOPING OF COBALT-NICKEL SPINEL OXIDES AT LOW TEMPERATURES

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ABSTRACT

Cobalt-nickel spinel oxides containing lithium ($Li_y(Ni_xCo_{1-x})_{3-y}O_4$, $y \approx 0.13$, $0 \leq x \leq 0.4$) are prepared by thermal decomposition of mixed cobalt-nickel hydroxide-nitrates with a double-chain structure, $Ni_xCo_{1-x}(OH)(NO_3){\cdot}H_2O$ in a lithium nitrate medium. XRD analysis, DTA and magnetic susceptibility measurements show that double-chain $Ni_xCo_{1-x}(OH)(NO_3){\cdot}H_2O$ $0 < x < 0.4$ decomposes to nickel-cobalt spinels via layered hydroxide-nitrates $Ni_xCo_{1-x}(OH)_{1.5}(NO_3)_{0.5}$, but in a $LiNO_3$ medium, lithium containing nickel-cobalt spinels $Li_y(Ni_xCo_{1-x})_{3-y}O_4$ are obtained, preceded by a complete oxidative hydrolysis of double-chain $Ni_xCo_{1-x}(OH)(NO_3){\cdot}H_2O$ to layered oxide-hydroxides $Ni_xCo_{1-x}OOH$. The lithium doping of nickel-cobalt spinels at low-temperature is explained in terms of the ion-exchange properties of the layered oxide-hydroxides $Ni_xCo_{1-x}OOH$ in a $LiNO_3$ melt. With increasing nickel content ($0.4 < x < 1$), the thermal decomposition of the coprecipitated cobalt-nickel hydroxide-nitrates in a lithium nitrate medium leads to the formation of two phases consisting of $Li_y(Ni_xCo_{1-x})_{3-y}O_4$ ($y \approx 0.13$, $x \approx 0.4$) spinels and a rock-salt $Ni_{1-b}Co_bO$ ($b \leq 0.1$), the relative amount of the latter increasing with the nickel content in the precursor mixture. Low-temperature lithium doping of NiO can not be achieved with this preparation procedure since $Ni(OH)(NO_3){\cdot}H_2O$ hydrolyses only to a layered nickel hydroxide-nitrate $Ni(OH)_{1.5}(NO_3)_{0.5}$ in a lithium nitrate medium.

KEYWORDS: A. oxides, A. layered compounds, B. chemical synthesis, C. X-ray diffraction.

INTRODUCTION

Lithium doped transition metal oxides gather both scientific and technological interests: they are model systems for investigations on the electronic structure of solids (1) and are used as electrodes in electrochemical power devices (2-3) and as catalysts in the reaction of oxidative coupling of methane (4). Among the numerous lithium-transition metal oxides, lithium-cobalt and lithium-nickel oxides are of special interest. Usually, lithium substitution in cobalt and nickel oxides is achieved by solid state reactions between lithium salts and cobalt or nickel oxides at temperatures above 500°C (5). To the best of our knowledge there are no data on lithium doping of cobalt-nickel oxides with a spinel type structure owing to their low thermal stability (up to 400°C).

Recently we have succeeded in preparation of lithium containing cobalt spinels Co_3O_4 (up to 12 at%) at low-temperature (300°C) by thermal decomposition of layered CoOOH in a $LiNO_3$ melt (6). Using data from TEM studies (6), the mechanism of lithium doping was explained with a topotactic transformation of CoOOH into $Li_xCo_{3-x}O_4$ spinel preceded by a partial ion-exchange between H^+ from CoOOH and Li^+ from the $LiNO_3$ melt. This result stimulated us to continue the investigation on lithium doping of mixed nickel-cobalt spinels $(Ni_xCo_{1-x})_3O_4$, $0 < x \leq 0.33$, by "soft-chemistry" reactions. We have chosen nickel-cobalt hydroxide-nitrates as suitable precursors because of their low-dimensional crystal structure.

