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# Preparation, identification and thermal investigation of solid solutions of cobalt–copper oxalates

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## Abstract

The solid-solution oxalates of the series $Co_xCu_{1-x}C_2O_4.nH_2O$ were prepared by coprecipitation from nitrate solutions. The characterization of the coprecipitates was carried out using X-ray powder diffraction (XRD), scanning electron microscopy and thermal analysis (TG/DTA) experiments in nitrogen. The results reveal the formation of a solid-solution with high cobalt content ($x = 0.7$) whereas other compositions with $x = 0.3$ or 0.5 did not form. The final solid products of the thermal treatment of the investigated oxalates are characterized by the formation of oxygen-deficient non-stoichiometric oxides. The thermal decomposition of the solid-solution and its mechanical mixture with the same mole ratio are very different. The first gave mixed lattice oxides in tri- and divalent states, whilst the latter gave separate oxides in the divalent state.

*Keywords:* Solid solution; XRD; DTA

## 1. Introduction

The common route for the formation of oxide composites for electronic ceramics involves a solid-state reaction of mixed oxides or carbonates at high temperatures. A number of disadvantages of this method have been reported, including microscopic compositional inhomogeneities [1,2] resulting in long calcination and sintering times, non-uniformity of particle size and shape, and lack of reproducibility. Therefore, preference is given to other techniques such as the precipitation-filtration technique [4]. Schule [1] successfully prepared Co–Fe, Ni–Fe, Zn–Fe, Mg–Fe and Mn–Fe oxalate solid solutions, but failed with the Cu–Fe system. He concluded that ions with nearly the same ionic radii can form solid solutions with each other. The coprecipitation of transition metal oxalates has received great interest because of the formation of magnetic and catalytic oxides [5–9] at relatively low temperatures. Such co-precipitates can be used as intermediate products containing metal ions of the required stoichiometry. Finely powdered forms of metal, alloys and oxides of transition metals are required to meet some industrial purposes. Dollimore [10] discussed the possibility of producing metal and alloy powders with a very high surface area by the decomposition of the corresponding oxysalts. Recently, the solid solutions of Ni–Co oxalates have been studied [11,12]. The results obtained indicated

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that, due to the similarity of both the charge and the solid-state ionic radii of nickel and cobalt ions, there is a complete range of solid solution and very little change in the lattice with composition. This would indicate the need to prepare and identify Co–Cu solid solutions in which cobalt and copper have somewhat different ionic radii. In the present study, information has been gained on the thermal decomposition of the prepared powdered forms of coprecipitated mixtures of cobalt and copper oxalates.

## 2. Experimental

### 2.1. Preparation

#### 2.1.1. Material

$Co(NO_3)_2 \cdot 6H_2O$ and $Cu(NO_3)_2 \cdot 2(1/2)H_2O$ were obtained from Fisher Scientific; the former is a pink crystalline powder, the latter a blue crystalline powder. Oxalic acid was obtained from J.T. Baker Chemical Co., and is a fine cyrstalline powder. All the compounds were chemically pure, and were used without further purification.

#### 2.1.2. Method

The general composition of the coprecipitated Co–Cu oxalates is $Co_xCu_{1-x}C_2O_4 \cdot nH_2O$. They were prepared as follows. Distilled water (250 ml) and 0.1 M oxalic acid solution (25 ml) were mixed together in a 2000–ml beaker. A 0.1 M solution of metal nitrate ion (500 ml) or a mixture of cobalt nitrate and copper nitrate in the required molar ratio of $Co^{2+}$ and $Cu^{2+}$, was added simultaneously and dropwise with a 0.1 M oxalic acid solution (475 ml) to the solution already present in the 2000–ml beaker, with stirring and warming (about 50°C). The addition was completed over a period of 5 h, and was followed by another 20 h of stirring. Then the reacted solution was left until all the precipitate had settled. The remaining clear solution was decanted off. The precipitate was then filtered and washed several times with distilled water sequentially with ethyl alcohol. The precipitate was carefully dried in air during the filtration, and was then left drying over anhydrous $CaCl_2$ for two weeks before investigation. In this study, five compositions with the general formula $Co_xCu_{1-x}C_2O_4 \cdot nH_2O$. ($x = 0, 0.3, 0.5, 0.7, 1.0$) were prepared. These precipitates are hereafter called samples **1**,**2**,**3**,**4** and **5**, respectively. X-ray diffraction (XRD) data as discussed below indicate that compositions **2** ($x = 0.3$) and **3** ($x = 0.5$) did not form. The elemental analyses gave the molecular formulae $CuC_2O_4 \cdot (1/3)H_2O$, $Co_{0.7}Cu_{0.3}C_2O_4 \cdot 2H_2O$ and $CoC_2O_4 \cdot 2H_2O$ for **1**, **4** and **5**, respectively.

