

# Preparation and characterization of cobalt-substituted $\alpha$ -nickel hydroxides stable in KOH medium

## Part I. $\alpha'$ -Hydroxide with an ordered packing

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### Abstract

An  $\alpha'$ -cobalt-substituted nickel hydroxide has been prepared from a  $\beta$ (II)-substituted nickel hydroxide by an oxidation to a  $\gamma$ -type phase followed by a reduction. This  $\alpha'_{\text{Co}^{3+}}$ -hydroxide crystallizes in the hexagonal system with a P3-type hydroxyl packing ( $a = 3.1 \text{ \AA}$ ,  $c = 23.5 \text{ \AA}$ ).  $\beta$ (II)- and  $\alpha'$ -cobalt phases have been characterized by chemical analysis, TGA, u.v.-visible and i.r. spectroscopies. In both materials cobalt ions remain in the trivalent state. In  $\alpha'_{\text{Co}^{3+}}$ -hydroxide, the excess of positive charge is compensated by carbonate anions which are either inserted between the  $\text{M}(\text{OH})_2$  slabs, or adsorbed on the particles. The infrared study shows that inserted anions are totally hydrogen bonded with intercalated water molecules ( $D_{3h}$  symmetry), while the adsorbed ions are linked to the nickel or cobalt ions in substitution of hydroxyl groups. In  $\beta_{\text{Co}^{3+}}$ -hydroxide, the charge compensation due to the presence of trivalent cobalt ions is provided by chemisorbed carbonate anions and by a proton deficiency in the sheets. The bonding between the inserted carbonate anions and the  $\text{Co}^{3+}$  cations increases the slab cohesion; as a result the  $\alpha'_{\text{Co}^{3+}}$ -phase ( $x_{\text{Co}} \geq 0.2$ ) is stable indefinitely in KOH medium.

### Introduction

To improve the electrochemical activity of Ni//Cd generators, the substitution of various elements for nickel in nickel hydroxides has been reported. However, the poor crystallinity of these nickel hydroxides and oxyhydroxides made understanding of what goes on rather difficult. We have previously shown in our laboratory that nickel oxyhydroxides and hydroxides ( $\alpha^*$ ) can

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be obtained by *chimie douce* reactions from  $\text{NaNiO}_2$  [1]. In this case, the materials remain well crystallized as with the starting phase, so that X-ray diffraction is a very helpful technique in understanding the nature of the chemical processes involved.

As a first step, the  $\gamma$ -type phase  $\text{H}_x\text{Na}_y(\text{H}_2\text{O})_z\text{NiO}_2$  is obtained via a rather complex mechanism requiring simultaneous oxidation (sodium departure), and a hydrolysis ( $\text{Na}^+/\text{H}_3\text{O}^+$  exchange and  $\text{H}_2\text{O}$  intercalation) [1]. The second step consists of the reduction of this material, leading to the formation of a well-crystallized  $\alpha^*$ -nickel hydroxide [1]. *Chimie douce* techniques also showed that the substitution of at least 20% of cobalt for nickel in the precursor material  $\text{NaNi}_{1-x}\text{Co}_x\text{O}_2$  allows the stabilization of the hydrated hydroxides in KOH medium [2, 3]. The formula for this compound should be compared with that of reevesite or hydrotalcite [4–6]. The stabilization of the  $\alpha_{20\%\text{Co}}^*$ -phase in KOH results from the presence of trivalent cobalt in the reduced nickel hydroxide [2, 3].

The  $\gamma \rightarrow \alpha^*$  reaction can be reversed by chemical oxidation. Moreover, preliminary tests have shown that these materials can be cycled in the electrochemical generator without noticeable structural change versus the cycle number. However, the electrochemical activity cannot be optimized due to the very large particle size:  $H = 10^3 \text{ \AA}$ ,  $D = 10^4 \text{ \AA}$ . The hydroxide particles are assumed to have a cylindrical shape ( $H$  = thickness,  $D$  = diameter). In an attempt to improve this electrochemical property and also to develop a method adapted to battery electrode manufacture, precipitation techniques have been used. The aim was to obtain a hydrated nickel hydroxide in which at least 20% of the cobalt is substituted for nickel. Moreover, the cobalt ions must stay in the trivalent state in the  $\alpha$ -phase.

Several reaction paths have been explored in order to obtain a nickel hydroxide substituted with trivalent cobalt. The direct precipitation of the  $\alpha$ -turbostratic nickel hydroxide has taken place, but it is necessary to solve many chemical problems resulting from the instability of trivalent cobalt ions in the starting solution. The results will be published in the next paper (Part II). Another method reported in the present paper consisted in following Bode's diagram: precipitation of a cobalt substituted  $\beta(\text{II})$ -phase, oxidation to  $\gamma$ -phase, then reduction to  $\alpha$ -hydroxide as in the case of the *chimie douce* reactions.