Three kinds of hydroxide-nitrate salts of cobalt and nickel with the general formula $M(OH)_{1+s}(NO_3)_{1-s}\cdot zH_2O$ are known, their crystal structure being dependent on the OH^-/NO_3 ratio. When $OH/NO_3 = 1$, the main structural elements are infinite double chains of octahedrally coordinated metal ions: $Ni(OH)(NO_3)\cdot H_2O$ (7) and $Co(OH)(NO_3)\cdot H_2O$ (8). When $2 \leq OH/NO_3 \leq 3$, brucite-type layers are built in which all the octahedral sites are occupied by M^{2+} ions: $Ni(OH)_{1.5}(NO_3)_{0.5}$ (9) and $Co(OH)_{1.5}(NO_3)_{0.5}$ (10). Finally, at $OH/NO_3 > 4$, the crystal structure consists of brucite-type layers again, but the M^{2+} ions are located in both octahedral and tetrahedral sites: $Co_7(OH)_{12}(NO_3)_2$ (11). Irrespective of the different chemical composition and crystal structure type, all hydroxide-nitrate salts present some structural similarities. For example, between 60 and 120°C double-chain $Zn(OH)(NO_3)\cdot H_2O$ transforms topotactically to the layered analogue $Zn(OH)_{1.33}(NO_3)_{0.67}$ (12).

In the present paper we have tried to prepare mixed lithium-nickel-cobalt spinel oxides at low-temperature by thermal decomposition of nickel-cobalt hydroxide-nitrates in a $LiNO_3$ melt.

EXPERIMENTAL

To obtain an intimate mixture of hydroxide nitrate and $LiNO_3$, solid Li_2CO_3 was added to a 75% solution of $Co(NO_3)_2$ and $Ni(NO_3)_2$ ($0 \leq Ni/(Ni+Co) \leq 1$) with intensive stirring, the Li/(Ni + Co) ratio being 1.05/1. This mixture was evaporated to a dry residue at 80°C. The dry residue was heated at 150°C for 4 hours and, then, at 300°C for 2 hours, after which the sample was quickly cooled. To eliminate the lithium nitrate from the hydroxide nitrates thus obtained, the samples were washed with acetone.

The lithium content was determined by atomic absorption analysis, the total (Ni + Co) amount was established by complexometric titration, and the mean oxidation degree of Ni and Co ions, by iodometric titration.

X-ray phase analysis was carried out with a DRON (ex-USSR) powder diffractometer using CuK_α- and CoK_α-radiation. The unit cell parameters were determined by least squares fits to all Bragg's peak positions.

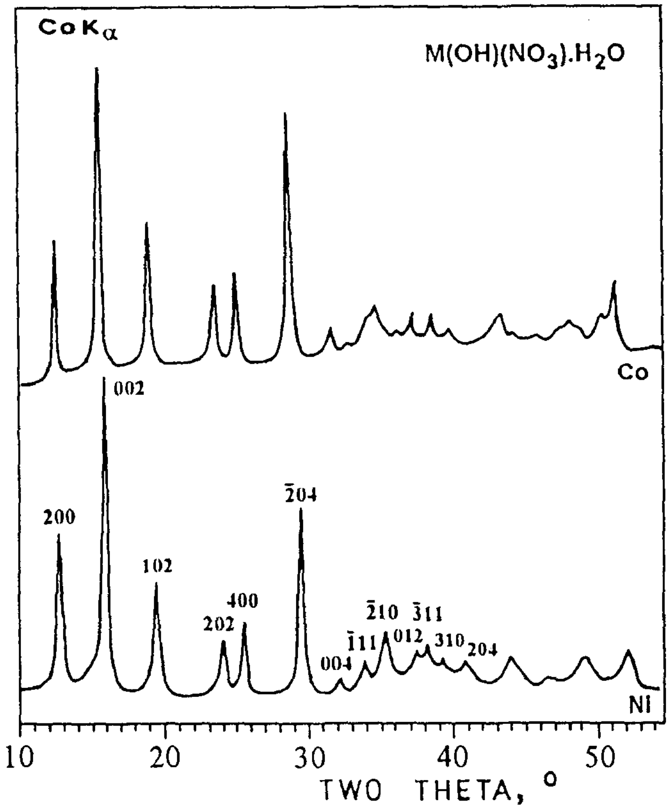

FIG. 1
XRD patterns of $Co(OH)(NO_3)\cdot H_2O$ and $Ni(OH)(NO_3)\cdot H_2O$ (CoK_α-radiation is used).

