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THERMAL BEHAVIOUR OF THE COPPER-SUBSTITUTED COBALT HYDROXIDE FLUORIDE SERIES $Cu_xCo_{1-x}(OH)F$

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Abstract

The basic salt cobalt(II) hydroxide fluoride was obtained by partial hydrolysis of a 0.2 *M* solution of CoF_2. Mixed Co(II)·Cu(II) hydroxide fluorides with an isomorphic substitution of Co(II) by Cu(II) ions up to 20% were also prepared.

XRD data obtained on these compounds indicate that they are single-phase compounds, their X-ray powder patterns being almost identical to the $Co(OH)_{0.7}F_{1.3}$ diagram, with Zn(OH)F-type structure. However, their stoichiometries are very close to $Co_{1-x}Cu_x(OH)F$ ($0 \leq x \leq 0.2$).

Thermal analysis studies carried out up to 1273 K in still air or under dynamic vacuum conditions show that in air CoO or a mixture of CoO and CuO is formed as final product. In vacuum, at high temperature, with a Ta heating surface, pure α–Co or a mixture of α–Co and Cu is formed at about 973 K.

Keywords: Cu_xCo_{1-x} (OH)F, thermal behaviour, X-ray

Introduction

The formation of cobalt metal and cobalt oxides by the thermal decomposition of different compounds has been widely studied because of their interesting applications.

The first references about the preparation of copper(II)–cobalt(II) spinels ($CuCo_3O_4$) appeared some 15 years ago [1]. Since then, many attemps have been made to prepare spinels under mild conditions by using suitable solid solutions as precursors. This method would guarantee the homogeneity of the spinels so formed [2–4].

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On the other hand, previous studies on the thermal decomposition of basic salts have also revealed the possibility of obtaining cobalt(II) or copper(II) and (I) as well as cobalt or copper metals at comparatively low temperatures [5–7]. All the above-indicated results have moved us to undertake a study of cobalt(II) hydroxide fluoride and also the mixed salts $Cu_xCo_{1-x}(OH)F$, $0 \leq x \leq 0.20$, in order to determine the possibility of their application as inorganic precursor in the formation of cobalt–copper spinels, Co–Cu mixed oxides and metals.

Experimental

Cobalt(II) hydroxide fluoride was obtained by partial hydrolysis of a 0.2 *M* solution of CoF_2. The solution was heated under reflux for 24 h with continuous stirring [8, 9]. The pink precipitate thus formed was filtered off, washed in turn with water, ethanol and acetone, dried in vacuum and kept over P_2O_5 at room temperature.

Mixed $Cu_xCo_{1-x}(OH)F$ was obtained by slow addition of freshly prepared CuO to a 0.4 *M* CoF_2 solution kept at 373 K. CuO was obtained by thermal decomposition of $CuCo_3 \cdot Cu(OH)_2$ at 473 K. Mixed $Cu_xCo_{1-x}(OH)F$ can also be prepared by addition of freshly obtained CuO to a 0.4 *M* Co(OH)F solution. By this method, a substitution up to 12.5% can be reached. These products can also be regarded as members of the previously indicated series obtained from a 0.2 *M* CoF_2 solution.

The stoichiometry of the mixed salts, calculated from analytical data, is shown in Table 1.

Table 1 Results of chemical analysis

%Co	%Cu	%F	Sample composition
61.63	20.06	17.61	Co(OH)F
57.56	2.12	19.91	$Cu_{0.030}Co_{0.97}(OH)F$
56.22	2.50	19.86	$Cu_{0.040}Co_{0.96}(OH)F$
53.51	4.73	19.86	$Cu_{0.070}Co_{0.93}(OH)F$
52.10	3.42	19.89	$Cu_{0.058}Co_{0.94}(OH)F$
51.84	5.85	19.87	$Cu_{0.090}Co_{0.91}(OH)F$
49.05	7.19	19.85	$Cu_{0.120}Co_{0.88}(OH)F$
46.69	8.64	19.87	$Cu_{0.150}Co_{0.85}(OH)F$
45.18	9.41	19.88	$Cu_{0.160}Co_{0.84}(OH)F$
44.73	4.70	19.93	$Cu_{0.090}Co_{0.91}(OH)F$
43.49	6.72	19.91	$Cu_{0.125}Co_{0.87}(OH)F$
42.12	10.85	19.90	$Cu_{0.190}Co_{0.81}(OH)F$