### Preparation of an $\alpha_{\text{Co}^{3+}}$ -phase from a $\beta_{\text{Co}}$ phase

The precipitation of  $\beta(\text{II})$ -nickel hydroxide is well known as it has been used by battery manufacturers for a century. In a previous paper we have shown that it is possible, by monitoring the pH of the solution, to obtain either an  $\alpha$ -phase with an almost quantitative yield, or a badly crystallized  $\beta(\text{II})$  type (designated by  $\beta_{\text{bc}}$ ) [7].

In this study, the  $\beta(\text{II})$  preparation method was transposed to cobalt-substituted  $\beta(\text{II})$ -type phases.

As mentioned earlier, the stabilization of the  $\alpha$ -phases requires at least 20% of cobalt ions [2]. Thus, this minimal concentration was chosen and all the experiments described in this paper will deal with  $\beta_{\text{Co}^{3+}}$ - and  $\alpha_{\text{Co}^{3+}}$ -type phases containing this amount of cobalt.

In order to form a  $\beta(\text{II})$ -type phase, cobalt and nickel solutions are mixed in the appropriate ratio and added to a 2 N NaOH solution. During the precipitation, the pH value remains close to 13. Another method of preparing a  $\beta_{\text{Co}}$ -type phase is to add, dropwise, a 2 N NaOH solution to the cobalt-nickel solution until the pH reaches a value close to 13. In both cases, the stoichiometric  $\text{NaOH}/(\text{Ni}^{2+} + \text{Co}^{2+})$  ratio is required. By contrast, for the preparation of  $\alpha$ -phases, the use of NaOH has to be limited to 80% of the stoichiometric ratio [7]. During the precipitation, the colour of the slurry is blue, it then gradually turns to green-brown as the material dries. This suggests a spontaneous oxidation of cobalt ions in air during the drying step. As will be discussed below, the cobalt ions are effectively within the substituted  $\beta(\text{II})$ -nickel hydroxide in the trivalent state, and this phase will therefore be designated by  $\beta_{\text{Co}^{3+}}$ . The fact that cobalt ions remain in the trivalent state within a nickel hydroxide lattice after initial oxidation has already been shown by Gunther and Gross [8].

The following step consists in obtaining the  $\gamma_{\text{Co}}$  phase by chemical oxidation of a  $\beta_{\text{Co}^{3+}}$  phase [9].

Moreover, as often reported although never explained, the  $\beta(\text{II}) \rightarrow \gamma$  oxidation reaction is more difficult to realize in presence of cobalt ions [10]. Usually, the  $\beta(\text{II}) \rightarrow \gamma$  reaction can be obtained under the following conditions: 1 g of nickel hydroxide is oxidized by a solution consisting of 20 ml of 4 M NaClO and 80 ml of 5 N KOH, in one day at room temperature. In the case of the  $\beta_{\text{Co}^{3+}}$  phase, for 1 g of starting phase, 80 ml of 4 M NaClO and 320 ml of 5 N KOH are required as oxidizing solution. Furthermore, the reaction time is increased from one to four days. A  $\gamma_{\text{Co}}$ -type phase is then formed, and its reduction by an  $\text{H}_2\text{O}_2$  solution (11 vol.) gives rise to an  $\alpha_{\text{Co}^{3+}}$ -type phase as shown below. An  $\text{H}_2\text{O}_2$  solution permits reduction of the nickel ions to the divalent state while cobalt ions stay trivalent [11]. This  $\alpha_{\text{Co}^{3+}}$  phase is stable in alkaline medium (5 N KOH) at room temperature. After a one month test period, no trace of  $\beta(\text{II})$ -type hydroxide was detected.

## Materials characterization

### *X-ray diffraction study of the cobalted nickel hydroxide*

X-ray diffraction patterns of the powdered compounds were recorded using Cu  $K\alpha$  radiation. The spectra of the  $\beta_{\text{Co}^{3+}}$ -,  $\gamma_{\text{Co}}$ -, and  $\alpha_{\text{Co}^{3+}}$ -materials, resulting from previously described reactions, are reported in Fig. 1.

The shape of the X-ray diffraction pattern of the  $\beta_{\text{Co}^{3+}}$  phase is similar to that of  $\beta(\text{II})\text{-Ni}(\text{OH})_2$ : the  $\beta_{\text{Co}^{3+}}$  phase crystallizes in the hexagonal system with the  $a$  and  $c$  cell parameters equal to 3.1 and 4.6 Å, respectively. No

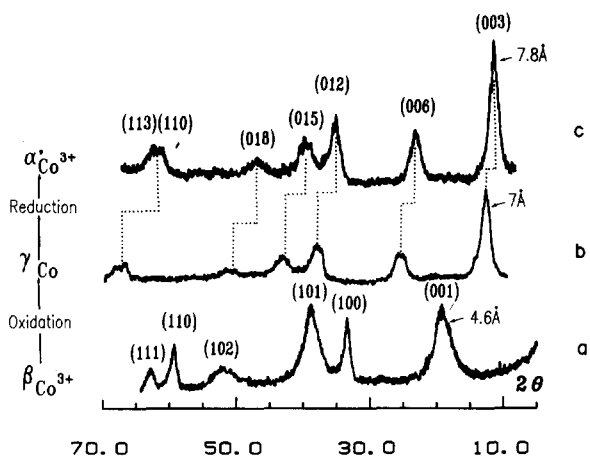


Fig. 1. X-ray diffraction spectra of  $\beta_{\text{Co}^{3+}}$ ,  $\alpha'_{\text{Co}^{3+}}$  and  $\gamma_{\text{Co}}$  phases ( $x_{\text{Co}} = 0.20$ ).

variation of the cell parameters can be deduced versus the cobalt concentration because the small particle size ( $H=30 \text{ \AA}$ ,  $D=80 \text{ \AA}$ ) causes substantial broadening of the diffraction lines.

