Infrared characterization of turbostratic α- and well crystallized α*-cobalted nickel hydroxides

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Abstract

Substitution of at least 20% of trivalent cobalt for nickel leads to α- and α*-nickel hydroxides which are stable in KOH. The compensation of the excess of positive charge results from the insertion of anions (CO_3^{2-} or SO_4^{2-}) in the van der Waals gap. The IR study shows that these anions are in D_{3h} and T_d symmetries, respectively, while the adsorbed ones are linked to the transition elements (C_{2v} and C_{3v} symmetries, respectively). This study also confirms the stability of $\alpha^*_{Co^{3+}}$- and $\alpha_{Co^{3+}}$-hydroxides in concentrated KOH solution, and the instability of $\alpha_{Co^{2+}}$ ones which leads to the formation of $\beta_{Co^{3+}}$-hydroxides.

Introduction

The addition of cobalt to the positive electrode of nickel–cadmium cells was reported by Edison at the beginning of this century [1] and interest in the additive has been continuing since that time. However, whereas most previous studies have been confined to compositions up to 15% cobalt [2, 3], a general study of the effects of a large amount of cobalt (10–55%) was undertaken in our lab a few years ago. Recently, it was shown that the substitution of at least 20% of cobalt for nickel in the hydroxide allows the formation of an α*-hydrated phase, stable in KOH solutions at room temperature [4, 5]. The γ- and α*-phases were prepared by chimie douce techniques from the $NaNi_{1-x}Co_xO_2$ precursor. Figure 1 gives, as an example, the X-ray diffraction spectra of these materials for $x = 0.30$. The small broadening of the X-ray diffraction lines show that these materials are well crystallized. The particle size has been calculated from SEM patterns along the $\vec{c}$ and $\vec{a}$ axes: $H = 10^3$ Å and $D = 10^4$ Å. It transpires that these materials are easily characterizable and can be used as reference compounds.

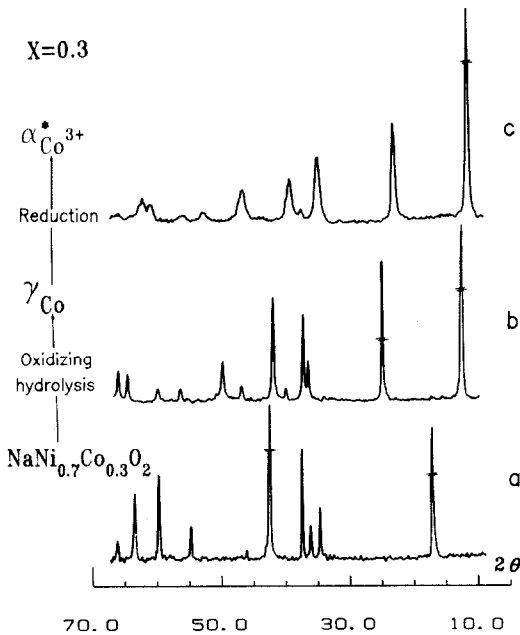*Author to whom correspondence should be addressed.

Fig. 1. X-ray diffraction patterns of the $\alpha^*_{Co^{3+}}$ and γ_{Co} phases and their precursor $NaNi_{0.7}$-$Co_{0.3}O_2$.

Chemical analyses showed that carbonate anions must be inserted in the interslab space of the α^*-phase in order to compensate the excess of charge due to the presence of trivalent cobalt ions. Moreover, their formula should be compared to that of the reevesite or the hydrotalcite [6–8].

In order to try to improve the electrochemical activity of the α_{Co}-type phase by reducing the particle size of cobalt substituted nickel hydroxides, precipitation techniques were used. Several preparation ways were investigated, leading to the formation of $\alpha_{Co^{3+}}$-turbostratic materials [9]. They can be obtained either by direct precipitation or from the oxidation of an $\alpha_{Co^{2+}}$-type phase:

- When the $\alpha_{Co^{3+}}$-type phase is formed by chemical cycling (oxidation–reduction) from an $\alpha_{Co^{2+}}$-type phase, or by direct precipitation including the pre-oxidation of cobalt ions by an acidic HClO solution, the charge compensation due to trivalent cobalt ions is assured by carbonate anions. The X-ray diffraction spectrum of this material, designated as $\alpha_{Co^{3+}}(CO_3)$, is reported in Fig. 2(a).
- When the $\alpha_{Co^{3+}}$-type phase is formed by selective oxidation of cobalt ions of an $\alpha_{Co^{2+}}$-type phase (with a H_2O_2 solution) or by direct precipitation after a pre-oxidation of cobalt ions with a H_2O_2 solution, the charge compensation is provided by sulfate anions. This material was designated as $\alpha_{Co^{3+}}(SO_4)$, and the X-ray diffraction pattern of the phase containing
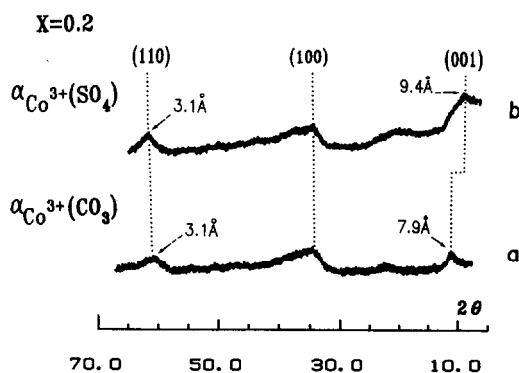
X=0.2

Fig. 2. X-ray diffraction patterns of the $\alpha_{Co^{3+}}(CO_3)$ (a) and $\alpha_{Co^{3+}}(SO_4)$ (b) phases ($x = 0.2$).

20% of cobalt ions is reported in Fig. 2(b). The detailed preparation and the chemical properties of these $\alpha_{Co^{3+}}$-type phases were developed in a previous paper [9].

This paper describes the IR characterization of $\alpha^*_{Co^{3+}}$ and $\alpha_{Co^{3+}}$ phases.

Results and discussion

The IR study has been realized on all reduced phases in order to characterize the nature of the adsorbed and inserted species and their bonding with the MO_2 slabs (M = Ni, Co). The experiments were performed on a Perkin-Elmer 983 spectrometer. They were initially realized in nujol in the 200 to 4000 cm^{-1} range, but as the main carbonate vibration was overlapped by a nujol band, they were also carried out in hexachlorobutadiene within the 1000 to 4000 cm^{-1} range.

IR characterization of $\alpha^*_{Co^{3+}}$- and $\alpha_{Co^{3+}}$-type phases

The IR spectra of $\alpha^*_{Co^{3+}}$, $\alpha_{Co^{3+}}(SO_4)$ and $\alpha_{Co^{3+}}(CO_3)$ phases containing 20% cobalt ions are reported in Fig. 3 (200 to 4000 cm^{-1} range) in comparison with the spectrum of a well crystallized β(II)-type phase.

The IR spectrum of the β(II)-type phase (Fig. 3(a)) is well known [10]. It is characterized by:
- a weak band at 3650 cm^{-1} corresponding to the ν(OH) stretching vibration
- a band at 520 cm^{-1} due to the hydroxyl groups δ(OH) lattice vibration
- a band at 350 cm^{-1} due to the out-of-plane γ(OH) vibration
- the Ni–O lattice vibration around 460 cm^{-1} [12].

The IR spectra of $\alpha^*_{Co^{3+}}$ and $\alpha_{Co^{3+}}$ phases differ from the previous one by:
- the appearance of large bands at 3350 and 1650 cm^{-1} which are respectively due to the stretching and bending modes (ν(H$_2$O) and δ(H$_2$O)) of water molecules [11, 12]
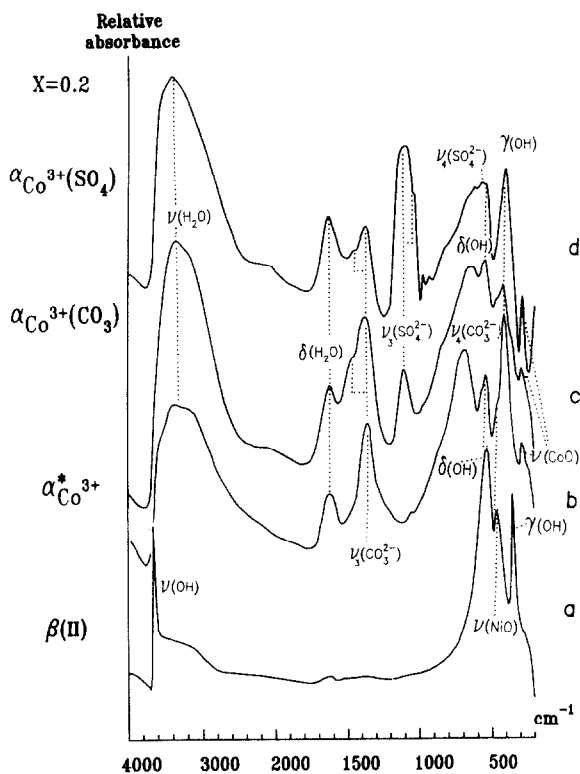
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Fig. 3. IR spectra of $\alpha^*_{Co^{3+}}$, $\alpha_{Co^{3+}}(CO_3)$ and $\alpha_{Co^{3+}}(SO_4)$ phases ($x=0.2$) compared with that of a $\beta(II)$-nickel hydroxide (spectra realized in nujol).