The %OH has been calculated by difference and corroborated by means of elemental analysis of H.

The copper and cobalt contents were determined with a Pye Unicam SP-9 atomic absorption spectrophotometer. The fluoride content of each compound was determined by titration with cerium [10, 11]; hydrogen was determined in a Perkin-Elmer 240 C elemental analyzer.

Differential thermal analysis (DTA) and thermogravimetry (TG) were performed up to 1323 K, on a Stanton STA-781 instrument, in still air, at a heating rate of 10 deg·min^{-1}. About 10 mg of sample was used for each run. Platinum–rhodium crucibles and Al_2O_3 as reference were used. The intermediates and final products were identified by X-ray diffraction and infrared spectroscopy.

Qualitative X-ray fluorescence analysis of the residues obtained at definite temperatures was performed in a Philips PW 1540 X-ray fluorescence spectrometer, with a W anode X-ray tube and a LIF (200) analyzing crystal.

X-ray diffraction diagrams were recorded on a Siemens D-500 diffractometer with monochromatized CuK_α radiation. Silicon powder (99.99% purity) was used as internal standard. Cell parameters were refined by a routine least square procedure.

X-ray high-temperature diffraction diagrams were obtained on an Anton PAAR HTK 10 attachment mounted on Philips PW 1310 equipment; the operating procedure has been described elsewhere [5].

Results

The X-ray powder diagram recorded for cobalt(II) hydroxide fluoride is analogous to that reported for $Co(OH)_{0.7}F_{1.3}$ [10]. However, our analytical results clearly indicate that the stoichiometry of the compound corresponds to Co(OH)F (Table 1). The diagram was indexed on the basis of the Zn(OH)F cell parameters. X-ray diffraction data are compiled in Table 2.

Substitution of Co^{2+} by Cu^{2+} ions causes a very slight variation in the cell parameters (Table 3). This could indicate the formation of a continuous solid solution $Cu_xCo_{1-x}OHF$ in the composition range $0 \le x \le 0.19$.

Thermal behaviour

Co(OH)F

The DTA curve (Fig. 1) shows an exothermic peak in the temperature range 473–573 K, which is accompanied by a weight loss of less than 1% in the TG curve. This is an irreversible process, as checked by recording the cooling curve from 553 K to room temperature. After this transformation, the colour of the sample was changed from the initial pink to dark-violet. Nevertheless, the X-ray diagrams and IR spectra recorded on the sample heated at 553 K did not in-

Table 2 X-ray powder data for Co(OH)F. a=10.305(3); b=4.677(2); c=3.126(1)

d_{ob} / Å	d_{calc} / Å	$h\ k\ l$	I/I_o
4.260	4.269	1 1 0	100
3.469	3.463	2 1 0	16
2.768	2.769	3 1 0	32
2.670	2.672	2 0 1	17
2.576	2.576	4 0 0	25
2.522	2.520	1 1 1	62
2.320	2.320	2 1 1	28
2.257	2.257	4 1 0	19
2.073	2.073	3 1 1	8
1.887	1.887	5 1 0	5
1.841	1.842	1 2 1	3
1.759	1.760	2 2 1	60
1.733	1.732	4 2 0	41
1.615	1.615	5 1 1	19
1.563	1.563	0 0 2	11
1.504	1.505	6 0 1	18
1.503		2 3 0	
1.404	1.404	7 1 0	6