A comparison of the  $\alpha_{\text{Co}^{3+}}$ -phase spectrum (Fig. 1(c)) with that of the  $\alpha$ -nickel hydroxide obtained directly by precipitation [7, 12] shows that the former material does not have any turbostratic character. In the  $\beta_{\text{Co}^{3+}}$  phase, the stacking of  $M(\text{OH})_2$  ( $M=\text{Ni}, \text{Co}$ ) sheets is well ordered. Each sheet is exactly superposed on the previous one. The hydroxyl groups form an ABAB packing (O1/T1 type) [13]. In such a packing the Van der Waals gap consists of octahedra (O) and tetrahedra (T) sharing faces. As the  $\beta_{\text{Co}^{3+}} \rightarrow \gamma \rightarrow \alpha_{\text{Co}^{3+}}$  reactions occur in the solid state (via topotactic reactions), the well-ordered stacking remains and the classical turbostratic character of the  $\alpha$ -phase does not appear. Therefore, in order to distinguish between the materials, the well ordered, hydrated nickel hydroxide will be denoted  $\alpha'$  subsequently.

It is well-known that the  $\gamma$  phases obtained by oxidation of  $\beta(\text{II})$  phases exhibit a unit cell with three  $\text{NiOOH}_x$  slabs and therefore a rhombohedral symmetry [9]. The observed and calculated interplanar distances are compared in Tables 1 and 2. In order to find the right unit cell, two indexations have been tried for both  $\gamma_{\text{Co}}$  and  $\alpha'_{\text{Co}^{3+}}$  phases, with one layer (as in  $\beta(\text{II})$  phases), or three layers (as expected for  $\gamma$  phases), within the unit cell (Table 3). Comparison of the observed and calculated interplanar distances unambiguously shows that both materials crystallize in the rhombohedral system with three  $M(\text{OH})_2$  or  $\text{MOOH}_x$  slabs per unit cell. With such a cell, two types of packing can be expected: ABBCA ( $P\bar{3}$  type) or ABCABC ( $O3$  type). Nevertheless, as previously discussed in several papers related to packing in layered oxides or chalcogenides, the ratio of the intensity of the (015) and (104) diffraction lines unambiguously indicates the nature of the oxygen packing. A strong (015) line shows an ABBCA oxygen packing while a strong (104) line indicates an ABCABC packing [14]. In the case of  $\alpha'_{\text{Co}^{3+}}$  and  $\gamma_{\text{Co}}$  phases,

TABLE 1

Observed interplanar distances of  $\alpha'_{20\%Co^{3+}}$ -hydroxide, and calculated interplanar distances with 3 or 1 slabs per unit cell.

$\alpha'_{20\%Co^{3+}}$ $d_{obs}$ (Å)	Cell with 3 slabs		Cell with 1 slab	
	$d_{calc.}$ (Å)	$hkl$	$d_{calc.}$ (Å)	$hkl$
7.83	7.830	0 0 3	7.830	0 0 1
3.91	3.915	0 0 6	3.915	0 0 2
	2.633	1 0 1	2.650	1 0 0
2.59	2.585	0 1 2		
	2.415	1 0 4	2.510	1 0 1
2.30	2.308	0 1 5		
	2.080	1 0 7	2.194	1 0 2
1.96	1.967	0 1 8		
	1.758	1 0 10	1.859	1 0 3
	1.663	0 1 11		
1.53	1.530	1 1 0	1.530	1 1 0
1.51	1.502	1 1 3	1.502	1 1 1

TABLE 2

Observed interplanar distances of  $\gamma_{20\%Co}$ -oxyhydroxide, and calculated interplanar distances with 3 or 1 slabs per unit cell

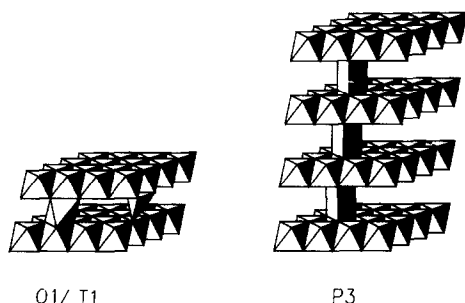
$\gamma_{20\%Co}$ $d_{obs}$ (Å)	Cell with 3 slabs		Cell with 1 slab	
	$d_{calc.}$ (Å)	$hkl$	$d_{calc.}$ (Å)	$hkl$
6.97	6.970	0 0 3	6.970	0 0 1
3.50	3.485	0 0 6	3.485	0 0 2
	2.362	0 1 2	2.425	1 0 0
2.36			2.290	1 0 1
2.10	2.098	0 1 5		
	1.778	0 1 8	1.990	1 0 2
			1.678	1 0 3
			1.415	1 0 4
1.40	1.400	1 1 0	1.400	1 1 0
1.38	1.372	1 1 3	1.372	1 1 1

as only the (015) line appears, the oxygen of the  $M(OH)_2$  or  $MOOH_x$  slabs form an ABBCCA packing with trigonal prisms. Such a structure has been reported previously for  $\gamma$ -oxyhydroxides [9] and for  $\alpha^*$  phases [1]. As shown