#### 2.1.3. Measurements

The X-ray powder diffraction analysis was performed on a Scintag XDS 2000 powder diffractometer with Cu Kα radiation, $\lambda = 1.540598$, using a solid-state Ge detector cooled by liquid nitrogen. The experimental conditions, for all samples, were: working voltage, 45 kV; working current, 40 mA; $2\theta = 5$–$70°$; continuous scan with speed 3.0° $min^{-1}$. The measurements were taken at room temperature in air under normal pressure. The data were processed using Scintag software DMS version 2.0 on a Micro VAX 3100 with a Tektronix terminal.

The scanning electron microscopic studies were carried out on a JOEL JSM-6100 scanning electron microscope. The surface of the sample was coated with a thin, uniform, electrically conductive gold film. The thermal analysis (TG/DTA) was performed on a SDT 2960 simultaneous DTA–TGA–TA instrument. The analysis was carried out at a heating rate of 10°C $min^{-1}$ in a dynamic nitrogen flow of 50 $cm^3$ $min^{-1}$.

## 3. Result and discusssions

Fig. 1, a and b, shows the X-ray patterns of single oxalates **1** and **5**, respectively. Fig. 1, c, d, and e, are X-ray patterns for mechanical mixtures of cobalt oxalate and copper oxalate in different mole ratios of cobalt oxalate: copper oxalate 3:7, 5:5 and 7:3 and their coprecipitates with the same stoichiometry. The investigation of the patterns leads to the following points:

(1) All the patterns of the mechanical mixtures have a similar nature, except for the relative heights of the two peaks of cobalt oxalate at about $2\theta = 18.6187°$ and 29.7984° which increase with increasing cobalt oxalate ratio in