• the disappearance of the narrow band at 3650 cm^{-1} which characterizes free OH groups [12]
• a band at 1360 cm^{-1} which is characteristic of the carbonate anions
• a band around 1100 cm^{-1} on the $\alpha_{Co^{3+}}$ spectra which corresponds to the ν_3 vibration of sulfate anions [11]
• a weak band around 280 cm^{-1} which corresponds to the $\nu(Co^{III}-O)$ vibration [11].

One of the main points is the disappearance of the free hydroxyl vibration in all α-cobalted phases. This result confirms the insertion of water molecules between the M(OH)$_2$ (M = Ni, Co) slabs. All the OH groups are thus linked by hydrogen bonds to water molecules. In the $\alpha^*_{Co^{3+}}$-type phases, the particles exhibit a very large size and the amount of adsorbed water molecules is therefore almost negligible, in comparison with the amount intercalated. On the contrary, for turbostratic $\alpha_{Co^{3+}}$ phases which have very small particles, the amount of adsorbed water molecules is not negligible. This point has been particularly emphasized by the TGA characterization previously reported [9].

The IR characterization of sulfate and carbonate anions in the various materials is reported in the following sections.

Carbonate anions

When the carbonate anion stays in a free configuration, its symmetry is D_{3h} and the IR active vibrations are ν_2, ν_3, ν_4 at 879, 1429–1492 and 706 cm^{-1}, respectively, in CaCO$_3$ (calcite) [11]. When one or two oxygen atoms are linked to a metallic ion the symmetry is lowered, consequently a splitting of the degenerated modes occurs with the appearance of a new band in the IR spectrum (corresponding to the ν_1 Raman active band of the free ion). When the anion is unidentate, the ν_3 and ν_4 vibrations split into two parts which appear at 1373 and 1453 and 756 and 678 cm^{-1}, respectively, in [Co(NH$_3$)$_5$CO$_3$]Br [11]. The ν_1 vibration which becomes IR active appears in such a compound around 1070 cm^{-1}. When the anion is bidentate, the ν_3 and ν_4 vibrations also split into two parts, at 1265 and 1593 and 760 and 673 cm^{-1}, respectively, in [Co(NH$_3$)$_4$CO$_3$]Cl and the ν_1 vibration appears around 1030 cm^{-1} [11].

CO_3^{2-} anions in $\alpha^*_{Co^{3+}}$ phases

The IR spectra of $\alpha^*_{Co^{3+}}$ phases containing 20 and 40% cobalt ions are reported in Fig. 4.

In both spectra, the strong band at 1360 cm^{-1} corresponds to the ν_3 vibration of carbonate anions in D_{3h} symmetry. However, from a comparison with the ν_3 vibrations of CaCO$_3$ (calcite) which appear at 1429 and 1492 cm^{-1} [11], one can assume that intercalated carbonate anions are not in a 'free' configuration although they stay in D_{3h} symmetry. This frequency difference suggests that all carbonate anions are totally and symmetrically
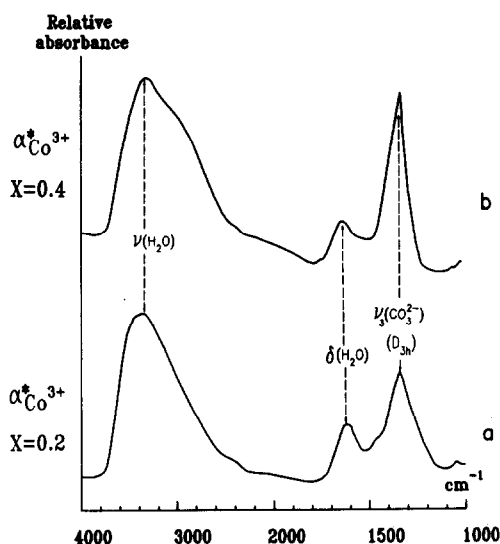