TABLE 3

Hexagonal parameters of  $\beta_{\text{Co}^{3+}}$ ,  $\gamma_{\text{Co}}$  and  $\alpha'_{\text{Co}^{3+}}$  phases ( $x_{\text{Co}}=0.20$ )

	$\beta_{\text{Co}^{3+}}$	$\gamma_{\text{Co}}$	$\alpha'_{\text{Co}^{3+}}$
$a$ (Å)	3.1	2.8	3.0
$c$ (Å)	4.6	20.9	23.5
intersheet distance (Å)	4.6	$\sim 7.00$	$\sim 7.8$

Fig. 2. Schematic representation of the  $O1/T1$  and  $P3$  packing.

in Fig. 2, slab gliding occurs during the  $\beta_{\text{Co}^{3+}} \rightarrow \gamma_{\text{Co}}$  reaction. The  $P3$ -type packing of the  $\gamma$  phase is conserved during the reduction to  $\alpha'_{\text{Co}^{3+}}$ . This gliding transforms the octahedral/tetrahedral sheet of the Van der Waals gap of the  $\beta_{\text{Co}^{3+}}$  phase in the trigonal prismatic sites that characterize the  $P3$ -type packing of  $\gamma_{\text{Co}}$  and  $\alpha'_{\text{Co}^{3+}}$  phases.

### Chemical analysis

Chemical determinations of the contents of all the elements (other than for oxygen) have been undertaken on  $\beta_{\text{Co}^{3+}}$ ,  $\gamma_{\text{Co}}$ , and  $\alpha'_{\text{Co}^{3+}}$  phases. The weight percentages of the determined elements are summarized in Table 4 for the various materials.

Several points arise concerning the presence of water molecules and carbonate anions. In all phases, a large amount of water is found. Whereas this result was expected for  $\gamma_{\text{Co}}$  and  $\alpha'_{\text{Co}^{3+}}$  phases, it is quite surprising in the case of  $\beta_{\text{Co}^{3+}}$  phase which contains 0.75 water molecule per (Ni+Co) atom. As these  $\text{H}_2\text{O}$  molecules cannot be inserted between adjacent slabs, they are only adsorbed. It should be borne in mind that the size of the hydroxide particles deduced from Scherrer's formula [15] is very small ( $H=30$  Å and  $D=80$  Å). In  $\gamma_{\text{Co}}$  and  $\alpha'_{\text{Co}^{3+}}$  phases, the water molecules are not only adsorbed but also intercalated. The  $\text{H}_2\text{O}/(\text{Ni}+\text{Co})$  molar ratio is equal to 1.20 and 0.95, respectively, in  $\alpha'_{\text{Co}^{3+}}$  and  $\gamma_{\text{Co}}$  phases.

Chemical analysis also shows the presence of carbonate anions in the reduced  $\beta_{\text{Co}^{3+}}$  and  $\alpha'_{\text{Co}^{3+}}$  phases in a molar ratio close to 0.08 and 0.13,

TABLE 4

Weight percent. of the various elements present in  $\beta_{\text{Co}^{3+}}$ ,  $\gamma_{\text{Co}}$ , and  $\alpha'_{\text{Co}^{3+}}$  phases ( $x_{\text{Co}}=0.20$ )

Weight percent.	$\beta_{\text{Co}^{3+}}$	→	$\gamma_{\text{Co}}$	→	$\alpha'_{\text{Co}^{3+}}$
Ni	41.21		34.2		33.2
Co	11.50		9.75		9.41
C	0.89		0.54		1.13
H	2.87		1.78		3.18
Na	0.12		0.48		0.05
K			6.21		0.02
S	0.09		<0.08		0.05

respectively, for the phases containing 20% of cobalt ions. As previously shown for the  $\alpha^*$ -cobalt phase [3], these anions compensate the excess of positive charge due to the presence of trivalent cobalt ions in both reduced phases. This latter point will be discussed later. The presence of sulfate anions and  $\text{Na}^+$  cations in  $\alpha'_{\text{Co}^{3+}}$  or  $\beta_{\text{Co}^{3+}}$  phases are washing residues from  $\text{Na}_2\text{SO}_4$  formed during the precipitation. For the  $\gamma_{\text{Co}}$  phase large amounts of alkali ions and water molecules are inserted between  $\text{MOOH}_x$  slabs. This material exhibits very small particles ( $H=50 \text{ \AA}$ ,  $D=80 \text{ \AA}$ ) by comparison with those obtained from *chimie douce* reactions from  $\text{NaNi}_{1-x}\text{Co}_x\text{O}_2$  ( $H=10^3 \text{ \AA}$ ,  $D=10^4 \text{ \AA}$ ). The result is that a larger amount of carbonate anions ( $\text{CO}_3^{2-}/(\text{Ni}+\text{Co})$  molar ratio is equal to 0.06) are adsorbed on the former material than on the latter ( $\text{CO}_3^{2-}/(\text{Ni}+\text{Co})$  molar ratio is lower than 0.01). This difference in particle size also plays an important role in the reactivity of the material:  $\gamma$ -phase particles spontaneously oxidize water during washing so that the mean oxidation level of the recovered material is close to 3.2 instead of the 3.5 expected.

