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# A comparative study of the thermal stability of nickel, copper and zinc spinel cobaltites

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## Abstract

The thermal stability of spinel $M_xCo_{3-x}O_4$ (M = Ni, Cu, Zn) obtained from hydroxycarbonate precursors is discussed. Thermal analysis was used to define the different decomposition stages. Information on the mechanism of the spinel synthesis was obtained from IR spectroscopy. Zinc cobaltite is the most stable compound (up to 1023 K), followed by nickel cobaltite; copper cobaltite exhibits considerably lower thermal stability. The beginning of the segregation process with formation of CuO was established by an experiment performed in a high-temperature X-ray chamber.

## INTRODUCTION

Nickel, copper and zinc cobaltites are of interest mainly due to their properties as catalysts in various oxidation processes [1-4] and as oxide electrode materials [5,6]. The application of these compounds is limited because of their low thermal stability. According to the investigations of Andrushkevich et al. [2] and, more recently, of Baussart et al. [7], the cobaltite decomposition proceeds according to the general scheme

$$M_xCo_{3-x}O_4 \text{ (spinel)} \rightarrow MO + M_yCo_{3-y}O_4 \text{ (spinel)} + O_2 \qquad (1)$$

At higher temperatures, the spinel lattice is no longer stable and a rock-salt structure is formed, according to the reaction

$$M_yCo_{3-y}O_4 \text{ (spinel)} \rightarrow M_zCo_{3-z}O_4 \text{ (spinel)} + MO + (M,Co)O \text{ (rock salt)} + O_2 \qquad (2)$$

The stability of spinel cobaltites is a function of temperature, pressure, the type of M(II) cation and its concentration in the spinel lattice. The use of different precursors leads to oxide products with structures with different homogeneities and different concentrations of defects. The phase diagram of the $Co_3O_4$/CuO system in the high-temperature region shows that copper cobaltite, $Cu_xCo_{3-x}O_4$, is stable at temperatures around 1170 K for $x < 0.3$

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[8]. At higher copper concentrations, a tenorite and other phases resulting from the destruction of the spinel phase, are formed. It has been established that even with a high copper content the segregation process is rather slow, so that a metastable copper cobaltite spinel with higher $x$ values can be obtained. A recent study on the relation between composition and thermal behaviour of $Cu_xCo_{3-x}O_4$ ($0 < x < 1$) spinels synthesised from coprecipitated hydroxide–nitrates, revealed that samples with $x > 0.85$ remain single phase up to about 670 K [9].

The stability of nickel, zinc and copper cobaltites is of interest, as zinc cobaltite shows the highest activity in the complete oxidation of hydrocarbons, followed by nickel cobaltite [1], while copper cobaltite is active in both CO-oxidation and NO-reduction [10]. Bearing in mind the low thermal stability of the spinel phase, the working temperatures that can be employed with these spinels must be determined so that phase segregation is avoided. The present study deals with the relative thermal stability of nickel, zinc and copper single-phase spinel cobaltites, synthesised from coprecipitated hydroxycarbonates under non-equilibrium conditions.

## EXPERIMENTAL

### Materials

The copper, nickel and zinc spinels were synthesised by thermal decomposition of coprecipitated hydroxycarbonate precursors of formulae, $NiO \cdot 2CoO \cdot 1.5CO_2 \cdot 3.24H_2O$, $ZnO \cdot 2CoO \cdot 1.14CO_2 \cdot 3.19H_2O$, $CuO \cdot 2CoO \cdot 1.33CO_2 \cdot 2.5H_2O$ and $xCuO \cdot (2-x)CoO \cdot 1.33CO_2 \cdot 2.5H_2O$. The coprecipitation was carried out at pH 9 with $Na_2CO_3$ as a precipitating agent. The detailed preparation procedure is described in refs. 11–13. The composition of the precursors was determined by atomic absorption analysis of Ni, Cu, Zn and Co, and by gravimetric measurement of the evolved carbon dioxide and water, absorbed in chemical traps. The decomposition of the precursors at 573 K leads to spinel cobaltites of a high dispersity with particle sizes between 60 and 100 Å.