Fig. 4. Influence of the cobalt amount ($x = 0.20$ and 0.40) on the IR spectra of $\alpha^*_{Co^{3+}}$ (spectra realized in hexachlorobutadiene).

hydrogen bonded with water molecules in the interslab space of the $\alpha^*_{Co^{3+}}$ phases as illustrated by the schematic representation of a part of the structure (Fig. 5).

CO_3^{2-} anions in $\alpha_{Co^{3+}}$ phases

The IR spectra of $\alpha_{Co^{3+}}(CO_3)$ phases containing 20, 40 and 55% cobalt ions are reported in Fig. 6.

The simultaneous presence of the strong band at 1360 cm^{-1} and of a shoulder around 1470 cm^{-1} suggests that the carbonate anions may be in two different symmetries. The band at 1360 cm^{-1} corresponds to the ν_3
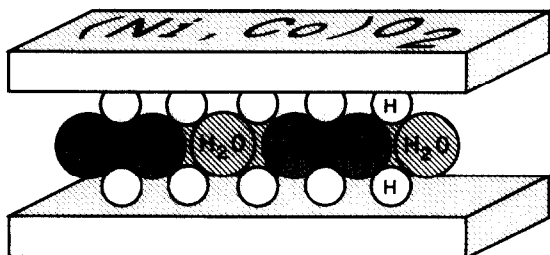

Fig. 5. Schematic representation of the interslab space of $\alpha^*_{Co^{3+}}$ and $\alpha_{Co^{3+}}(CO_3)$-hydroxides.

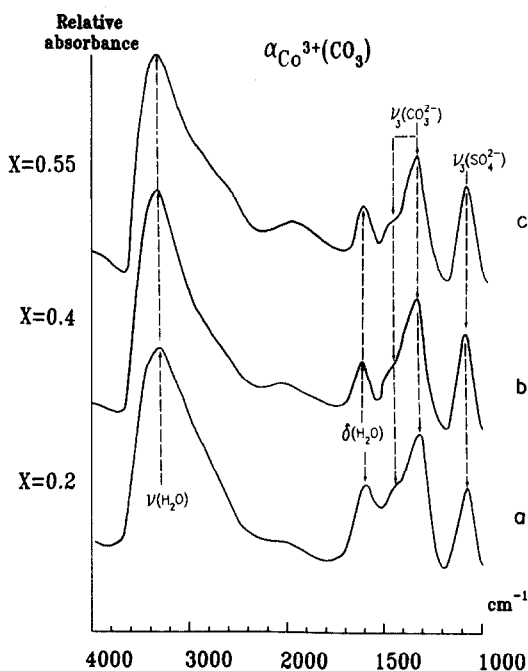

Fig. 6. Influence of the cobalt amount ($x = 0.20$, 0.40 and 0.55) on the IR spectra of $\alpha_{Co^{3+}}(CO_3)$ (spectra realized in hexachlorobutadiene).

vibration of carbonate anions in the D_{3h} symmetry. As in the case of $\alpha^*_{Co^{3+}}$ phases, these anions would be totally hydrogen bonded with water molecules in the interslab space of the hydroxide. However, the shoulder around 1470 cm^{-1} shows that a symmetry lowering has occurred. The ν_3 band, which appears at 1360 cm^{-1} for the anion in D_{3h} symmetry, splits into two at 1360 and 1470 cm^{-1}, respectively. A comparison with the values previously given shows that these carbonate anions are certainly unidentate. In our case, this means that one oxygen atom of the anions is directly linked to a metallic ion (Ni, Co) of the sheet in substitution of hydroxyl groups. As unidentate carbonate anions are not present (or as a negligible amount) in $\alpha^*_{Co^{3+}}$ phases, we can assume that these anions are mainly adsorbed on $\alpha_{Co^{3+}}$ phases. As the $\alpha_{Co^{3+}}$-phase particles have a small size, a lot of carbonate species may therefore be adsorbed. The anions in D_{3h} symmetry are inserted between the M(OH)$_2$ slabs, as in the case of the $\alpha^*_{Co^{3+}}$ phase.

