Thermochimica Acta, 224 (1993) 227–232
Elsevier Science Publishers B.V., Amsterdam

Preparation and thermal decomposition of $Cu_2(OH)_3NO_3$

I. Schildermans [a], J. Mullens [a,*], B.J. Van der Veken [b], J. Yperman [a],
D. Franco [a] and L.C. Van Poucke [a]

[a] *Laboratory of Inorganic and Physical Chemistry, Limburgs Universitair Centrum, B-3590 Diepenbeek (Belgium)*
[b] *Department of Chemistry, Universitair Centrum Antwerpen, B-2020 Antwerp (Belgium)*

(Received 5 January 1993; accepted 2 February 1993)

Abstract

The decomposition of basic copper nitrate is studied using TG–FTIR. The product is decomposed between 160 and 235°C at a heating rate of 10°C min^{-1}. The solid residue is CuO and the gases evolved during decomposition are HNO_3, H_2O, NO_2 and O_2. Decomposition seems to occur in one step.

INTRODUCTION

The YBaCu superconductor is generally prepared using the ceramic method which consists of a solid state reaction of mixed oxides or carbonates. A disadvantage of this method is the microscopic compositional inhomogeneities [1] resulting in long calcination and sintering times, because the metal ions have to diffuse over very long distances. Therefore alternative techniques such as coprecipitation and freeze-drying techniques, have been investigated.

One of the methods used for the precipitation of precursors is the precipitation–filtration technique [2]. In this technique, the metal ions are precipitated simultaneously in the correct stoichiometric proportions. One of the most used precipitating agents is the oxalate ion. The coprecipitated oxalates obtained [3, 4] are then fired. A difficulty in this method is the control of the stoichiometric ratio of the metal ions. Recently, a method for computing the starting concentrations for preparing a precursor in the correct proportions was published [5].

Another precipitating agent can be the hydroxide ion. The great advantages of the use of this ion over the oxalate ion are the formation of $Ba(OH)_2$ instead of $BaCO_3$ and the use of low-cost materials. Barium

---

[*] Corresponding author.

hydroxide decomposes at 650°C [6], while $BaCO_3$, formed by heating BaC_2O_4, only decomposes to BaO from 900°C. The calcination and sintering times will therefore be reduced. Another advantage is the transformation of the metal hydroxides through sols into gels. This sol–gel process [7] exhibits advantages over conventional ceramic processing. The first is an increased chemical homogeneity, maintained on an atomic scale, in a multi-component system. A second advantage is the high surface area of the gels, which leads to lower sintering temperatures.

In this paper we describe the reaction of a sodium hydroxide solution with a copper nitrate solution, which fits in the study of the preparation of hydroxide precursors. The obtained solids were examined by TGA coupled with FTIR, by DSC and by XRD.

By mixing a sodium hydroxide solution with a copper nitrate solution, Spark et al. [8] found that a hydroxide salt of empirical formula $Cu_2(OH)_3NO_3$ precipitates.

EXPERIMENTAL

The following products were used: $Cu(NO_3)_2 \cdot 3H_2O$ (Merck p.a.) and NaOH (Titrisol, Merck). The solutions were made with CO_2-free water, obtained by boiling deionised and bidistilled water for one hour and then cooling it under a flowing N_2 atmosphere.

The precipitates were prepared in a thermostated cage (25.0 ± 0.2°C) by mixing the sodium hydroxide solution (0.1 M) with the copper nitrate solution (0.1 M) using two motor-driven burettes (Schott Geräte T100) at the same speed and under continuous stirring. Three ratios of ($[OH^-]/[Cu^{2+}]$) were analysed, namely 1/1, 3/2 and 11/5. The precipitates obtained were filtered off, washed and dried on P_2O_5 in an excicator.

The TGA and DSC experiments were performed with a TA Instruments (formerly Du Pont) 2000-951. The evolved gases were examined by a Bruker FTIR IFS 48 coupled to the TGA unit [9]. The FTIR has a resolution of $8\,cm^{-1}$. The conformation of the composition of the precipitate was obtained by XRD measurements on a Philips PW 1050/70.