DTA measurements were performed with an STA 780 apparatus (Stanton Redcroft Ltd, England) at 20-600°C with a heating rate of 5°/min. Platinum crucibles with a diameter of 6 mm and samples weighting 20 mg each were used. The magnetic susceptibility measurements were performed by the Faraday method within the temperature range 100-600 K. The specific surface area were determined by the BET method from the adsorption of N_2 at 77 K.

RESULTS

When solid Li_2CO_3 is added to a concentrated cobalt and/or nickel nitrate solution, hydroxide-nitrates are precipitated which have the composition $M(OH)(NO_3)\cdot H_2O$ and a double-chain structure (Fig. 1). Table 1 shows the unit cell parameters of $Co(OH)(NO_3)\cdot H_2O$ and $Ni(OH)(NO_3)\cdot H_2O$ thus obtained, as well as the parameters of $Zn(OH)(NO_3)\cdot H_2O$ (12) and $Ni(OH)(NO_3)\cdot H_2O$ (7) obtained by thermal-hydrolysis from the corresponding nitrate salts. The unit cell dimensions increase from the nickel to the zinc salt and match with the ionic M^{2+} radii (r_{Ni} = 0.69 Å, r_{Co} = 0.72 Å, r_{Zn} = 0.74 Å). It should be noted that LiOH precipitates a mixture of hydroxide-nitrate salts consisting of double-chain $M(OH)(NO_3)\cdot H_2O$ and layered $M(OH)_{1.5}(NO_3)_{0.5}$.

TABLE I
Unit Cell Parameters of $M(OH)(NO_3)H_2O$, M ≡ Co, Ni and Zn

	Co	Ni	Ni (7)	Zn (12)
a ± 0.008, Å	17.854	17.628	17.523	17.9512
b ± 0.003, Å	3.226	3.156	3.150	3.26002
c ± 0.006, Å	14.273	14.110	14.110	14.2722
β ± 0.06, Å	114.39	113.54	112.55	114.911

Figure 2 compares the thermal behaviour of pure $Co(OH)(NO_3)\cdot H_2O$ and the $[Co(OH)(NO_3)\cdot H_2O\ LiNO_3]$ mixture. Pure $Co(OH)(NO_3)\cdot H_2O$ decomposes endothermally in two steps: at 147 and 183°C. In the $LiNO_3$ medium, the DTA curve consists of the endothermic peaks which correspond to the $Co(OH)(NO_3)\cdot H_2O$ decomposition (between 120 and 300°C) and to the $LiNO_3$ dehydration and melting (between 50 and 120°C and at 253°C, respectively). The effect of $LiNO_3$ on the $Co(OH)(NO_3)\cdot H_2O$ thermal behaviour is manifested by the lower intensity of the decomposition peak at 183°C and by the extra peak at 276°C, which indicates a change of the $Co(OH)(NO_3)\cdot H_2O$ decomposition process in the $LiNO_3$ medium. In addition, a strong endothermic peak at 465°C is also observed for the $[Co(OH)(NO_3)\cdot H_2O\ LiNO_3]$ mixture.

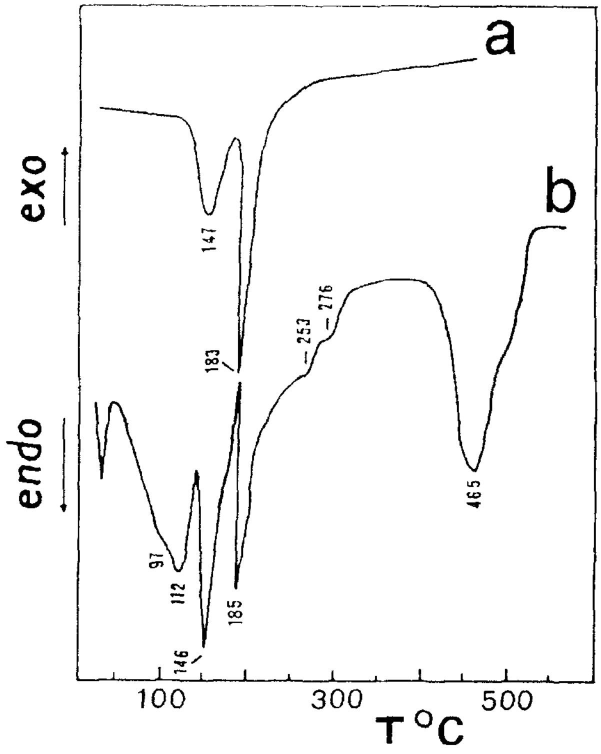

FIG. 2
DTA-curves of pure $Co(OH)(NO_3)\cdot H_2O$ (a) and $Co(OH)(NO_3)\cdot H_2O + LiNO_3$ (b).