Table 3 Refined cell parameters for the solid solution $Cu_xCo_{1-x}(OH)F$

Sample	a / Å	b / Å	c / Å
$Cu_{0.04}Co_{0.96}(OH)F$	10.287 (2)	4.679 (1)	3.1265 (6)
$Cu_{0.07}Co_{0.93}(OH)F$	10.283 (3)	4.677 (2)	3.1275 (8)
$Cu_{0.09}Co_{0.91}(OH)F$	10.279 (2)	4.6796 (9)	3.1255 (6)
$Cu_{0.12}Co_{0.88}(OH)F$	10.266 (2)	4.671 (1)	3.1232 (8)
$Cu_{0.15}Co_{0.85}(OH)F$	10.257 (2)	4.674 (1)	3.1263 (6)
$Cu_{0.16}Co_{0.84}(OH)F$	10.248 (3)	4.679 (2)	3.1274 (9)
$Cu_{0.19}Co_{0.81}(OH)F$	10.249 (4)	4.694 (2)	3.122 (1)

dicate any appreciable structural modification. Similar behaviour was observed for Co(II)–Ni(II) hydroxide nitrates and was attributed to an increase in the amount of M(III) ions [11].

The decomposition of Co(OH)F is a multistage process that takes place in the temperature range 573–843 K. After the first endothermic peak (573–643 K), X-ray data indicate that CoF_2, Co_3O_4 and the basic salt Co(OH)F are

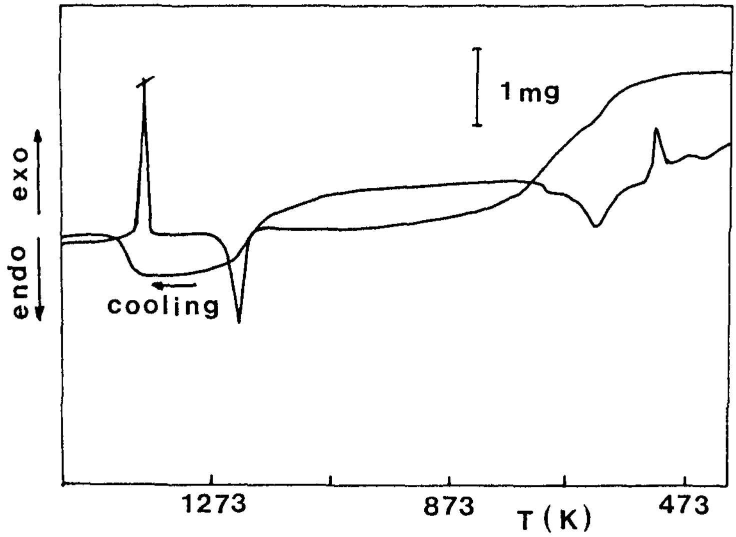

Fig. 1 Differential thermal analysis (DTA) and thermogravimetric (TG) curves recorded for the Co(II) hydroxide fluoride

the phases present. From 643 up to 853 K, a continuous weight loss is observed in the TG curve, the overall weight loss being 15.30%. Co_3O_4 is obtained from 853 up to 1163 K, when it transforms reversibly into CoO in a single-stage process.

The proposed decomposition scheme would be as follows:

$$12Co(OH)F \xrightarrow[+\,^3\!/\!_2O_2]{573\text{–}733\ K} 3Co_3O_4+3CoF_2+3H_2O_{(g)}+6HF_{(g)}$$

$$\xrightarrow[+\,^1\!/\!_2O_2]{733\text{–}853\ K} 4Co_3O_4+12HF_{(g)} \xrightarrow{1163\text{–}1273\ K} 12CoO+12HF_{(g)}+2O_{2(g)}$$

Experimental and calculated weight losses are presented in Table 4.

