

Preparation and X-Ray Diffraction Characterization of Two Modifications of the Cobalt Hydroxide Nitrate $\text{Co}(\text{OH})\text{NO}_3 \cdot \text{H}_2\text{O}$

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Samples of cobalt hydroxide nitrate, $\text{Co}(\text{OH})\text{NO}_3 \cdot \text{H}_2\text{O}$, have been prepared by thermal treatment of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ melts at different temperatures, in the presence of soft hydrolyzing agents, such as urea or ammonium hydrogen carbonate amide. The results of chemical analyses and the values of the unit cell parameters, refined from X-ray powder diffraction data, have shown that the investigated compound crystallizes in two different monoclinic modifications, whose relative amount varies depending on the temperature of preparation. © 1992 Academic Press, Inc.

Introduction

In a series of studies carried out during the past years, the suitability of hydroxide nitrate solid solutions $M_x\text{Co}_{1-x}(\text{OH})_y(\text{NO}_3)_z(\text{H}_2\text{O})_p$ ($M = \text{Cu}, \text{Mg}, \text{Ni}, \text{Zn}$; $0 < x \leq \frac{1}{3}$) as precursors for the synthesis of spinel oxides $M_n\text{Co}_{3-n}\text{O}_4$ ($0 < n \leq 1.0$) with a desired composition and cationic distribution was demonstrated (1–5). The methods used were based on some original conceptions concerning the mechanism of thermal decomposition of layered hydroxides (6)

and the role of topotactic transformations as a tool in preparative solid state chemistry (7). The choice of the precursors was based on the structural classification of the hydroxide nitrates of some divalent metals such as nickel and zinc (8).

Although there is great similarity between nickel and cobalt hydroxy salts from the viewpoint of crystal chemistry, crystallographic data on the hydroxide nitrates of cobalt are scarce. More or less precise descriptions of the structure types and lattice parameters of $\text{Co}_2(\text{OH})_3\text{NO}_3$ (9), $\text{Co}_7(\text{OH})_{12}(\text{NO}_3)_2$ (10), and the cobalt oxide hydroxide nitrates with varying composi-

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tion and oxidation degree have been given (11), but the crystal structure of not one has been determined.

Recently, we isolated very small amounts of fine needle-like crystallites from the crust formed on a $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ melt kept in air at 70–90°C for 24 hr. Initial X-ray diffraction (XRD) studies showed that the polycrystalline sample contained at least two phases. Their diffraction patterns were quite different from those of the known nitrates, hydroxides, and hydroxide nitrates of cobalt.

In the present paper we report the preparation procedure, analyses, and XRD characterization of these new phases. The data obtained would add new representatives to the hydroxy salt classification and extend the crystallographic data needed for the choice of precursors of cobalt containing oxides with interesting properties and applications.

Experimental

Sample Preparation

Preliminary attempts to isolate cobalt hydroxide nitrates from the crust formed on $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ melts were abandoned due to the very low yields. Since the formation of these phases is a result of partial decomposition and hydrolysis of the initial cobalt(II) nitrate hydrate (12), the yield was increased by the use of mild hydrolyzing

agents such as urea— $\text{CO}(\text{NH}_2)_2$ —and ammonium hydrogen carbonate amide— $\text{NH}_4\text{HCO}_3 \cdot \text{NH}_4\text{CO}_2\text{NH}_2$.

Distilled water (1.2 ml) and finely ground $\text{CO}(\text{NH}_2)_2$ or $\text{NH}_4\text{HCO}_3 \cdot \text{NH}_4\text{CO}_2\text{NH}_2$ (0.45 g) were added to samples of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (9 g) (A.R.). The mixtures obtained were heated in air at 45–120°C, which led to melting of the $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and its partial hydrolysis and dehydration to solid lower crystallohydrates. The duration of the thermal treatment was from 1 to 240 hr, depending on the temperature. Due to the insufficient degree of urea decomposition, the hydrolyzing agent preferred for syntheses at lower temperatures was $\text{NH}_4\text{HCO}_3 \cdot \text{NH}_4\text{CO}_2\text{NH}_2$. The solid hydroxide nitrates formed were isolated by dissolving the cobalt nitrate residue in acetone, filtering, washing with acetone, and drying in a vacuum furnace (10^{-2} Torr, 45°C). The preparation conditions for the samples investigated are presented in Table I.