As a conclusion, unidentate carbonate anions (C_{2v} symmetry) would be mainly adsorbed in substitution of surface OH$^-$ groups, while the anions in D_{3h} symmetry would be intercalated between the M(OH)$_2$ slabs and totally hydrogen bonded with water molecules [13].

The fact that intercalated carbonate anions are linked by hydrogen bonds is emphasized by the shoulder observed on both spectra of Figs. 4 and 6 around 3000 cm^{-1}. In pyroaurite-like minerals, it was shown that the absorption band at 3000 cm^{-1} results from a stretching vibration of OH groups bonded to carbonate anions [13–15]. The increasing intensity of this carbonate related shoulder, in each material family, with the cobalt concentration (Fig. 4(b) and 6(c)), confirms the chemical analysis which shows that the carbonate ions concentration increases with the cobalt amount. As a result of their mutual repulsion, the carbonate ions are distributed in the interlayer space as far from one another as possible. They are surrounded by water molecules, thereby reducing this repulsion [13], as shown in Fig. 5.

Sulfate anions

These anions have been detected in both $\alpha_{Co^{3+}}(SO_4)$ and $\alpha_{Co^{3+}}(CO_3)$ phases.

According to the literature, the number of bands and their positions give information about the symmetry, and about the linking between SO$_4^{2-}$ groups and metallic cations. If the sulfate anion is free (T_d symmetry), two vibrations are IR active (ν_3 and ν_4) [11]. When the anion is linked to a metallic cation, the symmetry becomes C_{3v} or even C_{2v} and both ν_3 and ν_4 bands split into two or three parts while the ν_1 and ν_2 vibrations become IR active [11]. The various vibrations of sulfate anions versus the anion symmetry are compared in Table 1.

From Fig. 3, we can notice that the band at 1100 cm^{-1} on the $\alpha_{Co^{3+}}(SO_4)$ spectrum, is in accordance with the presence of sulfate groups in T_d symmetry, but the shoulder around 1050 cm^{-1} indicates that some anions may be in C_{3v} symmetry. The value of the intersheet distance of the $\alpha_{Co^{3+}}(SO_4)$ material ranges from 8.8 to 9.4 Å, and allows the insertion of

TABLE 1

SO_4^{2-} anion vibrations vs. its symmetry

Material	Symmetry	ν_1	ν_2	ν_3	ν_4 (cm^{-1})
Free SO_4^{2-} anion	T_d			1104	613
[Co(NH$_3$)$_5$SO$_4$]Br	C_{3v}	970	438	1032–1044	645
				1117–1143	604
[(NH$_3$)$_4$Co⟨$^{NH_2}_{SO_4}$⟩Co(NH$_3$)$_4$][NO$_3$]$_3$	C_{2v}	995	462	1050–1060	641
				1170	610
				1105	571

sulfate anions, in T_d symmetry, in the interslab space of the material. Sulfate anions in C_{3v} symmetry would then be mainly adsorbed. Similar results were previously published for α-nickel hydroxides [12]. The fact that the ν_3 vibration of the sulfate anion is not displaced to lower frequencies (as is the case of the ν_3 vibration of CO_3^{2-} anions in D_{3h} symmetry), suggests that these anions must be only poorly linked with water molecules by hydrogen bonding. This last point will be discussed in the following section.

In the $\alpha_{Co^{3+}}$(CO_3) spectrum, the bands at 1100 and 610 cm^{-1} corresponding to the sulfate anion vibrations (T_d symmetry) arise from a residue of Na_2SO_4 which is formed during the precipitation. These anions can be removed by further washings and are systematically eliminated when the material stays in KOH medium.

IR study of $\alpha^*_{Co^{3+}}$ and $\alpha_{Co^{3+}}$ phases after a chemical stability test in KOH medium

Evolution of well crystallized $\alpha^*_{Co^{3+}}$ phases in KOH solution

The α-type phase is unstable in KOH medium and the IR spectrum of the material recovered after a stay in KOH is characteristic of a β(II)-type phase (presence of a narrow band at 3650 cm^{-1} due to free OH groups). However, as discussed in previous papers [4, 5, 9] from X-ray data, when the cobalt substitution rate is higher than 20%, $\alpha^*_{Co^{3+}}$ phases are stable in KOH medium and as a result the IR spectrum of the recovered material is identical to that of the starting phase.