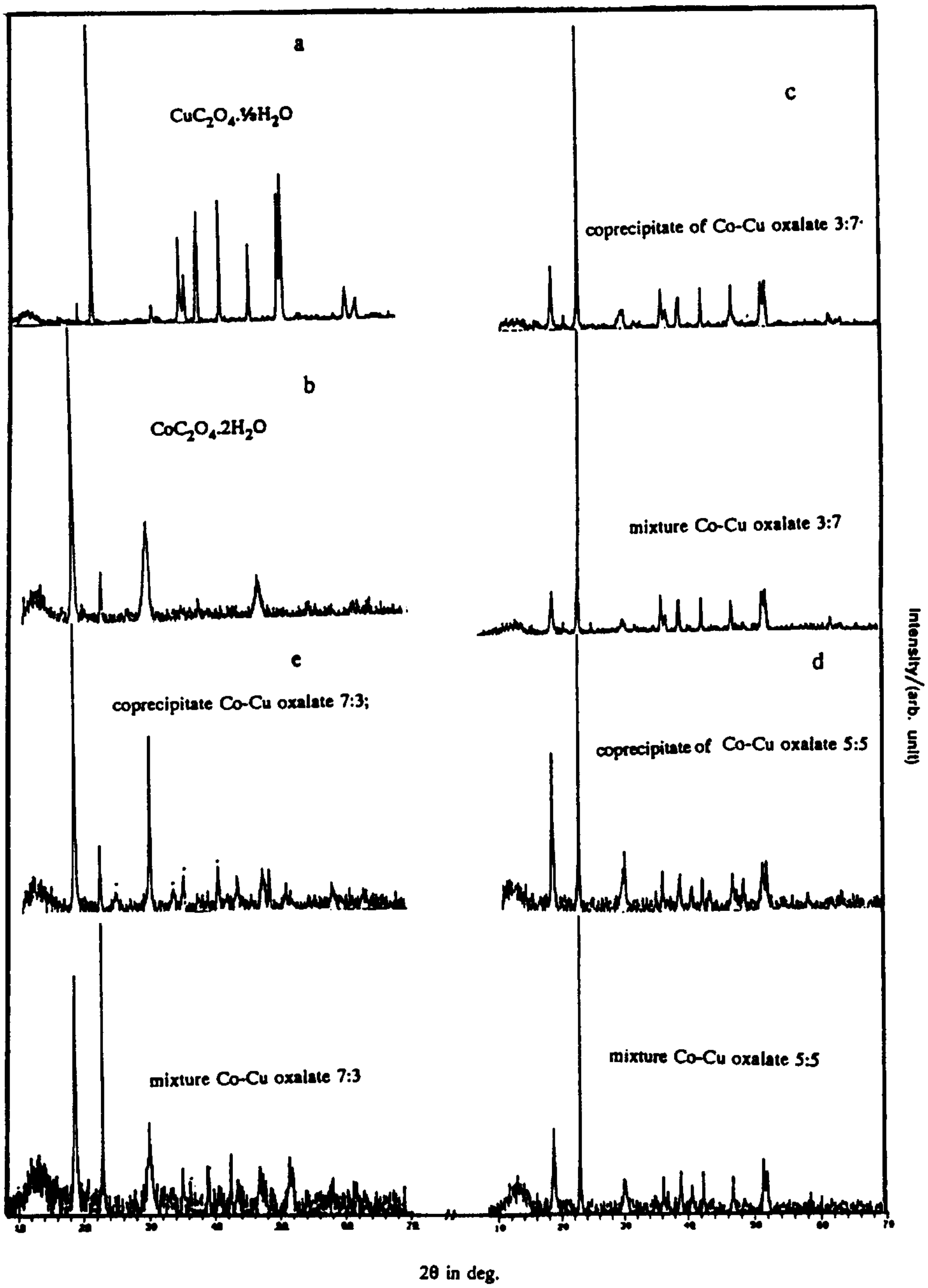


Fig. 1. The X-ray diffraction patterns: a, copper oxalate; b, cobalt oxalate; c,d,e, mechanical mixtures of cobalt oxalate and copper oxalate in mole ratios 3:7, 5:5, 7:3 and their coprecipitates with the same mole ratios, respectively.

the mixtures. However, the most intense peak in all these mixtures is that of copper oxalate at about $2\theta = 22.8587°$.

(2) The patterns of coprecipitates **2** and **3**, $x = 0.3$ and 0.5, follow the above behavior and are exactly like their mechanical mixtures. This indicates that these compositions did not form solid solution by coprecipitation.