Chemical Analyses

Cobalt content was determined by complexometric titration. The number of hydroxyl groups was established by pH-metric back-titration of the residue of a standard solution of hydrochloric acid, which has reacted with a given amount of the sample. The contents of the NO_3 groups were determined by the method of Dewarda (13). Wa-

TABLE I
CONDITIONS OF PREPARATION AND PHASE COMPOSITION OF $\text{Co}(\text{OH})\text{NO}_3 \cdot \text{H}_2\text{O}$ SAMPLES

Sample no.	Temperature of preparation (°C)	Duration (hr)	Hydrolyzing agent	Phase composition ^a
1	120	1	$\text{CO}(\text{NH}_2)_2$	(a) + (b)
2	100	8	$\text{CO}(\text{NH}_2)_2$	(a) + (b)
3	80	40	$\text{CO}(\text{NH}_2)_2$	(a) + (b)
4	65	120	$\text{CO}(\text{NH}_2)_2$	(a) + (b)
5	45	240	$\text{NH}_4\text{HCO}_3 \cdot \text{NH}_4\text{CO}_2\text{NH}_2$	(a)

^a (a), disordered modification; (b), ordered modification.

TABLE II
CHEMICAL COMPOSITION DATA FOR DIFFERENT COBALT HYDROXIDE NITRATE SAMPLES

Sample no.	Temperature of preparation (°C)	(Co)	(OH)	(NO ₃) (wt%)	(H ₂ O)
1	120	38.79	11.22	38.4	11.6
2	100	38.17	10.91	39.1	11.8
3	80	38.27	10.53	39.5	11.7
4	65	37.48	11.87	39.5	11.2
5	45	38.28	11.29	39.6	10.8
Average value		38.20	11.16	39.2	11.4
Calculated formula		$\text{Co}_{1.01}(\text{OH})_{1.02}(\text{NO}_3)_{0.98}(\text{H}_2\text{O})_{0.99}$			

ter content was calculated from the differences between the preliminary established sample weights and the sum of the corresponding OH^- , NO_3^- , and Co^{2+} weights. The data from the chemical analyses are shown in Table II.

Description of the Samples

Observations with an optical microscope showed that all samples consist of pink fibers, whose size increased with increasing temperature of preparation. Thorough study of crystallite morphology by transmission electron microscopy (TEM) was impossible because samples decomposed under intensive electron irradiation in a high vacuum. In a scanning regime (JEOL 200 CX STEM) at which the samples were relatively stable, the crystallites obtained at higher temperatures were found to be aggregates of fine parallel primary fibers (Figs. 1 and 2).

The samples were slightly hygroscopic. When allowed to stand for 2–3 months in open air, they decomposed partially to $\text{Co}(\text{OH})_2$ and $\text{Co}(\text{II})$ nitrate hydrates with different hydration degrees.

XRD Analyses

X-ray diffraction studies were performed with a DRON-3 powder diffractometer ($\text{CoK}\alpha$ radiation, Fe filter, scintillation de-

tector, continuous chart registration of the diffraction patterns). The following instrumental conditions were used: reflection geometry, goniometer radius of 192 mm, 1.5° Soller slits on the incident and the diffracted beam, 0.03° receiving slit. Routine measurements were carried out at a scanning speed of $1^\circ (2\theta) \text{ min}^{-1}$. In some cases, in order to improve the resolution of overlapping lines, a speed of $1/16^\circ (2\theta) \text{ min}^{-1}$ was used.

The effect of the shape of the crystallites on their preferred orientation was clearly observed in samples prepared by pressing and side-filling techniques. The relative intensities were estimated from the diffraction patterns of samples prepared by mixing the investigated compounds with finely dispersed silica gel.

The first 20 lines of the XRD patterns were indexed by the autoindexing programs DICVOL and TREOR (14, 15). The unit cell parameters obtained were used as an input to the program PDI (16) for refinement and estimation of the figures of merit (FOM).