RESULTS AND DISCUSSION

The precipitates were analysed by the thermogravimetry. The results are presented in Table 1. The thermoanalytical studies were carried out in an N_2 atmosphere. The inert working conditions of the TGA experiment were checked as described elsewhere [10].

The decomposition reaction of the 1/1 and 3/2 products can be represented by the following equation, with the indicated onset and

TABLE 1

Results of the thermogravimetric analyses

Sample	Colour of solid	Weight loss/%	Formula
Cu 1/1	Blue	32.94	$Cu_2(OH)_3NO_3$
Cu 3/2	Blue-green	33.28	$Cu_2(OH)_3NO_3$
Cu 11/5	Brown-black	4.21	$CuO \cdot nH_2O$

terminal temperatures

$$Cu_2(OH)_3NO_3(s) \xrightarrow{160°C-235°C} 2CuO(s) + \text{gases} \qquad 33.74\%$$

This theoretical value of 33.74% corresponds very well with the experimental values of 33.28% and 32.94% obtained at 235°C. The TGA plot of the 1/1 product is given in Fig. 1. The weight loss occurs in a single step. The DSC curve shows one broad endothermic peak from 175 to 235°C.

The 11/5 product loses 4.21% of its total weight. The weight loss can be attributed to the release of free water.

$$CuO \cdot nH_2O(a) \rightarrow CuO(s) + nH_2O(g)$$

The identities of all the compounds were confirmed by their X-ray diffraction patterns [11, 12].

The evolved gases from the TGA experiment were carried along with nitrogen to the FTIR. A three-dimensional FTIR plot of the gases released

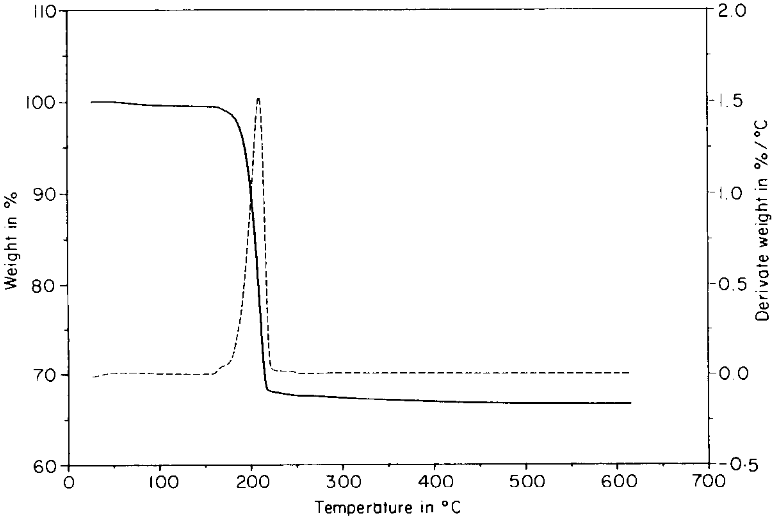

Fig. 1. TGA plot of the 1/1 product.