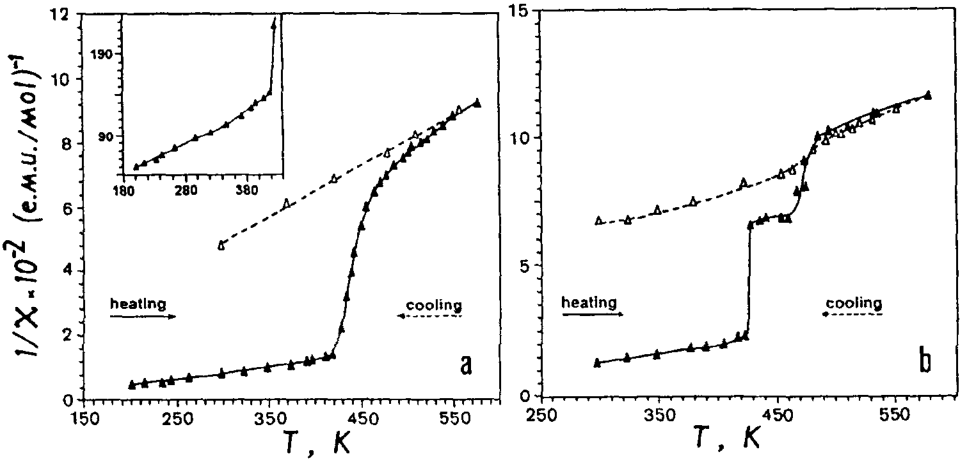

FIG. 3
Temperature variation in the magnetic susceptibility of $Co(OH)(NO_3){\cdot}H_2O$ (a) and $Co(OH)(NO_3){\cdot}H_2O + LiNO_3$ (b).

The effect of $LiNO_3$ on the $Co(OH)(NO_3){\cdot}H_2O$ decomposition is more visible in the magnetic susceptibility measurements (coordinates $1/\chi_M$ *versus* T, Fig. 3). For $Co(OH)(NO_3){\cdot}H_2O$ the Curie-Weiss law is obeyed up to 350 K with a Curie constant C = 3.5 e.m.u./mol, which is typical for octahedrally coordinated high-spin Co^{2+}. On further heating, the kink in the linear dependence $1/\chi_M$ (T) at 350 K (inset in Fig. 3a) and the irreversible drastic change of the magnetic susceptibility above 420 K reflect the two-step decomposition of $Co(OH)(NO_3){\cdot}H_2O$ For the intimate $Co(OH)(NO_3){\cdot}H_2O + LiNO_3$ mixture, χ changes in a different way (Fig. 3b): during heating, the magnetic susceptibility abruptly drops at 420 K, between 430 and 470 K it remains unchanged, and, above 480 K, a smooth decrease in χ is observed. (We shall mention that $LiNO_3{\cdot}H_2O$ is diamagnetic and does not contribute to the changes in the magnetic susceptibility.) In the $LiNO_3$ medium, the cooling curve also changes as compared to the pure samples.