Results and Discussion

The attempts to index directly the XRD patterns of samples 1 to 4 always gave unsatisfactory results. The choice of a unit cell with reasonable lattice parameter values allowing indexing of all lines proved to be

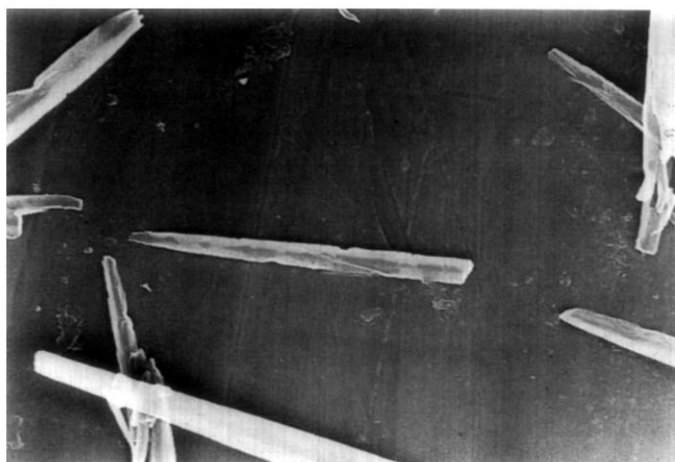


FIG. 1. SEM photograph of cobalt hydroxide nitrate sample No. 5, prepared at 45°C. \times 3000.

impossible. However, this negative result provided the following positive information: (i) the set of interplanar spacings corresponding to lines which could not be indexed was the same for all XRD patterns of samples 1 to 4; (ii) the intensities of these lines increased with decreasing temperature of sample preparation (Fig. 3); (iii) the set of the nonindexed lines in the XRD spectra of samples 1 to 4 practically coincides with the XRD pattern of sample 5 (Table III).

These details permit the assumption that samples 1 to 4 are mixtures. They contain two phases, one of which has the diffraction pattern of sample 5. For the sake of convenience this phase will be called phase (a). The powder diffraction pattern of the second phase was obtained by subtracting the lines of phase (a) from the patterns of samples 1 to 4. The remaining lines (Table IV) were indexed in the space group $P2_1/c$, in which $Zn(OH)NO_3 \cdot H_2O$ (17) and

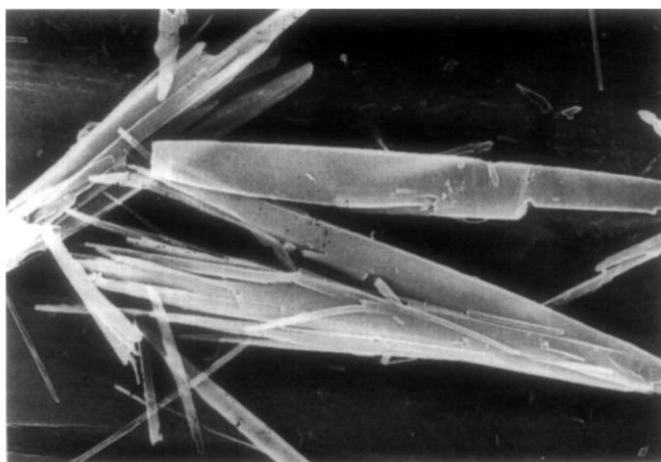


FIG. 2. SEM photograph of cobalt hydroxide nitrate sample No. 1, prepared at 120°C. \times 1500.

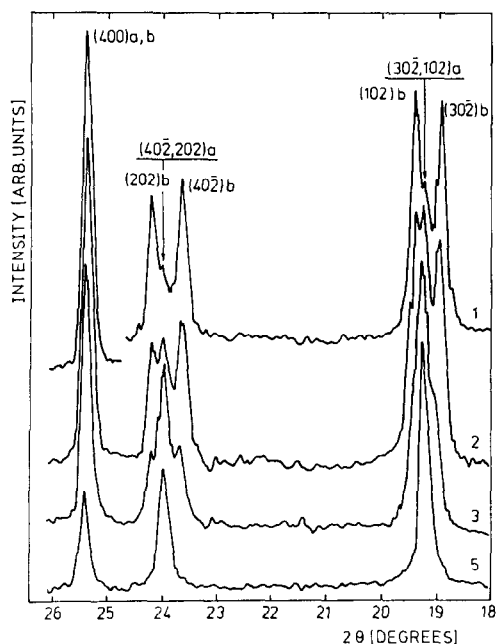


FIG. 3. Evolution of part of the XRD pattern of the samples with temperature of preparation: 1, 120°C; 2, 100°C; 3, 80°C; 5, 45°C.