$Cu_xCo_{1-x}(OH)F$ $(0.04 \le x \le 0.19)$

Co(II)–Cu(II) hydroxide fluorides undergo dehydroxylation and decomposition in the temperature range 573–873 K (Fig. 2), showing a decomposition pattern analogous to that described for cobalt hydroxide fluoride, Co(OH)F. The X-ray powder diagrams recorded on the solid product formed at 863 K corresponds to that reported for Co_3O_4.

From 1073 K, the DTA curves show differences, depending on the composition. When $x \ge 0.07$, the samples decompose in two stages: two endothermic peaks appear in the DTA curves, at 1123 and 1148 K. The presence of these two

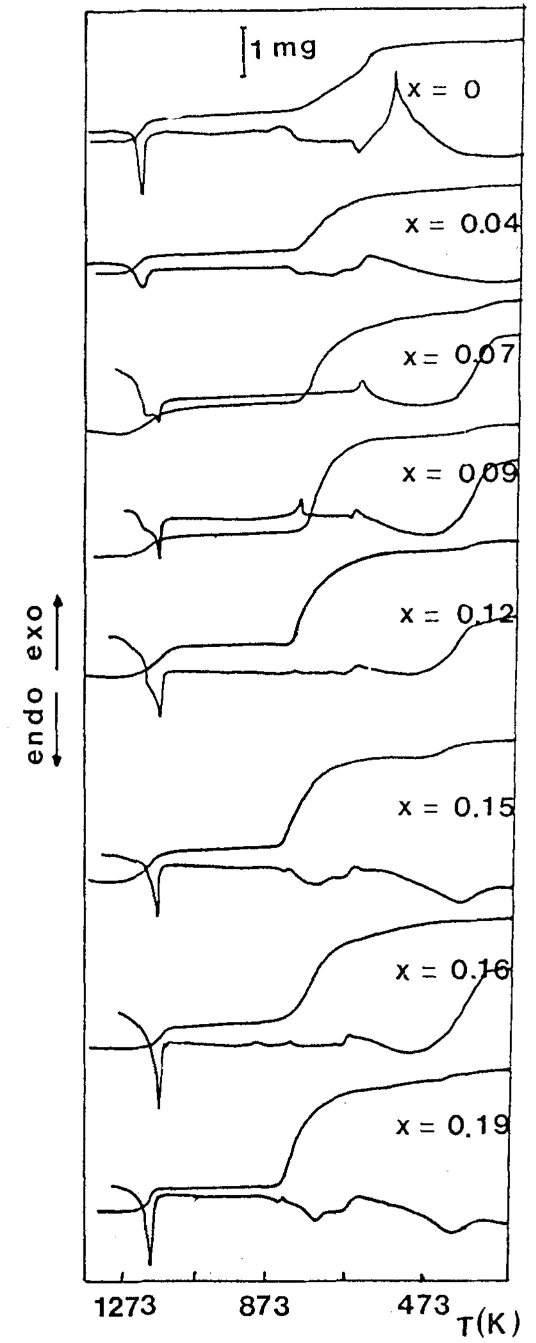

Fig. 2 Differential thermal analysis (DTA) and thermogravimetric (TG) curves recorded for the $Cu_xCo_{1-x}(OH)F$ serie