### Methods

Thermal analyses of the coprecipitated products and the spinels were carried out on a MOM 1500 derivatograph in air, at a heating rate of 10 K $min^{-1}$, using $Al_2O_3$ as a reference.

The IR spectra were recorded on a Specord M-80 spectrometer in KBr discs.

The decomposition of the cobaltites was carried out in an isothermal regime, the samples being heated at temperatures ranging from 573 to 1223 K in intervals of 25 K. The duration of heating for each sample was 4 hours.

The phase composition was determined from the X-ray patterns registered at room temperature. The X-ray diffractograms were taken on a DRON 3 apparatus using monochromatic Cu K$\alpha$ radiation. In addition, the decomposition of a copper cobaltite sample of composition $Cu_{0.8}Co_{2.2}O_4$ was performed in a high-temperature X-ray chamber in air and atmospheric pressure at a heating rate 3 K $min^{-1}$.

## RESULTS AND DISCUSSION

Because the precursors are X-ray amorphous, information concerning the decomposition mechanism can be obtained by IR spectroscopy. In the case of zinc and nickel hydroxycarbonates, the decomposition proceeds in one step, passing through an intermediate stage with randomly oriented octahedra, indicated by the appearance of a strong broad band at about 580 $cm^{-1}$ for both compounds; this corresponds to the $ABO_2$ vibrations in the spinel lattice [14]. Zinc–cobalt hydroxycarbonate decomposes with the simultaneous formation of tetrahedral and octahedral domains as elements of the spinel lattice, recognized by the two bands at 664 and 572 $cm^{-1}$ (Fig. 1, curve a). In the IR spectrum of semi-decomposed copper–cobalt hydroxycarbonate with $Cu/Co > 0.45$, new bands at 1088, 1048 and 880 $cm^{-1}$,

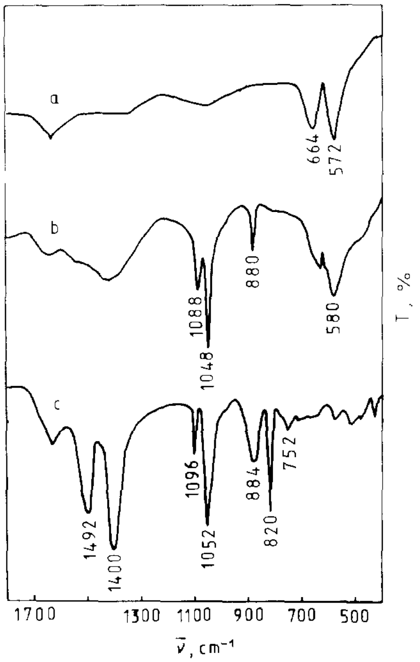

Fig. 1. IR spectra. Curve a, zinc–cobalt hydroxycarbonate after heating at 470 K for 15 min; curve b, copper–cobalt hydroxycarbonate after heating at 520 K for 15 min; curve c, copper hydroxycarbonate, $Cu(OH)_2 \cdot CuCO_3$ (malachite), obtained by co-precipitation.

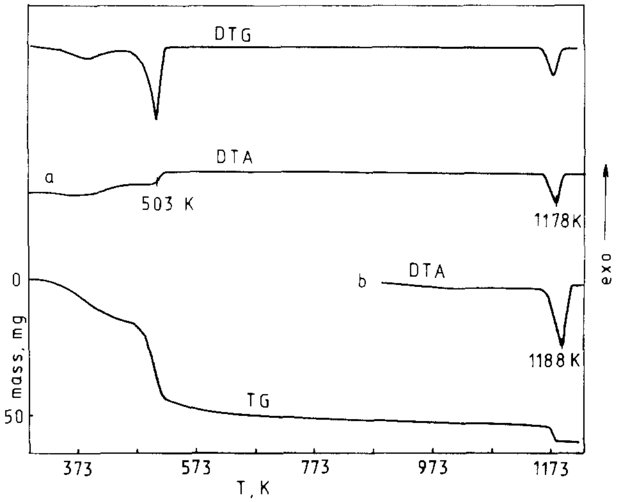

Fig. 2. Thermal analysis of zinc–cobalt hydroxycarbonate and zinc cobaltite. Curve a, DTA of $ZnO \cdot 2CoO \cdot 1.14CO_2 \cdot 3.19H_2O$; curve b, DTA of $ZnCo_2O_4$.