#### Study by u.v.-visible spectroscopy

In order to confirm the oxidation level of cobalt ions in the reduced phases, these materials were characterized by u.v.-visible spectroscopy. The apparatus used was a Cary 2415 Varian spectrophotometer. The optical spectra of the  $\beta_{\text{Co}^{3+}}$  and  $\alpha'_{\text{Co}^{3+}}$  phases are reported in Fig. 3(c), (d).

The absorption bands of  $\text{Ni}^{2+}$  ion in octahedral site  $t_{2g}^6e_g^2$  have been reported by Feitknecht [16]. They correspond to the following transitions:

$${}^3A_{2g} \longrightarrow {}^3T_{2g} (\text{F}) : 1150 \text{ nm}$$

$${}^3A_{2g} \longrightarrow {}^3T_{1g} (\text{F}) : 650 \text{ nm}$$

$${}^3A_{2g} \longrightarrow {}^3T_{1g} (\text{P}) : 390 \text{ nm}$$

The same bands are obtained in  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  and in the  $\alpha$  phase (Fig. 3(a), (b)). This result emphasizes the divalent state of nickel ions in the latter material.

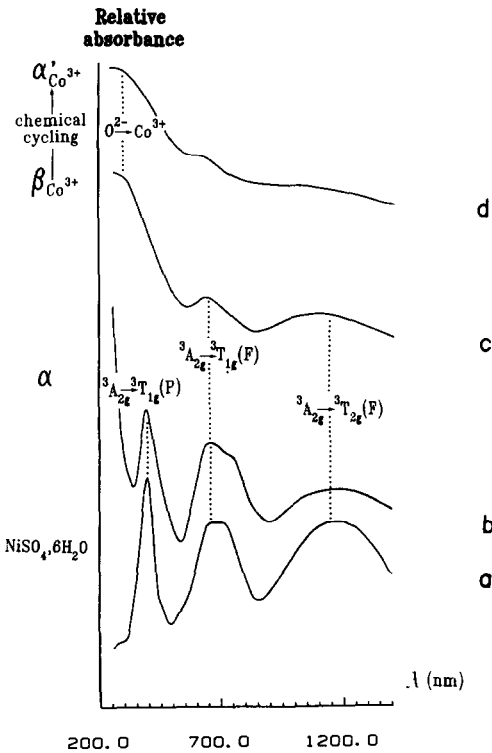


Fig. 3. U.V.-visible absorption spectra of  $\beta_{\text{Co}^{3+}}$  and  $\alpha'_{\text{Co}^{3+}}$  phases compared with those of reference materials:  $\alpha$ -nickel hydroxides and  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ .

In the cobalted phases a very strong charge transfer band appears for the smallest wavelength ( $\lambda < 500$  nm). Moreover, two broad bands that correspond to the  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$  and  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{F})$  transitions of the  $\text{Ni}^{2+}$  ion are observed. The third band, expected at higher energy, is overlapped by the charge transfer band.

The optical spectrum of  $\text{Co}^{2+}$  in  $\beta\text{-Co}(\text{OH})_2$  has also been published by Feitknecht [16]. In this compound the divalent cobalt ions are in the high spin state ( $t_{2g}^5 e_g^2$ ). The following optical transitions are observed:

$$\begin{aligned} {}^4\text{T}_{1g} &\longrightarrow {}^4\text{T}_{2g}(\text{F}) &: & 1299 \text{ nm} \\ {}^4\text{T}_{1g} &\longrightarrow {}^4\text{A}_{2g}(\text{F}) &: & 645 \text{ nm} \\ {}^4\text{T}_{1g} &\longrightarrow {}^4\text{T}_{1g}(\text{P}) &: & 532\text{--}488 \text{ nm} \end{aligned}$$

None of these bands appears on the u.v.-visible spectra of  $\beta_{\text{Co}^{3+}}$  and  $\alpha'_{\text{Co}^{3+}}$  phases.

The behavior is more complicated in the case of trivalent cobalt ion since LS or HS configurations are possible. Nevertheless, no data concerning  $\text{Co}^{3+}$  ions are available in the literature for similar materials.