Evolution of turbostratic $\alpha_{Co^{3+}}$ phases in KOH medium

A long range stability test was performed on the $\alpha_{Co^{3+}}$(CO_3)-type phase containing 30% cobalt ions. The IR spectra of the recovered materials after a one week and a three month long test are reported in Fig. 7 in comparison with that of the starting material. The corresponding X-ray diffraction spectra are given in Fig. 8. The IR study agrees with the X-ray diffraction one and shows that, even after a long range stability test, the $\alpha_{Co^{3+}}$(CO_3) phases ($x \geqslant 0.2$) are stable in concentrated alkaline medium: there is no sign of the narrow line at 3650 cm^{-1} which indicates the presence of free OH groups or in other words unoccupied van der Waals gap.
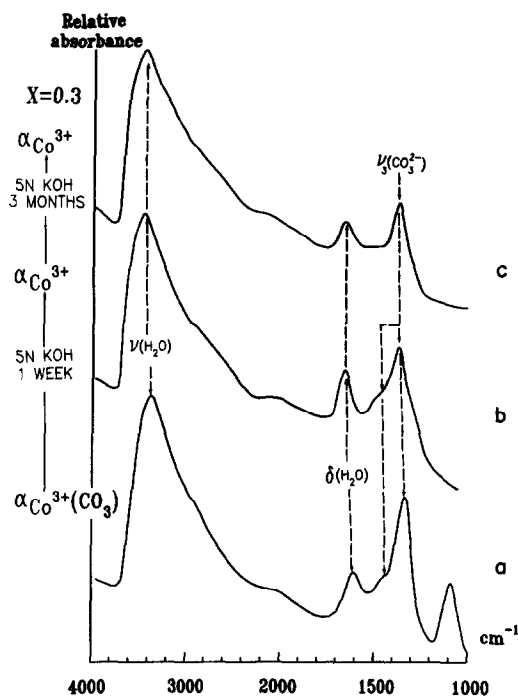
Fig. 7. IR spectra of $\alpha_{Co^{3+}}$ phases obtained after a one week and a three month long stability test of $\alpha_{Co^{3+}}(CO_3)$ ($x = 0.3$).
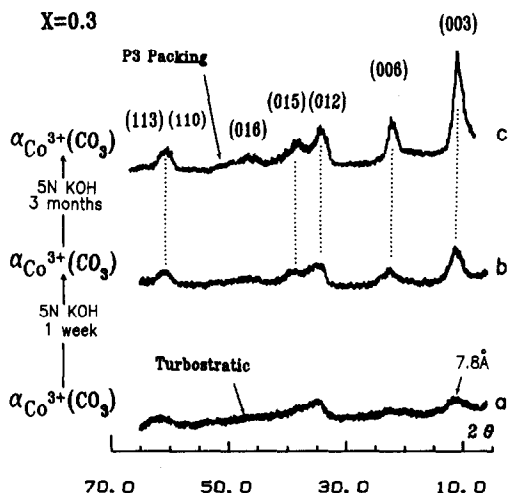
Fig. 8. X-ray diffraction spectra of $\alpha_{Co^{3+}}$ phases obtained after a one week and a three month long stability test of the $\alpha_{Co^{3+}}(CO_3)$-hydroxide ($x = 0.3$).

However from the X-ray diffraction patterns, we can notice an increase in the particle size of the material which stayed in KOH medium simultaneously with the loss of its turbostratic character. This result means that a dissolution and recrystallization mechanism has occurred. The X-ray diffraction pattern of the recovered material (Fig. 8(c)) is similar to that of the $\alpha'_{Co^{3+}}$ phases prepared from $\beta_{Co^{3+}}$ phases [16]. Moreover, it looks like an $\alpha^*_{Co^{3+}}$ phase but with a small particle size. As previously reported, the hydroxyl groups of the (Ni,Co)(OH)$_2$ slabs are well ordered and exhibit a P3-type packing [5, 16]. The IR spectrum of the material obtained after a three month stability test (Fig. 7(c)) shows that the band at 1470 cm^{-1}, characteristic of adsorbed unidentate carbonate anions, has disappeared while that at 1360 cm^{-1} remains. All carbonate anions are therefore in D_{3h} symmetry and are totally hydrogen bonded with water molecules in the interslab space of the material as observed in the $\alpha^*_{Co^{3+}}$ phase. One should notice the similarity between the IR spectra of the $\alpha^*_{Co^{3+}}$ phase (Fig. 4) and of the material recovered after three months in KOH (Fig. 7(c)).