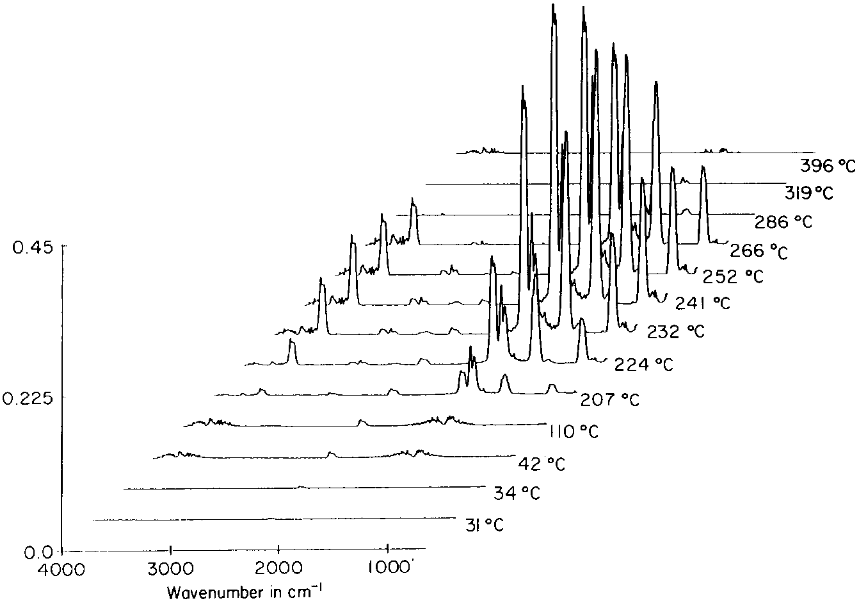

Fig. 2. A three-dimensional FTIR plot of the gases released from the basic copper nitrate after heating in the TGA equipment.

from the basic nitrate salt after heating in the TGA equipment is given in Fig. 2. All the different gases are liberated at the same time in one broad temperature interval with a maximum at about 241°C.

To identify the gases, Fig. 3 shows the FTIR plot from 4000 to 500 cm^{-1} at 241°C. One of the evolved gases is water (3800–3600 cm^{-1} and 1600–1500 cm^{-1}). The peak at 3550 cm^{-1} can be attributed to HNO_3 [13]. HNO_3 has nine fundamental modes, three of which are not visible in our spectrum. Those modes are the OH torsion (456 cm^{-1} [13]), the NO′

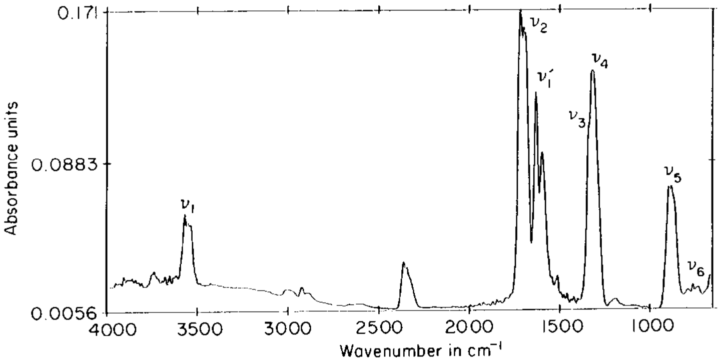

Fig. 3. FTIR plot of the gas evolved by heating the basic copper nitrate salt.

TABLE 2

Frequencies of HNO_3

	Experimental	Reference [13]	Assignment
ν_1	3550(m)	3500(m)	HO stretching
ν_2	1707(vs)	1708(vs)	NO anti-symmetric stretching
ν_3	1330(s)	1331(s)	HON-bending
ν_4	1321(vs)	1325(vs)	NO-symmetric stretching
ν_5	882(m)	879(s)	ONO-angle deformation
ν_6	760(m)	762(s)	out of plane NO_2 bending

stretch (647 cm^{-1} [13]) and the ONO′ angle bend (579 cm^{-1} [13]). The other HNO_3 frequencies and their assignments are given in Table 2.

Figure 4 shows an FTIR plot of HNO_3 from 4000 cm^{-1} to 500 cm^{-1}. This plot was made under the same conditions as Fig. 3. Comparison of the two demonstrates clearly that one of the liberated gases must be HNO_3.

A third gas is NO_2 (1318, 749 and 1610 cm^{-1}). The absorption at 1612 cm^{-1} (ν_1') is strong. The other frequencies cannot be seen because they overlap with the frequencies of the NO symmetric stretching and out-of-plane NO_2 bending of HNO_3.

From these results it can be concluded that $Cu_2(OH)_3NO_3$ decomposes according to