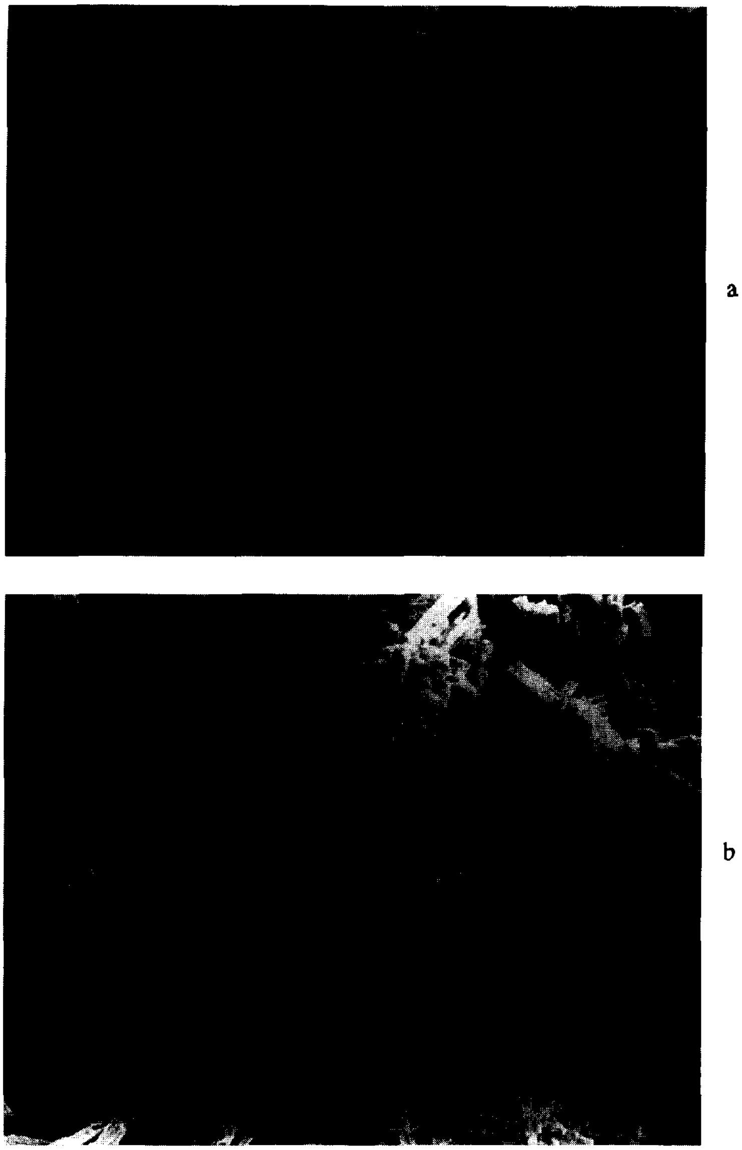


Fig. 2. Scanning electron micrographs of: a, $CuC_2O_4 \cdot (1/3)H_2O$; and b, $CoC_2O_4 \cdot 2H_2O$.

(3) The pattern for coprecipitate **4**, $x = 0.7$, does not follow the above behavior and is different from its mechanical mixture. The most intense peak appears at about $2\theta = 18.8213°$, whereas that of the mechanical mixture appears at about $2\theta = 22.8634°$. In addition to the main lines of cobalt oxalates and copper oxalates, the pattern also displays new lines at about $2\theta = 25.0000°$, $33.9081°$, $35.4275°$, $40.7347°$ and $48.5009°$. These lines may be attributed to the new phase of the solid solution. Also, in spite of the main features of the main lines in the pattern at about $2\theta = 18.8213°$, $22.6194°$ and $30.3300°$ similar to those of cobalt oxalate, they show slight differences in the values of $2\theta$ and, therefore, $d$-spacings. These