The shifting of the charge transfer band to a higher wavelength is characteristic of the presence of trivalent cations. As the presence of  $\text{Ni}^{3+}$  ions is excluded by the green-brown colour of the material (simultaneous presence of  $\text{Ni}^{3+}$  and  $\text{Ni}^{2+}$  ions in the same site would, anyway, lead to a hopping phenomenon and therefore to a black-coloured material), the charge transfer band is a result of the presence of  $\text{Co}^{3+}$  cations. This result confirms that cobalt ions stay in the trivalent state not only in the  $\alpha'_{\text{Co}^{3+}}$  phases, but also in the  $\beta_{\text{Co}^{3+}}$  phase obtained directly by precipitation from an  $\text{NiSO}_4$  and  $\text{CoSO}_4$  solution.

#### Thermal analysis of $\beta_{\text{Co}^{3+}}$ and $\alpha'_{\text{Co}^{3+}}$ phases

The thermogravimetric analyses of  $\beta_{\text{Co}^{3+}}$  and  $\alpha'_{\text{Co}^{3+}}$  phases were performed under identical conditions:  $1\text{ }^\circ\text{C min}^{-1}$  under nitrogen flow. The variations of the sample weight with temperature are shown in Fig. 4.

For the  $\beta_{\text{Co}^{3+}}$  phase (Fig. 4(a)), a loss of mass is first observed in the  $30\text{--}110\text{ }^\circ\text{C}$  temperature range and, after a pseudo plateau between  $110$  and  $200\text{ }^\circ\text{C}$ , the second loss occurs. The first loss can only correspond to the removal of adsorbed water molecules and the second to the dehydroxylation of the  $\text{M}(\text{OH})_2$  sheets. The dehydroxylation of  $\beta_{\text{Co}^{3+}}$  phase seems to occur earlier than for  $\beta(\text{II})\text{-Ni}(\text{OH})_2$ , which is observed around  $270\text{ }^\circ\text{C}$  [17].

The TGA curve of the  $\alpha'_{\text{Co}^{3+}}$  phase also shows two main losses of water (Fig. 4(b)). The first, which lies between  $30$  and  $140\text{ }^\circ\text{C}$ , corresponds to the removal of the adsorbed water and part of the intercalated water molecules: a pseudo plateau is then observed between  $140$  and  $190\text{ }^\circ\text{C}$ . At this point,  $0.8$  water molecule per formula unit has been removed from the material. The departure of part of the intercalated water molecules is indicated by the contraction of the intersheet distances (from  $7.8$  at RT to  $7.2\text{ \AA}$  at  $190\text{ }^\circ\text{C}$ ). As in the case of  $\alpha$  phases, the removal of adsorbed water molecules cannot be distinguished from the removal of intercalated water molecules by the TGA experiments [7, 17]. Beyond  $190\text{ }^\circ\text{C}$ , the remaining water molecules and carbonate anions are removed from the interslab space simultaneously

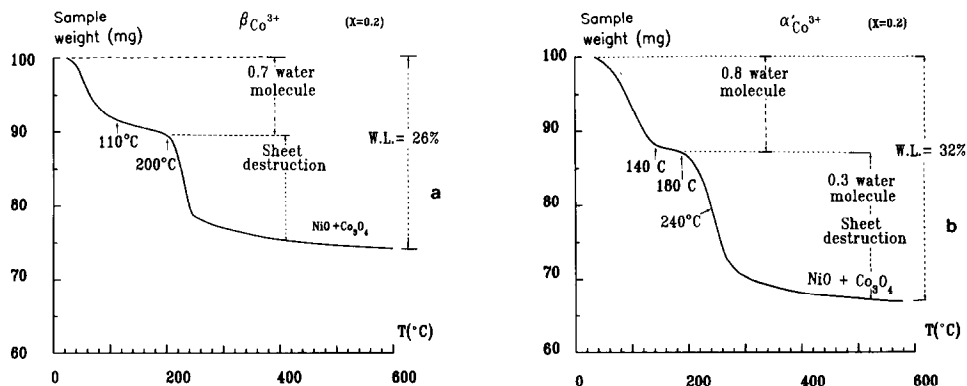


Fig. 4. TGA curves of  $\beta_{\text{Co}^{3+}}$  and  $\alpha'_{\text{Co}^{3+}}$  phases ( $x_{\text{Co}}=0.20$ ) ( $1\text{ }^\circ\text{C min}^{-1}$ , under nitrogen flow).

with the destruction of the  $M(OH)_2$  sheet, leading to the formation of a mixture of  $NiO$  and  $Co_3O_4$ . The second weight loss allows us to estimate that about 0.3 water molecule per nickel and cobalt atom remains in the intersheet space at 190 °C.

It should be noted that the dehydroxylation reaction occurs at the same temperature for both the  $\beta_{Co^{3+}}$  and  $\alpha'_{Co^{3+}}$  phases. The TGA curve of the  $\alpha'_{Co^{3+}}$  phase exhibits a large difference compared with that previously reported for  $\alpha$  phases prepared from  $NiSO_4$  and  $NaOH$  solutions [7]. In the case of the  $\alpha$  phase, the loss of water was almost continuous and the plateau observed for the  $\alpha'_{Co^{3+}}$  phase in the 140–190 °C range was not observed. We can assume that the presence of trivalent cobalt ions, which increase the material stability in  $KOH$  medium, also increase the thermal stability of this material.