The XRD patterns of samples prepared by interrupting the DTA experiments at 140, 155 and 200°C are given in Figures 4 and 5. The better resolution of the (300), (102), (402) and (202) diffraction lines of the double-chain $Co(OH)(NO_3){\cdot}H_2O$ heated at 140°C reflects a gain of cristallinity during heating (Fig. 4b). Between 140 and 160°C, the double-chain $Co(OH)(NO_3){\cdot}H_2O$ transforms into a hydroxide-nitrate with a layered structure $Co(OH)_{1.5}(NO_3)_{0.5}$ (Fig. 4c), which corresponds to the first endothermic peak in the DTA curve (Fig. 2a) and to the kink in the magnetic susceptibility curve (Fig. 3a). The decomposition of the layered hydroxide-nitrate $Co(OH)_{1.5}(NO_3)_{0.5}$ proceeds above 170°C and leads to the formation of Co_3O_4 with a spinel structure (Fig. 4d). In a $LiNO_3$ medium, a layered hydroxide-nitrate $Co(OH)_{1.5}(NO_3)_{0.5}$ is obtained at 140°C (Fig. 5b). However, the thermal hydrolysis of the hydroxide-nitrate in $LiNO_3$ goes on further: a layered oxide-hydroxide CoOOH results from the complete oxidative hydrolysis of the initial $Co(OH)(NO_3){\cdot}H_2O$ at about 150°C (Fig. 5c). The diamagnetic properties of CoOOH (octahedral Co^{3+} ions in low-spin state) are the reason for the abrupt drop of the magnetic susceptibility above 420 K (Fig. 3b). Above the melting point of $LiNO_3$ (250°C), CoOOH decomposes to a lithium containing Co_3O_4 (Fig. 5d) with magnetic properties differing from those of pure Co_3O_4 (cooling curves, Fig. 3a and 3b). The thermal effect of the CoOOH decomposition in the $LiNO_3$ melt corresponds to the endothermic peak at 276°C (Fig. 2b). During

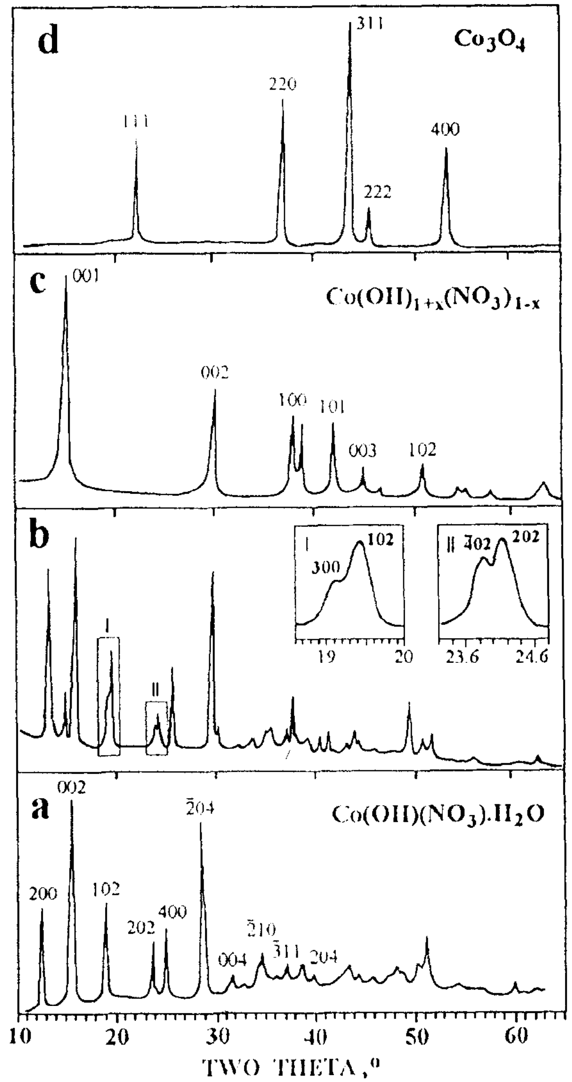

FIG. 4

XRD patterns of $Co(OH)(NO_3)·H_2O$ during heating at 100°C (a), 140°C (b), 155°C (c), and 200°C (d).

further heating, the interaction between lithium containing Co_3O_4 and $LiNO_3$ leads to the formation of $LiCoO_2$ which is demonstrated by the strong endothermic peak at 465°C (Fig. 2b).

Double-chain $Ni(OH)(NO_3)·H_2O$ decomposes also in two steps, as is the case of $Co(OH)(NO_3)·H_2O$ layered $Ni(OH)_{1.5}(NO_3)_{0.5}$ is a first decomposition product at 130°C, which, above 200°C, decomposes to NiO with a rock-salt structure. In the $LiNO_3$ medium, the decomposition process remains the same: double-chain $Ni(OH)(NO_3)·H_2O$ decomposes to rock-salt NiO via layered $Ni(OH)_{1.5}(NO_3)_{0.5}$.