different from those of the initial hydroxycarbonate and the spinel product, appear (Fig. 1, curve b). These bands are characteristic of pure copper hydroxycarbonate with malachite structure. For that compound, the effect of the thermal decomposition registered at 593 K on the DTA curve. The new IR bands are possibly due to undecomposed copper–cobalt hydroxycarbonate with a high copper/cobalt ratio and a structure close to that of malachite (Fig. 1, curve c). This may explain the impossibility of stoichiometric copper cobaltite being synthesised from hydroxycarbonate precursors. A CuO impurity probably appears in the $Cu_xCo_{3-x}O_4$, with $x > 0.9$ samples, from the decomposition of this phase.

The thermal analysis of the hydroxycarbonate precursors shows three types of endothermal transitions (Figs. 2–4). The dehydration of all the samples takes place in the range 373–400 K. The decomposition with evolution of carbon dioxide and water occurs between 470 and 570 K, the DTA peaks being small and asymmetric due to the parallel oxidation of Co(II) to Co(III). In the interval 600–1200 K, a continuous weight loss is registered as a result of reaction (1). At 1070–1200 K, the phase transition spinel → rock-salt structure is observed. In the DTA curves of the already synthesised zinc and copper cobaltites, the position of the last peak is shifted to higher temperatures, while for $NiCo_2O_4$, the shift is towards a lower-temperature, compared with the DTA curves of the hydroxycarbonates from which the spinels were obtained. For zinc and copper cobaltites, the last process occurs at temperatures close to that of pure $Co_3O_4$ (1193 K), while for nickel cobaltite a lower temperature (1093 K) is registered. The shift is insignificant for zinc cobaltite, but for nickel and copper cobaltites differences of $-20$ K and 55 K were found. With Ni–Co hydroxycarbonate

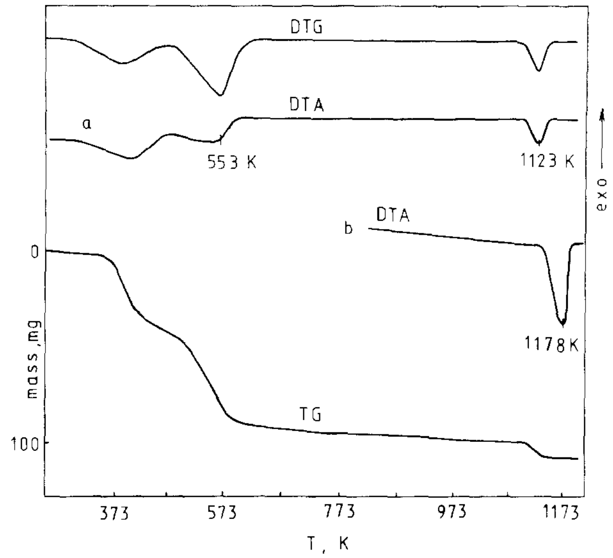

Fig. 3. Thermal analysis of copper–cobalt hydroxycarbonate and copper cobaltite. Curve a, DTA of a $0.9CuO \cdot 2.1CoO \cdot 1.33Co_2 \cdot 2.5H_2O$ sample; curve b, DTA of $Cu_{0.9}Co_{2.1}O_4$.