### Infrared characterization

An infrared study has been carried out on all the reduced phases in order to characterize the nature of the adsorbed and inserted species and their bonding with the  $NiO_2$  slabs. The experiments have been undertaken on a Perkin Elmer 983 spectrometer. They have mainly been carried out in nujol, but as the main carbonate vibration is overlapped by a nujol band, they were also carried out in hexachlorobutadiene. The infrared spectra of both  $\beta_{Co^{3+}}$  and  $\alpha'_{Co^{3+}}$ -reduced phases are shown in Fig. 5 in the 200–4000  $cm^{-1}$  range. That of the  $\beta_{Co^{3+}}$  phase is characteristic of the  $\beta(II)$ -type phase with a lot of adsorbed water molecules on the very small nickel hydroxide particles [7].

The weak band at 3650  $cm^{-1}$  corresponding to the stretching vibration  $\nu(OH)$ , the band at 350  $cm^{-1}$  due to the out-of-plane vibration  $\gamma(OH)$ , the band at 520  $cm^{-1}$  due to the hydroxyl group's lattice vibration  $\delta(OH)$ , and the  $Ni-O$  lattice vibration around 460  $cm^{-1}$ , are characteristic of a  $\beta(II)$ - $Ni(OH)_2$  phase [18, 7].

The bands at 3350 and 1650  $cm^{-1}$  correspond, respectively, to the stretching mode and to the bending mode of water molecules [19].

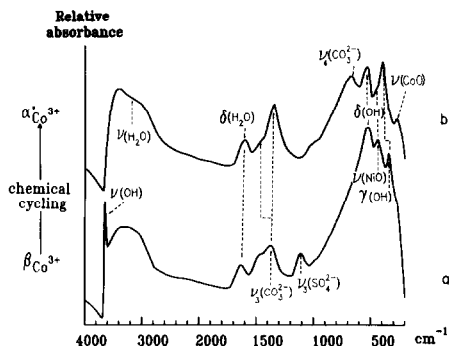


Fig. 5. Infrared spectra of  $\beta_{Co^{3+}}$  and  $\alpha'_{Co^{3+}}$  hydroxides ( $x_{Co} = 0.20$ ).

The bands at 1360 and 1470  $\text{cm}^{-1}$  correspond to the two components of the  $\nu_3$  vibration of unidentate carbonate anions [20].

The bands around 1100  $\text{cm}^{-1}$  and 610  $\text{cm}^{-1}$  correspond to the  $\nu_3$  and  $\nu_4$  vibrations, respectively, of free sulfate ions in  $T_d$  symmetry [19]. In the  $\beta_{\text{Co}^{3+}}$  material, these free sulfate ions arise from a residue of  $\text{Na}_2\text{SO}_4$  formed during precipitation. These anions can be removed by further washing and are systematically eliminated during the chemical cycling of this hydroxide.

On the infrared spectrum of the  $\alpha'_{\text{Co}^{3+}}$  phase, the bands at 3350  $\text{cm}^{-1}$  and 1650  $\text{cm}^{-1}$ , due to the  $\text{H}_2\text{O}$  stretching and bending modes, show the presence of a large amount of water molecules. The main difference between this spectrum and that of  $\alpha_{\text{Co}^{3+}}$  phase results from the disappearance of the narrow band at 3650  $\text{cm}^{-1}$ , which shows that all OH groups of the  $\text{Ni}(\text{OH})_2$  slabs are linked by hydrogen bonds to inserted water molecules. This material also contains carbonate anions as the  $\beta_{\text{Co}^{3+}}$  phase.

## Discussion

In order to understand the infrared spectra, it is convenient to consider more structural and chemical data. The  $c$  parameter value of the  $\beta_{\text{Co}^{3+}}$  phase (4.6 Å) does not allow the presence of intercalated water molecules. These molecules are therefore only adsorbed, whereas they are both intercalated and adsorbed in the  $\alpha'_{\text{Co}^{3+}}$ -type phase.

Both hydroxides ( $\beta_{\text{Co}^{3+}}$  and  $\alpha'_{\text{Co}^{3+}}$ ) contain carbonate anions, as was shown by chemical analysis. As in the case of water molecules, carbonate anions are only adsorbed on  $\beta_{\text{Co}^{3+}}$  phases. The problem is to determine the nature of the chemical bonding between  $\text{CO}_3^{2-}$  anions and the hydroxide slabs. In the  $\alpha'_{\text{Co}^{3+}}$ -type phase, these anions can be inserted between adjacent slabs and/or adsorbed at the surface of the particles. Moreover, they can be directly linked to the nickel or cobalt cations and/or to hydrogen atoms, or even 'free' as in the case of  $\text{CaCO}_3$  [19].