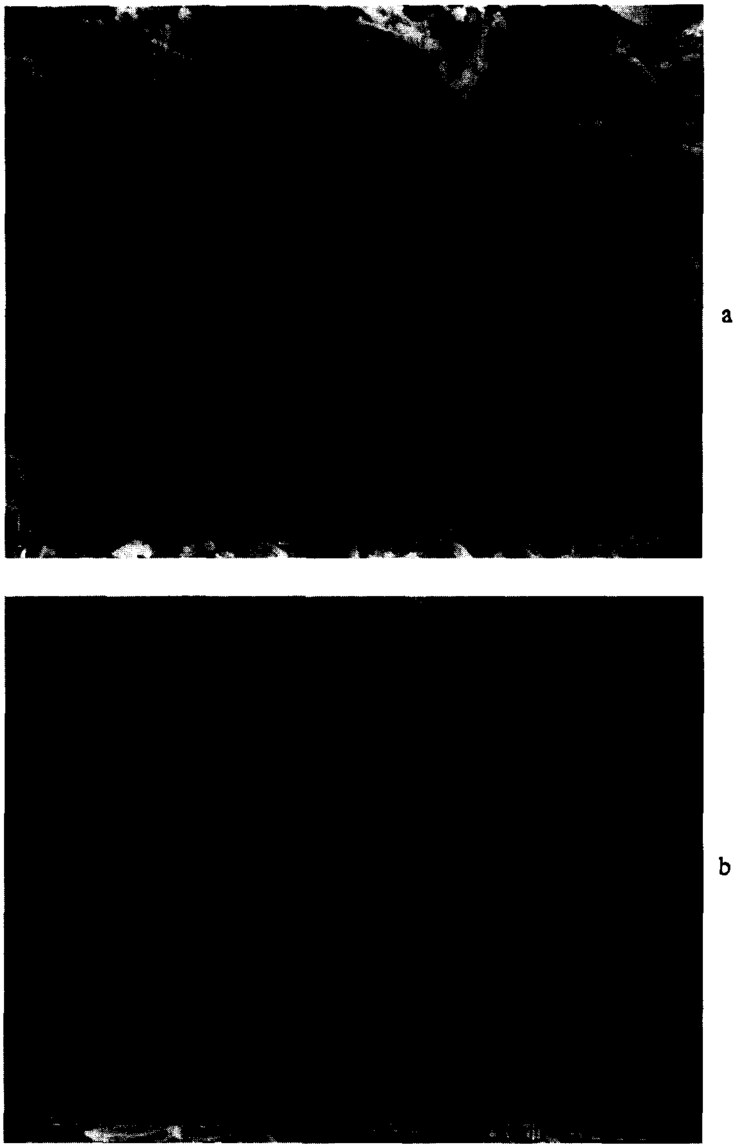


Fig. 3. Scanning electron micrographs of: a, mechanical mixture of Co–Cu oxalate in mole ration 7:3; b, coprecipitate of Co–Cu oxalate in mole ration 7:3.

differences may be due to the distribution and interaction of the copper ions (minor) in the lattice of cobalt oxalate (major) forming the solid solution phase.

Fig. 2 shows the SEM photos of samples **1** and **5**. These indicate that copper oxalate particles have a uniform thin circular plate-like shape with a radius of about 2.8 μm. Cobalt oxalate, however, is in the form of rods, about 2 μm wide and about 20 μm long. Fig. 3 shows the SEM photos of the coprecipitate **4** and its mechanical mixture in the mole ratio copper oxalte:cobalt oxalate of 3:7. It can be seen that the mechanical mixture is simply