$\text{b-Ni}(\text{OH})\text{NO}_3 \cdot \text{H}_2\text{O}$ crystallize (18). This phase will be denoted phase (b).

The indexing of the XRD pattern of phase (a) was based on the plausible assumption that its unit cell has a smaller monoclinic angle than the unit cell of phase (b). The final values of the refined unit cell parameters of phase (a) and phase (b) and the FOM are also given in Tables III and IV.

The next problem that was solved by combining XRD and chemical data concerned the composition of phases (a) and (b). As is obvious from Fig. 3, the relative amount of phase (b) decreases with decreasing temperature of preparation and reaches zero for sample 5. In contrast to this result, the data from the chemical analyses (Table II) indicate no systematic changes in composition. Therefore, phases (a) and (b) can be considered structural modifications of a compound whose composition, as determined from the data averaged over all samples (see Table

II), shows satisfactory agreement with the formula $\text{Co}(\text{OH})\text{NO}_3 \cdot \text{H}_2\text{O}$.

The $(h00)$ and $(h0l)$ diffraction lines of phases (a) and (b) have comparable half-widths (see Fig. 3), while the (hkl) lines for phase (a) with $k \neq 0$ are broader than those for phase (b). This allows the assumption that phase (a) has a lower degree of structural perfection. The crystallographic and compositional characteristics of $\text{Co}(\text{OH})\text{NO}_3 \cdot \text{H}_2\text{O}$ discussed above are very similar to those obtained for the (a) and (b) forms of the nickel hydroxide nitrate $\text{Ni}(\text{OH})\text{NO}_3 \cdot \text{H}_2\text{O}$ (18).

The structural differences between the (a) and the (b) phases of $\text{Co}(\text{OH})\text{NO}_3 \cdot \text{H}_2\text{O}$ are still unknown. The structures of the corresponding modifications of $\text{Ni}(\text{OH})\text{NO}_3 \cdot \text{H}_2\text{O}$ also have not been determined. However, the structure of the zinc hydroxide nitrate $\text{Zn}(\text{OH})\text{NO}_3 \cdot \text{H}_2\text{O}$ has been determined recently (17). Its XRD pattern, its unit cell parameters, the content of its formula unit, and even the morphology of its crystallites allow the assumption that this compound and the (b) forms of $\text{Co}(\text{OH})\text{NO}_3 \cdot \text{H}_2\text{O}$ and $\text{Ni}(\text{OH})\text{NO}_3 \cdot \text{H}_2\text{O}$ are isostructural (see Table V).

The structure of $\text{Zn}(\text{OH})\text{NO}_3 \cdot \text{H}_2\text{O}$ is built of infinite double octahedral chains $[\text{Zn}_2(\text{OH})_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}]$ parallel to the direction $[010]$. A similar motif exists in the structures of some magnesium hydroxide chlorides and hydroxide carbonates (19).

The hydroxyl groups, the water molecules, and the oxygen atoms of the nitrate groups occupy positions shared by three, two, and one $[\text{ZnO}_6]$ octahedra, respectively. Hydrogen bonds between water molecules and nitrate groups of neighboring chains link them together in a three-dimensional structure (18). The double chains built up of edge-sharing octahedra form a rigid construction, while the neighboring chains are socket-jointed. This allows cooperative rotation of the chains around the $\langle 010 \rangle$ axis as well as small mutual displace-

TABLE III
POWDER X-RAY DIFFRACTION PATTERN OF $\text{Co(OH)NO}_3 \cdot \text{H}_2\text{O}$, PHASE (a)