$$Cu_2(OH)_3NO_3(s) \rightarrow 2CuO(s) + H_2O(g) + HNO_3(g)$$

The FTIR analysis clearly shows that only a part of the HNO_3 is dissociated as

$$HNO_3(g) \rightleftharpoons 0.5H_2O(g) + NO_2(g) + 0.5O_2(g)$$

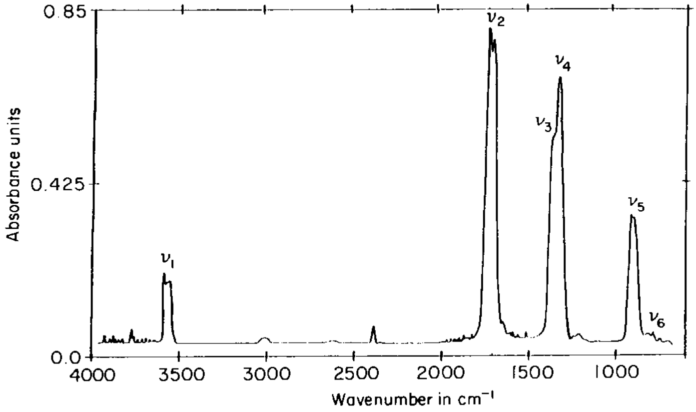

Fig. 4. FTIR plot of HNO_3 gas.

CONCLUSION

Our results demonstrate that the decomposition of $Cu_2(OH)_3NO_3$ can only be explained as a combination of either the proposal of Ilcheva et al. [14] and Ramamurthy and Secco [15], who reported a complete decomposition into NO_2, H_2O and O_2, or the proposal of Auffrédic et al. [16] who reported no dissociation of HNO_3. Basic copper nitrate is a typical sample for which advanced evolved-gas analysis using a technique such as Fourier transform infrared analysis coupled to TGA is indispensable for a complete description of the decomposition process.

ACKNOWLEDGEMENTS

The authors are indebted to the I.W.O.N.L. – Belgium for financial support. This text presents research results of the Belgian Program on Interuniversity Poles of Attraction initiated by the Belgian State, Prime Minister's Office, Science Policy Programming. The scientific responsibility is assumed by its authors. This work is also supported by the Incentive Program on High Temperature Superconductors supported by the Belgian State Science Policy Office.

REFERENCES

1 W.J. Schuele, J. Phys. Chem., 63 (1959) 83.
2 D.W. Johnson, Jr., and P.K. Gallagher, Ceramic Processing before Firing, Wiley, New York, 1978, p. 125.
3 A. Vos, J. Mullens, J. Yperman, R. Carleer, J. Vanhees, L.C. Van Poucke, T.C. Krekels, G. Van Tenderloo, F. Persijn, I. Van Driessche and S. Hoste, in B. Raveau et al. (Eds.), Superconductivity, Technology Transfer Series, I.I.T.T.-I.C.M.A.S., Paris, 1991, p. 85.
4 A. Vos, J. Mullens, R. Carleer, J. Yperman, J. Vanhees and L.C. Van Poucke, Bull. Soc. Chim. Belg., 101(3) (1992) 187.
5 A. Vos, J. Carleer, J. Mullens, J. Yperman, J. Vanhees and L.C. Van Poucke, Eur. J. Sol. State Inorg. Chem., 28 (1991) 657.
6 C. Duval, Inorganic Themogravimetric Analysis, Elsevier, Amsterdam, 1963, p. 528.
7 C.W. Turner, Ceram. Bull., 70(9) (1991) 1487.
8 K. Spark, B. Johnson and J. Wells, Aust. J. Chem., 43 (1990) 749.
9 J. Mullens, R. Carleer, G. Reggers, J. Yperman, J. Vanhees and L.C. Van Poucke, Thermochim. Acta, 212 (1992) 219.
10 J. Mullens, A. Vos, R. Carleer, J. Yperman and L.C. Van Poucke, Thermochim. Acta, 207 (1992) 337.
11 Z. Oswald, Z. Kristallogr. Kristallgeom. Kristallphys. Kristallchem., 116 (1961) 210.
12 Merck Index, 8th. edn., Merck, Rahway, NY, 1968 p. 301.
13 G.E. McGraw, D.L. Bernitt and I.C. Hisatsune, J. Chem. Phys., 42 (1965) 237.
14 L. Ilcheva, M. Maneva and P. Bozadziev, J. Therm. Anal., 16 (1979) 205.
15 P. Ramamurthy and E. Secco, Can. J. Chem, 48 (1970) 3510.
16 J.P. Auffrédic, D. Löuer and M. Löuer, J. Therm. Anal., 16 (1979) 329.