As will be developed in a forthcoming paper [20], the band centred at 1360  $\text{cm}^{-1}$  in the spectra of  $\alpha^*_{\text{Co}^{3+}}$ -type phases obtained by *chimie douce* is characteristic of the  $\nu_3$  vibration of carbonate anions in  $D_{3h}$  symmetry [21]. However, in these materials, as in pyroaurite-like minerals, it has been shown that the carbonate anions are totally and symmetrically linked by hydrogen bonds to intercalated water molecules [20–23]. In the  $\alpha'_{\text{Co}^{3+}}$  and  $\beta_{\text{Co}^{3+}}$  spectra (Fig. 5), the presence of the shoulder around 1470  $\text{cm}^{-1}$  shows that the carbonate symmetry is lowered. A splitting of the degenerate modes occurs simultaneously with the appearance of a new band in the infrared spectrum which is only active in Raman for the free anion. This  $\nu_1$  vibration, which should appear around 1070  $\text{cm}^{-1}$  is, in fact, overlapped by the  $\nu_3$  vibration of free sulfate anions. These carbonate anions, in a lowered symmetry, may be uni- or bi-dentate. However, the position of the  $\nu_3$  vibration (respectively at 1360 and 1470  $\text{cm}^{-1}$ ) shows, in comparison with reference compounds

[19], that these anions are certainly unidentate. This means, in our case, that one oxygen atom of the carbonate group is linked to a metal ion (Ni or Co) in substitution for an OH group.

Therefore, in the reduced phases obtained by precipitation techniques, two kinds of carbonate anions may exist: those which are intercalated in the material and are totally hydrogen bonded with water molecules ( $D_{3h}$  symmetry) and those which are linked to the sheets in substitution of OH groups.

In the  $\beta_{\text{Co}^{3+}}$ -type phase, the carbonate anions must only be adsorbed and are linked to a metallic ion.

In the  $\alpha'_{\text{Co}^{3+}}$  spectrum, the band at  $1360\text{ cm}^{-1}$  ( $\nu_3(\text{CO}_3^{2-})$ ) exhibits a higher intensity than in the  $\beta_{\text{Co}^{3+}}$  spectrum; such behaviour supports the hypothesis of the presence of both types of carbonate anions (i.e., bonded to M cations, or totally hydrogen bonded). One can assume that the first type should be mainly adsorbed, while the second should be inserted in the intersheet-space of the stabilized material. Such a hypothesis is corroborated by the following: if an  $\alpha'_{\text{Co}^{3+}}$ -type phase is set aside for an extended period in a concentrated KOH solution, the intensity of the band at  $1460\text{ cm}^{-1}$  is weakened, while that of the band at  $1360\text{ cm}^{-1}$  remains strong [20]. One may assume that the chemisorbed carbonate anions are slowly exchanged by hydroxyl ions in KOH medium leading to an  $\alpha_{\text{Co}^{3+}}$  phase which contains carbonate anions almost entirely inserted between  $\text{M}(\text{OH})_2$  slabs (all the oxygen atoms of these anions being hydrogen bonded).

In the case of  $\beta_{\text{Co}^{3+}}$  phases, the following problem remains. If the carbonate anions, which compensate the excess of charge due to the trivalent cobalt ions, are only at the grain periphery, the second Pauling rule is not satisfied. Nevertheless the  $c_{\text{hex}}$ -parameter value of the  $\beta_{\text{Co}^{3+}}$  phase forbids any insertion of anions between the  $\text{M}(\text{OH})_2$  sheets. The only explanation concerning this charge compensation would be the removal of some  $\text{H}^+$  ions from the  $\text{M}(\text{OH})_2$  sheet. This proton deficiency had already been observed in  $\beta(\text{II})$ -type phases formed during the nickel electrode discharge: in that case, the oxidation level of nickel ions is close to 2.2 instead of 2 [24].

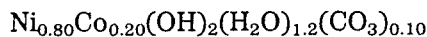
## Conclusions

An  $\alpha'_{\text{Co}^{3+}}$  hydroxide can be obtained from a  $\beta_{\text{Co}^{3+}}$  hydroxide, by oxidation to  $\gamma_{\text{Co}}$  phase followed by a reduction in contrast to the classical  $\alpha$ -turbostratic hydroxide. This material exhibits a well ordered (Ni, Co)(OH)<sub>2</sub> slabs arrangement (ABBCCA hydroxyl packing). A layer of water molecules and  $\text{CO}_3^{2-}$  anions is inserted between adjacent slabs. The infrared study has shown that these species are hydrogen bonded with hydroxyl groups of the (Ni, Co)(OH)<sub>2</sub> slabs.

Moreover, many water molecules and carbonate anions are adsorbed on the particles. The infrared study also shows that these anions are directly linked to a nickel or cobalt cation in substitution of an OH group.

The hydrogen bonds between OH groups and carbonate ions increase the interslab cohesion so that the  $\alpha'_{\text{Co}^{3+}}$  material is indefinitely stable in KOH medium when the cobalt content is greater than 20%.

An idealistic formula of the  $\alpha'_{\text{Co}^{3+}}$  phase ( $x_{\text{Co}}=0.20$ ) may be easily deduced from chemical analysis, if we neglect the adsorbed ions:



Such a formula may be compared with those of reevesite or hydrotalcite minerals, and is similar to that of cobalted  $\alpha^*$  phases.

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