Evolution of turbostratic $\alpha_{Co^{3+}}(SO_4)$ phases in KOH medium

A one month long stability test in a 5 N KOH solution was performed on the $\alpha_{Co^{3+}}(SO_4)$ phase with 20% cobalt ions. The IR spectrum of the recovered material is reported in Fig. 9(b) in comparison with that of the starting phase (Fig. 9(a)).

This Figure shows that the $\alpha_{Co^{3+}}(SO_4)$ phase is also stable in KOH medium as there is no sign of the narrow band at 3650 cm^{-1} characteristic of a β(II)-type phase [10]. The main difference between the two spectra is
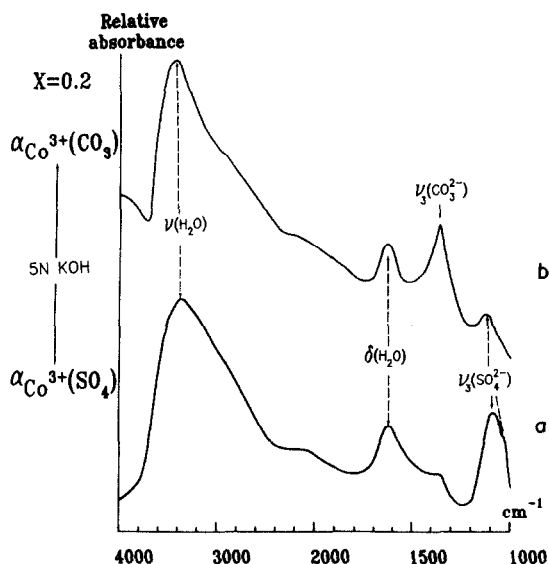

Fig. 9. IR spectrum of the $\alpha_{Co^{3+}}(CO_3)$-hydroxide obtained after a one week long stability test of the $\alpha_{Co^{3+}}(SO_4)$ phase ($x=0.2$) (spectra realized in hexachlorobutadiene).

the disappearance of the strong band at 1100 cm^{-1} with an increase in that at 1360 cm^{-1} in the material which stayed in the concentrated KOH solution. This result, in agreement with the chemical analysis, shows that an exchange of SO$_4^{2-}$ anions by CO$_3^{2-}$ ones has occurred in the intersheet space of the material. This exchange reaction is also emphasized by the X-ray diffraction study which shows an important decrease of the intersheet distance (from 9.4 Å in the starting phase to 7.9 Å after the stability test) [9]. Moreover, we can notice the appearance of a shoulder around 3000 cm^{-1} on the spectra of the material recovered after the stability test. As previously discussed, this shoulder is induced by the hydrogen bonding between carbonate ions and water molecules. One has to notice that in the spectrum of the starting material ($\alpha_{Co^{3+}}(SO_4)$) there is no shoulder around 3000 cm^{-1} which could characterize hydrogen bonding between sulfate anions and water molecules or hydroxyl groups (Fig. 9). This result seems to indicate that if these hydrogen bondings exist, they are necessarily very weak. On the contrary, the hydrogen bonding between carbonate anions and H$_2$O molecules are very strong certainly because of the planar shape of these entities. This difference between the hydrogen bonding strength could then explain the higher lability of sulfate anions in comparison with that of the carbonate ones.

Evolution of $\alpha_{Co^{2+}}$ phases in KOH medium

In a previous paper, it was shown that the $\alpha_{Co^{2+}}$ phase was used as preparation intermediate to obtain the $\alpha_{Co^{3+}}$ phase. The X-ray diffraction pattern of this material after a stay in KOH shows its instability in this medium. This reaction has also been studied by IR spectroscopy.