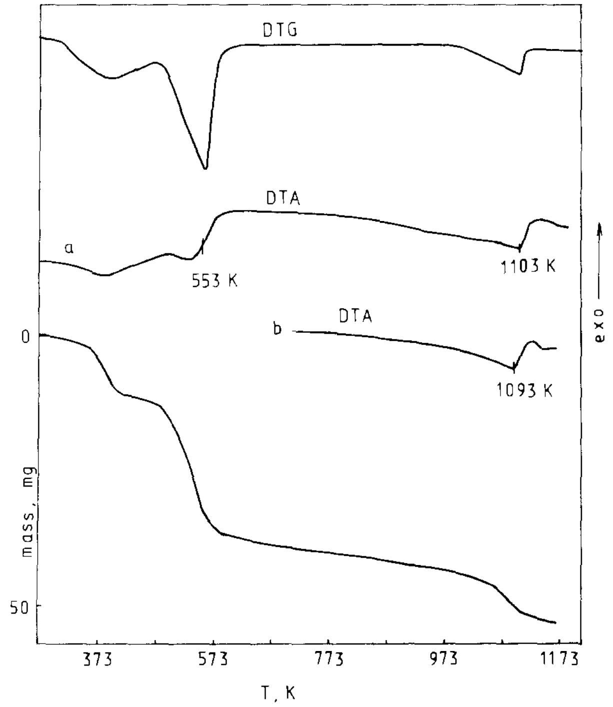

Fig. 4. Thermal analysis of Ni–Co hydroxycarbonate and nickel cobaltite. Curve a, DTA of $NiO \cdot 2CoO \cdot 1.5CO_2 3.24H_2O$; curve b, DTA of $NiCo_2O_4$.

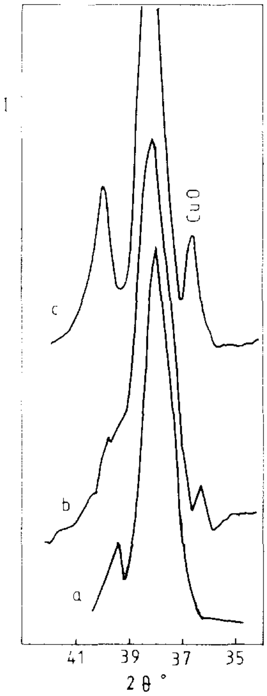

Fig. 5. Decomposition of copper cobaltite in the high-temperature X-ray chamber. Curve a, diffractogram of $Cu_{0.8}Co_{2.2}O_4$ at room temperature; curve b, diffractogram of $Cu_{0.8}Co_{2.2}O_4$ at 653 K; curve c, diffractogram of $Cu_{0.8}Co_{2.2}O_4$ heated to 723 K in the X-ray chamber, registered after cooling to room temperature.

and $NiCo_2O_4$, reaction (2) has begun by 1023 K. The endothermal peak is very broad and is followed by a small exothermal peak. Only in the case of nickel cobaltite may the two processes of spinel destruction and rock-salt structure formation be distinguished. As all spinels have a high dispersity and similar specific surface areas (120 $m^2$ $g^{-1}$) as well as similar particle sizes (60–100 Å), the different position of the endothermal transition reflects the spinel structure stabilisation (or destabilisation) caused by the substitution of another type of bivalent metal cation in the lattice. This effect is more pronounced for the spinels synthesised in isothermal conditions, for which a spinel structure with better ordering and larger crystallites is attained.

To ensure that copper oxide impurities are absent from the initial sample, cobaltite with composition $Cu_{0.8}Co_{2.2}O_4$ was chosen for the experiment performed in the high-temperature X-ray chamber. The spinel lines, (311) and (222), and the most intense CuO line were monitored. The CuO phase was detected at 653 K (Fig. 5). The intensity of the CuO line slowly increases with temperature. Due to the additional temperature-induced braodening of the X-ray lines, the presence of CuO was clearly recognized after cooling the sample to room temperature.

The thermal decomposition in isothermal conditions revealed the relatively high stability of zinc cobaltite. Up to 1023 K no traces of zincite were detected in the X-ray analysis. At 1073 K, the beginning of the spinel → rock-salt structure transition is indicated, for all three cobaltites, by the appearance of CoO lines in the diffractograms. For nickel cobaltite, the phase segregation with appearance of NiO takes place at 823 K. The most unstable compound, copper cobaltite, decomposes as low as 623 K. For a sample of composition $Cu_{0.95}Co_{2.05}O_4$, a tenorite phase was registered after heating at 573 K for 15 hours.

## CONCLUSIONS

On the basis of these investigations, it may be concluded that, due to its low thermal stability, copper cobaltite with a high copper content per formula unit can be obtained only as a metastable phase in the temperature range 570–650 K: it should be used in low-temperature processes below 570 K. For zinc cobaltite, a considerably wider temperature range with an upper limit of 1020 K is applicable. Nickel cobaltite shows intermediate stability (up to 770 K) and its working temperatures should also be chosen with care.

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