Sample no.	2θ	d_{obs}	h	k	l	d_{calc}	$\Delta 2\theta$	I/I_0
1	12.621	8.144	2	0	0	8.139	0.007	265
2	15.801	6.512	2	0	-2	6.503	0.022	1000
			0	0	2	6.503	0.022	
3	19.253	5.353	3	0	-2	5.348	0.018	404
			1	0	2	5.348	0.018	
4	23.960	4.313	4	0	-2	4.310	0.015	209
			2	0	2	4.310	0.015	
5	25.389	4.073	4	0	0	4.067	0.024	186
6	29.223	3.548	2	0	-4	3.547	0.012	837
7	29.926	3.467	3	0	-4	3.466	0.010	28
			1	0	-4	3.466	0.011	
8	31.960	3.251	0	0	4	3.252	-0.002	60
			4	0	-4	3.252	-0.002	
9	35.118	2.9671	1	0	4	2.9690	-0.023	177
			5	0	-4	2.9690	-0.023	
10	35.602	2.9281	2	1	0	2.9311	-0.038	23
11	35.853	2.8320	2	1	-2	2.8291	0.039	9
12	37.653	2.7739	2	1	1	2.7751	-0.017	19
			3	1	-1	2.7751	-0.017	
13	39.119	2.6738	2	0	4	2.6739	-0.002	102
			6	0	-4	2.6740	-0.002	
14	43.812	2.3993	7	0	-4	2.3985	0.015	149
			3	0	4	2.3985	0.015	
15	44.960	2.3411	4	0	-6	2.3401	0.020	24
			2	0	-6	2.3401	0.020	
16	46.445	2.2702	1	0	-6	2.2708	-0.013	24
			5	0	-6	2.2708	-0.013	
17	47.802	2.2094	6	0	2	2.2098	-0.010	9
			8	0	-2	2.2098	-0.010	
18	48.804	2.1667	0	0	6	2.1678	-0.026	47
			6	0	-6	2.1678	-0.026	
19	49.075	2.1555	8	0	-4	2.1550	0.012	98
			4	0	4	2.1550	0.013	
20	51.303	2.0678	4	1	-5	2.0673	0.012	14
			1	1	-5	2.0673	0.012	
21	51.929	2.0446	7	0	-6	2.0446	0.000	260
			1	0	6	2.0446	0.000	

Crystal system Monoclinic

a 17.757(7) Å
 b 3.142(2) Å
 c 14.188(4) Å
 β 113.55(2)°

Space group $P2_1/c$

V 725.7(5) Å³
 $F_{2\theta}$ 20.69(0.015, 67)
 M_{20} 17.26
Radiation $\text{CoK}\alpha$ (Fe filter)

ment parallel to the same axis, which could result in a specific structural disorder. This is the type of structural imperfection to

which the differences of the (a) and (b) forms of $\text{Co(OH)NO}_3 \cdot \text{H}_2\text{O}$ should be ascribed. The presence of anionic positional disorder,

TABLE IV
POWDER X-RAY DIFFRACTION PATTERN OF $\text{Co}(\text{OH})\text{NO}_3 \cdot \text{H}_2\text{O}$, PHASE (b)

Sample no.	2θ	d_{obs}	h	k	l	d_{calc}	$\Delta 2\theta$	I/I_0
1	12.637	8.140	2	0	0	8.140	0.001	808
2	15.635	6.581	2	0	-2	6.585	-0.010	678
3	15.884	6.478	0	0	2	6.468	0.026	808
4	18.988	5.427	3	0	-2	5.426	0.002	340
			3	0	0	5.426	0.002	
5	19.455	5.298	1	0	2	5.297	0.005	367
6	23.651	4.368	4	0	-2	4.368	-0.002	226
7	24.232	4.265	2	0	2	4.267	-0.010	225
8	25.418	4.069	4	0	0	4.070	-0.006	538
9	29.127	3.560	2	0	-4	3.562	-0.014	1000
10	29.664	3.497	3	0	2	3.497	-0.002	107
			3	0	-4	3.497	-0.002	
11	29.960	3.463	1	0	-4	3.462	0.013	34
12	31.571	3.290	4	0	-4	3.292	-0.020	56
13	32.128	3.235	0	0	4	3.234	0.010	56
14	34.602	3.010	5	0	-4	3.011	-0.017	100
15	34.865	2.9880	6	0	-2	2.9889	-0.011	141
16	35.423	2.9424	1	0	4	2.9447	-0.028	181
17	36.783	2.8372	2	1	-2	2.8369	0.005	56
18	36.939	2.8256	0	1	2	2.8273	-0.023	124
19	37.702	2.7704	2	1	1	2.7710	-0.008	164
20	38.519	2.7138	6	0	-4	2.7132	0.008	102
			6	0	0	2.7132	0.009	
21	38.677	2.7032	1	1	2	2.7033	-0.001	45
22	39.511	2.6483	2	0	4	2.6483	0.000	102
23	40.802	2.5679	4	1	-1	2.5682	-0.005	28
24	43.182	2.4326	7	0	-4	2.4328	-0.004	170
25	44.290	2.3747	3	0	-6	2.3744	0.007	192
			3	0	4	2.3744	0.007	
26	44.960	2.3411	2	0	-6	2.3413	-0.005	23
27	45.874	2.2969	5	1	-3	2.2968	0.001	45
28	45.925	2.2945	5	0	-6	2.2945	0.000	90
29	46.560	2.2649	1	0	-6	2.2645	0.008	28
30	47.403	2.2269	8	0	-2	2.2269	0.001	11
31	48.133	2.1951	6	0	-6	2.1950	0.002	141
			6	0	2	2.1950	0.003	
32	48.384	2.1844	8	0	-4	2.1841	0.006	170
33	49.632	2.1328	4	0	4	2.1338	-0.012	170
34	51.160	2.0732	7	0	-6	2.0730	0.005	265
35	52.203	2.0346	8	0	0	2.0349	-0.008	282
36	54.209	1.9647	5	1	2	1.9639	0.024	33