The IR spectra of the starting $\alpha_{Co^{2+}}$ material (20% Co^{2+}) and that of the material recovered after a one week stability test in a 5 N KOH solution are reported in Fig. 10. The spectrum of the starting phase is characteristic of an α-type phase as shown by:
• the presence of water vibrations
• the absence of the band of free OH groups.
The band at 1100 cm^{-1} is characteristic of free sulfate anions (in T_d symmetry) but the shoulder at 1050 cm^{-1} indicates that some sulfate anions are also in C_{3v} symmetry. As in the case of $\alpha_{Co^{3+}}(SO_4)$ phases, free sulfate anions would be intercalated (the intersheet distance is equal to 9 Å) while those in C_{3v} symmetry are assumed to be mainly adsorbed and linked in substitution of surface OH$^-$ groups. The presence of unidentate carbonate anions is proved by the observed bands at 1360 and 1470 cm^{-1} (Fig. 10). These anions are probably adsorbed. In the $\alpha_{Co^{2+}}$-type phase, as previously reported [9], the presence of CO$_3^{2-}$ and SO$_4^{2-}$ anions requires that of water molecules linked to the M cation in substitution of hydroxyl groups. This provides the charge equilibrium in the material. When the material stays in KOH medium, a β(II)-type phase is formed as shown by the appearance of the narrow ν(OH) band at 3650 cm^{-1} (Fig. 10(b)). This IR spectrum is similar to that previously reported for a β_{bc}-nickel hydroxide obtained by evolution of a α-nickel hydroxide in KOH [12].
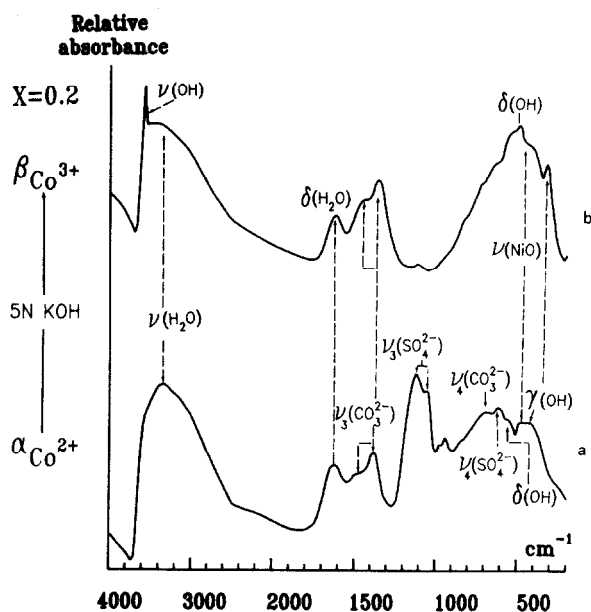
Fig. 10. IR spectra of the $\alpha_{Co^{2+}}$- and the $\beta_{Co^{3+}}$-hydroxides ($x = 0.2$) resulting from the evolution of the former in KOH medium (spectra realized in hexachlorobutadiene).

Conclusions

IR analyses show that the compensation of the charge excess due to trivalent cobalt ions is provided by carbonate anions which are totally hydrogen bonded with water molecules in the interslab space of $\alpha^*_{Co^{3+}}$- and $\alpha_{Co^{3+}}(CO_3)$-type phases and by sulfate ones in $\alpha_{Co^{3+}}(SO_4)$ phases. For cobalt concentrations higher than 20%, $\alpha^*_{Co^{3+}}$ phases do not evolve in KOH medium, while $\alpha_{Co^{3+}}(CO_3)$-hydroxides slowly transform into better crystallized $\alpha'_{Co^{3+}}$ phases. In these conditions, a CO_3^{2-}/SO_4^{2-} exchange occurs in the intersheet space of $\alpha_{Co^{3+}}(SO_4)$ phases. The fact that carbonate anions are totally hydrogen bonded with water molecules in the intersheet space of $\alpha^*_{Co^{3+}}$- and $\alpha_{Co^{3+}}$-type phases increases the stability of these materials which is due to the interaction between trivalent cobalt ions and carbonate anions. The chemical formula of $\alpha^*_{Co^{3+}}$ or $\alpha_{Co^{3+}}(CO_3)$ phases should be compared to that of reevesite or hydrotalcite and more generally both phases and even $\alpha_{Co^{3+}}(SO_4)$ phases, are double layer hydroxide minerals [6–8].

Acknowledgements

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