For the coprecipitated nickel-cobalt hydroxide-nitrates, the phase composition of the reaction products at 300°C in a $LiNO_3$ melt depends on Ni/(Ni + Co) ratio (Fig. 6): up to $x \leq 0.4$, only

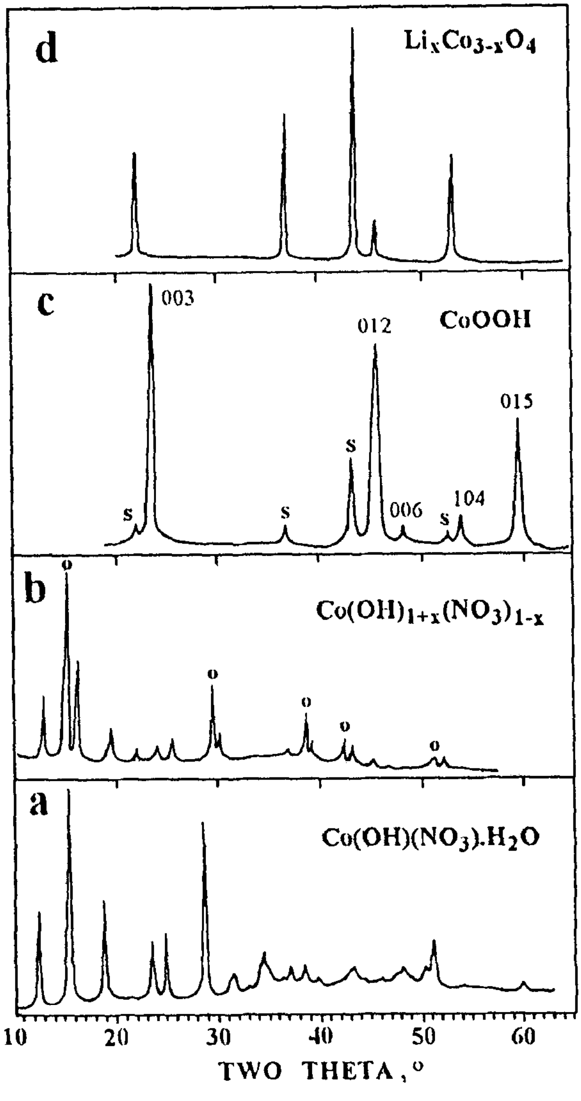

FIG. 5
XRD patterns of $Co(OH)(NO_3)\cdot H_2O + LiNO_3$ during heating at 100°C (a), 140°C (b), 155°C (c), and 250°C (d).

a single oxide phase with a spinel type structure is obtained, for $0.4 < x \leq 0.9$, a mixture of two oxides (with a spinel and rock-salt type structure) appears, and when $x = 1$, the only product is nickel oxide with rock-salt type structure. Data on the unit cell parameters, the relative amounts of both kinds of oxides, specific surface area and chemical composition of the samples are given in Table 2. For $Ni/(Ni + Co) \leq 0.4$, the decrease in the unit cell parameter of the spinel oxides, as compared with pure Co_3O_4 and $NiCo_2O_4$, reveal the incorporation of lithium into the spinel lattice. This is also related with an increase of the mean oxidation state of (Ni + Co) as compared to that of pure spinel $(Ni_xCo_{1-x})_3O_4$ (OS = 2.67). According to chemical analysis data, the maximum lithium concentration in the nickel-cobalt spinels is about 4 at% (Table 2):