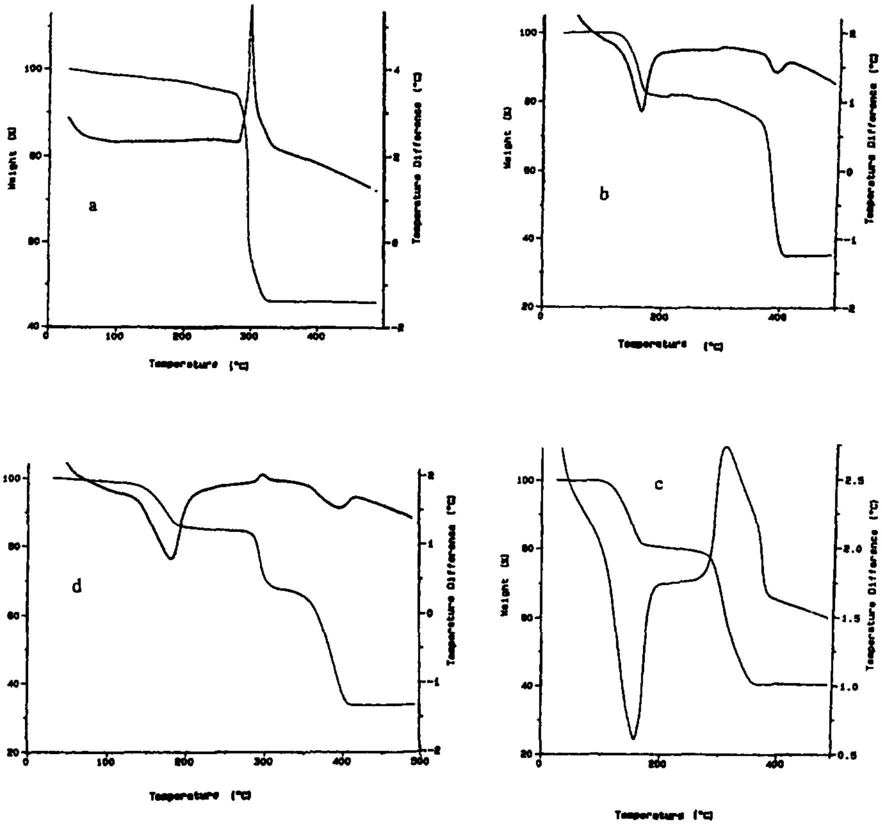


Fig. 4. DTA and TG curves of: a, $CuC_2O_4 \cdot (1/3)H_2O$; b, $CoC_2O_4 \cdot 2H_2O$; c, $Co_{0.7}Cu_{0.3}C_2O_4 \cdot 2H_2O$; and d, mechanical mixture of Co–Cu oxalate in mole ratio 7:3.

a mixture of plates and rod crystals, whereas the coprecipitate has a uniform well-crystallized, rectangular shape of size about $5.0 \times 5.0 \times 1.5\,\mu m^3$. This supports the contention that the coprecipitate is a solid solution, in conformity with the X-ray data.

### *3.1. Thermal studies*

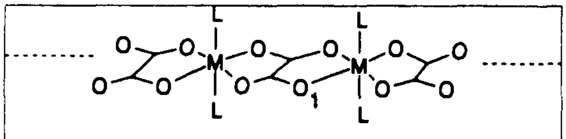
Fig. 4 shows the TG and DTA curves of samples **1**, **5** and their mechanical mixture in a mole ratio 3:7, and the coprecipitate **4** with the same mole ratio. The thermal data are also presented Table 1. It can be seen that the single oxalates **1** and **5** display an ndothermic dehydration DTA peak in the range 40–220°C (broad) and 120–220°C (max 160°C), respectively. The TG weight losses (Table 1) correspond to $(1/3)H_2O$ and $2H_2O$ for **1** and **5**, respectively, in the same temperature ranges. The DTA curves also show exothermic (for **1**) and endothermic (for **5**) mass loss processes with peak maxima at 300°C and 390°C, respectively. These peaks are assigned to material decomposition as indicated from the TG weight losses in the temperature ranges 220–320°C and 290–400°C (Table 1). The solid products of thermal decomposition thus obtained are oxygen-deficient non-stoichiometric metal oxides ($MO_{1-x}$, $x = 0.35$ or 0.25, Table 1) and are soluble in hot $HNO_3$. It is also seen that the onset temperature of decomposition of copper oxalate is lower (about 70°C) than that of cobalt oxalate. This can be explained in terms of the electronegativities

Table 1
Thermal reactions and their thermoproducts of the investigated oxalates as obtained from thermogravimetric analysis (TG) in $N_2$

| Compound | Temperature range/°C | Weight loss% Calcd. (F) | Reaction | Reaction product | |
|---|---|---|---|---|---|
| $CuC_2O_4 \cdot (1/3)H_2O$ | 40–220 | 3.8 (3.8) | a | $CuC_2O_4$ | |
| | 220–320 | 53.1 (53.2) | b | $CuO_{0.65}$ | |
| $CoC_2O_4.2H_2O$ | 120–210 | 19.7 (19.5) | a | $CoC_2O_4$ | |
| | 290–400 | 61.2 (61.2) | b | $CoO_{0.75}$ | |
| $Co_{0.7}Cu_{0.3}C_2O_4.H_2O$ | 100–190 | 19.5 (19.5) | a | $Co_{0.7}Cu_{0.3}C_2O_4$ | |
| | 190–340 | 54.2 (53.9) | b | $Co_{0.7}Ci_{0.3}O_{1.5}$ | $[M^{3+}]$ |
| | 340–355 | 58.6 (58.3) | c | $Co_{0.7}Cu_{0.3}O$ | $[M^{2+}]$ |
| | 355–390 | 59.6 (59.6) | c | $Co_{0.7}Cu_{0.3}O_{0.89}$ | |
| Mechanical mixture of Cu and Co oxalates in mole ratio 3:7 | 60–220 | 15.5 (15.3) | a | $CuC_2O_4 + CoC_2O_4$ in mole ratio (3:7) | |
| | 220–390 | 56.7 (56.1) | b | CuO + CoO in mole ratio (3:7) | |
| | 390–400 | 63.5 (63.4) | c | $CuO_{0.25} + CoO_{0.25}$ in mole ratio (3:7) | |