Crystal system Monoclinic

a 17.933(3) Å
 b 3.1435(9) Å
 c 14.250(3) Å
 β 114.80(1)°

Space group $P2_1/c$

V 729.2(3) Å³
 F_{30} 51.10(0.009, 69)
 M_{20} 34.63
Radiation $\text{CoK}\alpha$ (Fe filter)

TABLE V
CRYSTAL DATA OF SOME HYDROXIDE NITRATE HYDRATES, $M(\text{OH})\text{NO}_3 \cdot \text{H}_2\text{O}$ ($M = \text{Zn}$,
 Ni , Co), SPACE GROUP $P2_1/c$

Sample Phase Ref.	$\text{Co}(\text{OH})\text{NO}_3 \cdot \text{H}_2\text{O}$		$\text{Ni}(\text{OH})\text{NO}_3 \cdot \text{H}_2\text{O}$	$\text{Zn}(\text{OH})\text{NO}_3 \cdot \text{H}_2\text{O}$
	(a)	(b)	(b) ^a	(17)
	Present paper		(18)	
$a(\text{Å})$	17.757(7)	17.933(3)	17.790(3)	17.951(3)
$b(\text{Å})$	3.142(2)	3.1435(9)	3.150(3)	3.2600(2)
$c(\text{Å})$	14.188(4)	14.250(3)	14.110(3)	14.272(2)
$\beta(^{\circ})$	113.55(2)	114.80(1)	114.5(2)	114.91(1)
$V(\text{Å}^3)$	725.7(5)	729.2(3)	719.5	757.5

^a Prepared under 10 kbar pressure of nitrogen at 175°C (18).

i.e., statistical mutual replacement of hydroxyl groups, water molecules, and the nitrate groups, is improbable from steric considerations, as pointed out by De Wolf in his discussion of the structure of $\text{Mg}_2(\text{OH})_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$ (19).

The actual reason for the weak spatial correlation between neighboring chains may be a result of imperfect twinning of primary fibers, having different orientations of the end nitrate groups. The existence of this type of crystal growth defect is to be expected in phase (a), obtained at lower temperatures. At higher temperatures, i.e., when conditions favoring recrystallization arise, the amount of phase (b), which has a higher structural perfection, increases. The internal stresses, induced by the reordering, cause the larger imperfect particles to split into aggregates of thinner, more perfect crystallites (see Fig. 2).

Generally, a disordered structure has a thermal stability lower than its ordered modification. In the particular case discussed here, this was experimentally confirmed. The XRD patterns of a two-phase (a) + (b)- $\text{Co}(\text{OH})\text{NO}_3 \cdot \text{H}_2\text{O}$ sample heated at 130°C for different times show that phase (a) transforms into $\text{Co}_2(\text{OH})_3\text{NO}_3$ more rapidly than phase (b).

Conclusions

The cobalt hydroxide nitrate $\text{Co}(\text{OH})\text{NO}_3 \cdot \text{H}_2\text{O}$ is a new representative of 3D transition metal hydroxy salts with chain structures. Its (a) and (b) modifications have monoclinic unit cells with close parameters. The differences in their diffraction patterns are due to structural imperfection probably associated with the presence of crystal growth defects which are more pronounced for phase (a), obtained at a lower temperature.

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