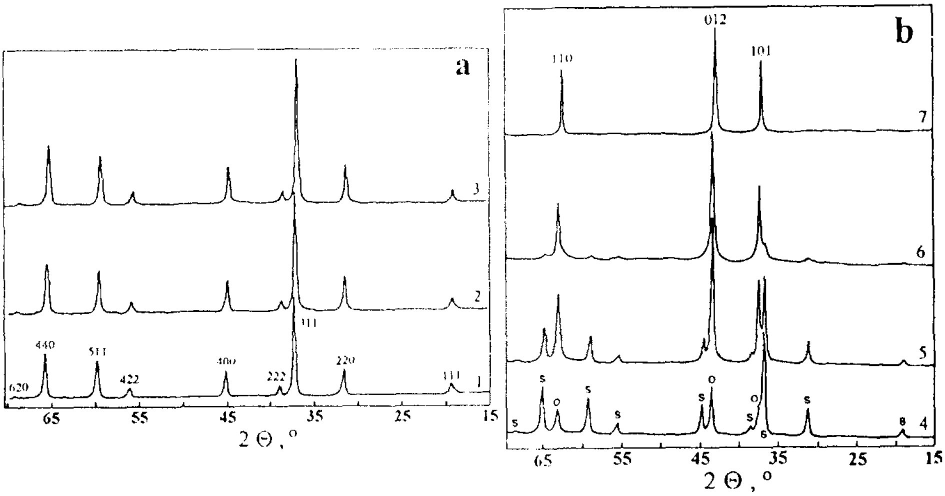

FIG. 6

XRD patterns of the decomposition products of the co-precipitated cobalt and nickel hydroxide-nitrates with $0 \leq x \leq 0.4$ (a) and $0.6 \leq x \leq 1$ (b) in $LiNO_3$ at 300°C, x = Ni/(Ni + Co). Sample notation: 1 - x = 0; 2 - x = 0.2; 3 - x = 0.4; 4 - x = 0.6; 5 - x = 0.8; 6 - x = 0.9; 7 - x = 1. (CuK_α-radiation is used).

$Li_y(Ni_xCo_{1-x})_{3-y}O_4$ with $y \approx 0.13$ and $0 \leq x \leq 0.4$. For $0.4 < x \leq 0.9$, the unit cell parameter of the spinel phase has the same value as for the sample with x = 0.4 but the oxide with the rock-salt structure has a smaller unit cell parameter than that of the sample with x = 1. This result, as well as the monotonous decrease in the oxidation state and lithium amount, allow us to describe the phase composition as a mixture of a spinel $Li_{0.13}(Ni_{0.4}Co_{0.6})_{2.87}O_4$ and a rock-salt $Ni_{1-b}Co_bO$, $b < 0.1$. The relative amount of the latter phase increases with the nickel content in the precursor (Table 2). For x = 1, the end product at 300°C is a non-stoichiometric NiO containing no lithium.

TABLE 2

Mean Oxidation State (OS), Lithium Amount (Li, wt.%), Unit Cell Parameters of the Spinel and NaCl-Type Structure (a_s and a_c), Relative Amounts of the Spinel Phase [RA, $I_{311}/(I_{311} + I_{012})$] and Specific Surface Areas (S, m^2/g) of the Decomposition Products of Co-Precipitated Cobalt and Nickel Hydroxide-Nitrates in a $LiNO_3$ Melt at 300°C

		X = Ni/(Ni+Co)					
	0	0.2	0.4	0.6	0.8	0.9	1.0
OS	2.87	2.87	2.80	2.64	2.38	2.21	2.08
Li, wt.%	0.31	0.31	0.26	0.18	0.04	0.01	0
$a_S \pm 0.003$, Å	8.030	8.072	8.110	8.093	8.107	9.097	—
$a_C \pm 0.002$, Å	—	—	—	4.166	4.164	4.164	4.175
RA	1.0	1.0	1.0	0.69	0.36	≈0.05	0
S, m^2/g	8	8	9	13	26	28	15

DISCUSSION

In concentrated cobalt and/or nickel nitrate solutions, solid LiOH and Li_2CO_3 act as mild hydrolysing agents and cobalt and/or nickel hydroxide-nitrates are precipitated. Only for Li_2CO_3 the hydroxide-nitrates thus precipitated have a double-chain structure (Fig. 1):

$$Li_2CO_3 + 2\ M^{2+} + 4\ NO_3^- + H_2O \rightarrow 2\ M(OH)(NO_3)\cdot H_2O + 2\ Li^+ + 2\ NO_3^- + CO_2.$$