Key: a, dehydration; b, decomposition; c, reduction through loss of oxygen.

of the central metal ions ($Cu^{2+}$ and $Co^{2+}$). According to previous work [13], the metal oxalates (especially of copper) can take the following polynuclear polymeric structure



M is Co or Cu; L is axial ligand or vacant

Because the final product of thermal analysis is a metal oxide, the rupture of the C–O bond is the first step in the decomposition [14]. The higher interaction between Cu and O (due to the higher electronegativity of copper than that of cobalt) results in a strong Cu–$O_1$, bond and therefore a weak C–$O_1$ bond. Therefore, the copper oxalate shows a lower onset temperature of decomposition (thermal stability).

The DTA trace of the mechanical mixture (Fig. 4) has an endothermic peak with a maximum at 180°C, which corresponds to the dehydration of the single oxalates. The TG weight loss in the temperature range 60–220°C (Table 1) confirms this dehydration process. In the range 220–400°C, two distinct TG steps also appear in the mechanical mixture, which can be assigned to the decomposition of copper oxalate (220–320°C) and cobalt oxalate (290–400°C) to give the oxygen-deficient non-stoichiometric metal oxides at 400°C (Table 1). This assignment was confirmed by the appearance of two successive DTA peaks in the same temperature range. The endothermic peak at 300°C corresponds to the decomposition of coper oxalate, whereas the exothermic one at 390°C corresponds to the decompositio of cobalt oxalate. The above discussion indicates that the mechanical mixture behaves like two separate oxalates. For the coprecipitate 4, the DTA curve shows a strong endothermic peak with a maximum at 1550°C, which corresponds to the dehydration process. The TG weight loss (19.5%) in the temperature range 100–190°C corresponds to two molecules of water (19.5%). The observed asymmetric exothermic DTA peak (with a maximum at 310°C and a shoulder near 370°C) is attributed to material decomposition as obtained from the TG weight losses in the range 190–390°C. The TG weight losses in Table 1 at 340, 355 and 390°C indicate the formation of the following solid-solution oxides: $Co_{0.7}Cu_{0.3}O_{1.5}$(metal in trivalent state), $Co_{0.7}Cu_{0.3}O$ (metal in divalent state) and oxygen-deficient non-stoichiometric $Co_{0.7}Cu_{0.3}O_{0.89}$, respectively. It is clear that there are obvious differences in the decomposition of the coprecipitate [4] and its mechanical mixture with the same composition. The fact that the coprecipitate behaves as a single entity is further proof that this is in fact a true solid solution. However, the XRD patterns of the products of thermal decomposition of both the coprecipitate and its mechanical mixture at 420°C in a nitrogen atmosphere are very different, confirming the above result for the formation of a solid solution.

## 4. Conclusion

A technique to prepare solid solution $Co_xCu_{1-x}C_2O_4.nH_2O$ was developed by coprecipitation. The solid solution with a high cobalt content (high ionic radius) is formed as indicated from XRD, SEM and TG/DTA results. The final solid products of thermal decomposition of these investigated oxalates are oxygen-deficient non-stoichiometric oxides. Copper oxalate shows a lower thermal stability than cobalt oxalate due to its high electronegativity.

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