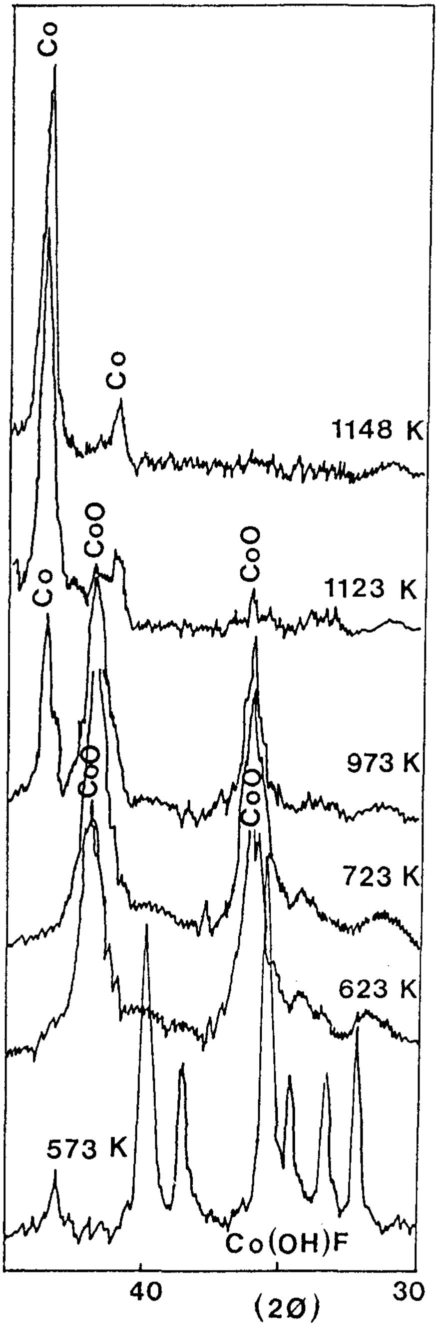

Fig. 3 X-ray high temperature diffraction diagrams for the Co(II) hydroxide fluoride

Table 4 Experimental and calculated weight loss for Co(OH)F

Step	Overall w. loss / %		Temp. /			
	observed	calculated	K			
1	11.13	11.06	733	$4Co(OH)F+\frac{1}{2}O_2$	→	$2HF+H_2O+CoF_2+Co_3O_4$
2	15.60	15.45	853	$3Co(OH)F+\frac{1}{2}O_2$	→	Co_3O_4+3HF
3	21.05	21.07	1273	$Co(OH)F$	→	$CoO+HF$