The formation of a single spinel phase as a thermal decomposition product up to $x \leq 0.4$ proves that during coprecipitation solid solutions of Ni and Co hydroxide-nitrates with a double-chain structure are obtained: $Ni_xCo_{1-x}(OH)(NO_3)\cdot H_2O$ Pure $Ni_xCo_{1-x}(OH)(NO_3)\cdot H_2O$ and the intimate $[Ni_xCo_{1-x}(OH)(NO_3)\cdot H_2O + LiNO_3]$ mixture posses different thermochemical properties. Above 120°C , mixed $Ni_xCo_{1-x}(OH)(NO_3)\cdot H_2O$ hydrolyse partially into hydroxide-nitrates with a layered structure $Ni_xCo_{1-x}(OH)_{1.5}(NO_3)_{0.5}$ evolving gaseous nitric acid and water (Fig. 4c). In a $LiNO_3$ medium, where the water vapour evolution is hindered, a complete oxidative hydrolysis of double-chain $Ni_xCo_{1-x}(OH)(NO_3)\cdot H_2O$ to layered oxide-hydroxides $Ni_xCo_{1-x}OOH$ is favoured at about 150°C. On further heating, both reaction products $[Ni_xCo_{1-x}(OH)_{1.5}(NO_3)_{0.5}$ and $Ni_xCo_{1-x}OOH]$ yield single phases of nickel-cobalt spinel oxides, but in a $LiNO_3$ melt, the nickel-cobalt spinels thus formed contain lithium: $Li_y(Ni_xCo_{1-x})_{3-y}O_4$ with $y \approx 0.13$ and $0 \leq x \leq 0.4$. From these results it follows that lithium doping of nickel-cobalt spinel oxides comes from the decomposition of the hydrolysing product $Ni_xCo_{1-x}OOH$ in the $LiNO_3$ melt. As we have mentioned in the Introduction section, we have studied the thermal decomposition of layered CoOOH in a $LiNO_3$ melt and have shown that a partial ion-exchange between H^+ from CoOOH and Li^+ from the melt (up to 10 at%) precedes the topotactic transformation to a lithium containing cobalt spinel $Li_xCo_{3-x}O_4$ (6). As the CoOOH → Co_3O_4 transformation in air also proceeds topotactically (14), this means that the $H^+ \leftrightarrow Li^+$ ion-exchange does not perturb the transformation mechanism of CoOOH to the spinel structure in the $LiNO_3$ melt. Further experimental proof for the appearance of a lithium containing Co oxide-hydroxide before its decomposition is the preparation of a single $Li_{1-x}H_zCoO_2$ phase ($x < 0.55$, $x + z < 1$) by acid delithiation of $LiCoO_2$ (15). Thus, it can be concluded that a similar mechanism of lithium doping operates during the thermal decomposition of mixed $Ni_xCo_{1-x}OOH$ to $Li_y(Ni_xCo_{1-x})_{3-y}O_4$ in a $LiNO_3$ melt.

However, low-temperature lithium doping of NiO cannot be achieved with this preparation procedure since $Ni(OH)(NO_3)\cdot H_2O$ hydrolyses in a $LiNO_3$ medium, as in air, to a layered nickel hydroxide-nitrate $Ni(OH)_{1.5}(NO_3)_{0.5}$ in a lithium nitrate medium. This is, most probably, a result from the decreased stability of the trivalent state of nickel as compared to cobalt.

CONCLUSIONS

Thermal decomposition of double-chain $Ni_xCo_{1-x}(OH)(NO_3)\cdot H_2O$ $0 \leq x \leq 0.4$, in a $LiNO_3$ medium yields lithium containing nickel-cobalt spinels $Li_y(Ni_xCo_{1-x})_{3-y}O_4$, $y \approx 0.13$. The mechanism of lithium doping can be explained in terms of three type of soft-chemistry reactions: (i) complete thermal hydrolysis of double-chain $Ni_xCo_{1-x}(OH)(NO_3)\cdot H_2O$ to layered oxide-hydroxides $Ni_xCo_{1-x}OOH$ (ii) ion-exchange reactions of H^+ from layered $Ni_xCo_{1-x}OOH$ with Li^+ from the $LiNO_3$ melt and (iii) topotactic decomposition of the lithium containing oxide-hydroxide to a lithium containing nickel-cobalt spinel.

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