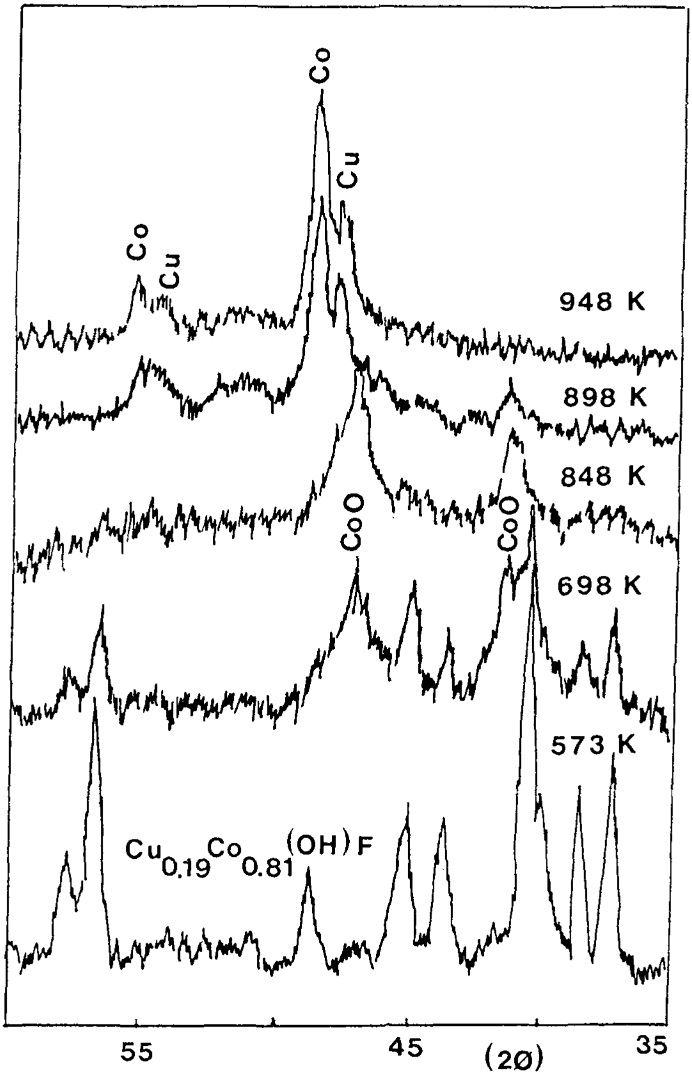

Fig. 4 X-ray high temperature diffraction diagrams for $Cu_{0.19}Co_{0.81}(OH)F$

peaks has been interpreted as originating from the formation of two different Co(II)–Cu(II) spinels with different copper contents. Similar behaviour has been observed for copper(II)–cobalt(II) hydroxide nitrates [12, 13].

X-ray powder diagrams recorded on products formed after the thermal treatment correspond to Co_3O_4 or to a mixture of Co_3O_4 and CuO ($0.07 \le x \le 0.19$).

X-ray high-temperature diffraction studies

Under vacuum dynamic conditions, the decomposition of basic hydroxyfluorides starts at about 623 K.

The changes in the samples with temperature are shown in Figs 3 and 4. The hydroxide fluorides decompose to CoO; no intermediate fluorides were detected. The formation of Co_3O_4 was never observed.

All samples exhibit common features when heated in vacuum. Although CoO is the only intermediate observed at about 873 K, X-ray fluorescence analysis indicates the presence of Co and Cu, which suggests the formation of a mixed oxide (Co,Cu)O. This result would be in agreement with those reported by Landolt *et al.* [14].

From samples with compositions in the range $0.12 \le x \le 0.19$, X-ray diffraction lines of copper and α–cobalt metals are observed at >948 K (Fig. 4).

Conclusions

Cobalt(II) hydroxide fluoride, Co(OH)F, was prepared. Although the X-ray powder diagram is identical to that reported for the composition $Co(OH)_{0.7}F_{1.3}$, the analytical data clearly show an M:OH:F ratio =1:1:1.

The solid solution $Cu_xCo_{1-x}(OH)F$ in the composition range $0 \le x \le 0.2$ was obtained by reacting CuO with either CoF_2 or Co(OH)F.

Thermal decomposition of the mixed basic hydroxide fluorides with $0.07 \le x \le 0.19$ led to the formation of spinels with different Co(II)–Cu(II) contents.

A mixture of copper and cobalt metals was formed when the Co–Cu hydroxide fluorides underwent thermal decomposition under dynamic vacuum conditions; the formation of a mixed oxide (Co, Cu)O was suggested.

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Zusammenfassung — Das basische Salz Cobalt(II)-hydroxidfluorid wurde durch partielle Hydrolyse einer 0,2-molaren Lösung von CoF_2 erhalten. Ebenso wurden auch gemischte Co(II)Cu(II)-hydroxidfluoride mit einem isomorphen Substition von Co(II) gegen Cu(II) bis zu 20% hergestellt.

Die von diesen Verbindungen erhaltenen Röntgendiffraktionsdaten zeigen, daß es sich um einphasige Verbindungen handelt, ihre Debye-Scherrer-Aufnahmen sind fast identisch mit denen des $Co(OH)_{0.7}F_{1.3}$-Diagrammes, mit einer Struktur vom Zn(OH)F-Typ. Die Stöchiometrie liegt der von $Co_{1-x}Cu_x(OH)F$ $(0 \le x \le 0.2)$ auf jeden Fall sehr nahe.

Thermische Untersuchungen bis zu Temperaturen von 1273 K in unbewegter Luft oder unter dynamischen Vakuumbedingungen zeigen, daß in Luft CoO oder ein Gemisch aus CoO und CuO als Endprodukt gebildet wird. In Vakuum wird bei hoher Temperatur (etwa 973 K) und einer Heizfläche Ta reines α-Co oder ein Gemisch aus α-Co und Cu gebildet.