# THE DECOMPOSITION OF THE OXALATE PRECURSOR AND THE STABILITY AND REDUCTION OF THE YBa₂Cu₄O₈ SUPERCONDUCTOR STUDIED BY TG COUPLED WITH FTIR AND BY XRD

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The 124 superconductor $YBa_2Cu_4O_8$ was prepared from the oxalate precursor $Y_2(C_2O_4)_3 \cdot 4BaC_2O_4 \cdot 8CuC_2O_4 \cdot xH_2O$ at one atmosphere oxygen pressure. In $O_2$ the precursor decomposes in one step at 300°C and more gradually (300°–600°C) in Ar. The stability of the superconductor is strongly dependent on the gas atmosphere: in $O_2$ and in air there is no significant weight change as long as the temperature does not exceed 800°C, whereas in a 1% $O_2$-99% $N_2$ mixture decomposition starts at about 670°C with the formation of CuO and $YBa_2Cu_3O_x$ with $x<7$. The reduction of $YBa_2Cu_4O_8$ in a 5% $H_2$-95% Ar mixture takes place in at least four major steps with formation of products such as $Y_2O_3$, BaO, $Cu_2O$, Cu, $BaY_2O_4$ and $Ba_4Y_2O_7$.

Keywords: oxalate, precursor, superconductor

## Introduction

Recently the oxalate coprecipitation technique has been used for preparation of the '124' superconductor at one atmosphere oxygen pressure [1]. A general method for computing the starting concentrations for preparing the precursor in the correct proportions has been described previously [2].

TG coupled with FTIR gives information about the decomposition products and the evolved gases.

An important characteristic of the $YBa_2Cu_4O_8$ superconductor is its thermally stable oxygen content.

Several methods, such as TG in $H_2/Ar$ [3, 4], spectroscopic analysis, coulometric determination [5, 6] and potentiometric titrations [7, 8, 9], have been developed to determine the oxygen content of a superconducting material. In this paper, the following experiments carried out with TG coupled with FTIR, are described: the decomposition of the oxalate precursor $Y_2(C_2O_4)_3 \cdot 4BaC_2O_4 \cdot 8CuC_2O_4 \cdot xH_2O$ in $O_2$ and Ar; the stability of the $YBa_2Cu_4O_8$ superconductor in different gas atmospheres with various oxygen contents ($O_2$; air; 1% $O_2$-99% $N_2$; $N_2$); and the reduction of $YBa_2Cu_4O_8$ in 5% $H_2$-95% Ar.

XRD is used to obtain information on the intermediate formed products.

## Experimental

### Materials

The oxalate precursor was made by adding a solution of the metal nitrates to a solution of $H_2C_2O_4$ and $(NH_4)_2C_2O_4$. Sintering of the oxalate took place in an oxygen flow at 800°C [1].

For investigation of the individual oxides, the following products were used: CuO (Merck, extra pure), BaO (Matthey reagent 95%), and $Y_2O_3$ (made at 900°C from a $Y_2(C_2O_4)_3 \cdot 9H_2O$ precursor).

### Methods

Thermal analysis measurements were carried out with a TA Instruments 2000-951 (former DuPont), coupled with a Bruker IFS 48 FTIR spectrometer [10, 11] working at a resolution of 8 $cm^{-1}$.

A Siemens D5000 diffractometer was used to record XRD spectra. This diffractometer was equipped with a high-temperature unit HTK10 for measurements up to 1600°C.

Oxygen content and copper valence state were determined by iodometric titrations as described elsewhere [7–9].

## Results and discussion

### Decomposition of the oxalate precursor $Y_2(C_2O_4)_3 \cdot 4BaC_2O_4 \cdot 8CuC_2O_4 \cdot xH_2O$

Figure 1 shows TG plots of the oxalate recorded in $O_2$ and Ar. FTIR spectra of the evolved gases are given in Figs 2a and 2b.
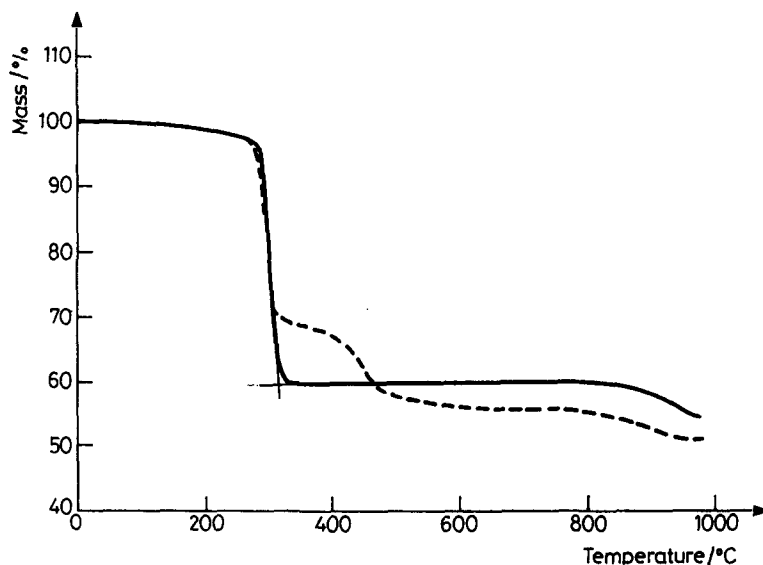
**Fig. 1** Decomposition of $Y_2(C_2O_4)_3 \cdot 4BaC_2O_4 \cdot 8CuC_2O_4 \cdot xH_2O$ in $O_2(—)$ and Ar (- - -); heating rate 10 degmin$^{-1}$; gas flow 60 ml min$^{-1}$. Sample mass 32.539 mg in $O_2$ and 31.952 mg in Ar

In $O_2$ the decomposition to $Y_2O_3$, $BaCO_3$ and a mixture of $Cu_2O$ and $CuO$ occurs in one step at 300°C. At this temperature the FTIR spectrum shows large peaks for $CO_2$ (all CO reacts with $O_2$ to form $CO_2$) at 2300–2400 and 600–700 cm$^{-1}$, and for $H_2O$ at 3600–3800 and 1400– 1600 cm$^{-1}$. The small weight gain from 300° to 800°C results from the conversion of Cu(I) and Cu(II) to Cu(II) and Cu(III). From 800°C an increasing $CO_2$ peak indicates formation of BaO from $BaCO_3$.

In Ar the precursor decomposes gradually to $Y_2O_3$, $BaCO_3$ and Cu between 300°–600°C. Using FTIR, as well as $CO_2$ and $H_2O$ peaks, CO peaks at 2140 cm$^{-1}$ were also detected.

*Stability of the* $YBa_2Cu_4O_8$ *superconductor*

The influence of different atmospheres on the thermal stability of the $YBa_2Cu_4O_8$ superconductor is demonstrated in Fig. 3. $YBa_2Cu_4O_8$ samples were submitted to a temperature program in gases with different oxygen contents.

Temperature program (line 1 in Fig. 3):

– heating up at a rate of 10 deg·min$^{-1}$ from ambient to 800°C.
– isothermal period of 30 min.
– cooling from 800°C to ambient at 10 deg·min$^{-1}$.

– heating at 10 deg·min$^{-1}$ to 950°C.

Before the superconductor was submitted to the temperature program the sample was heated to 800°C and cooled in $O_2$ to ensure that no adsorbed $H_2O$ or $CO_2$ remained at the surface.
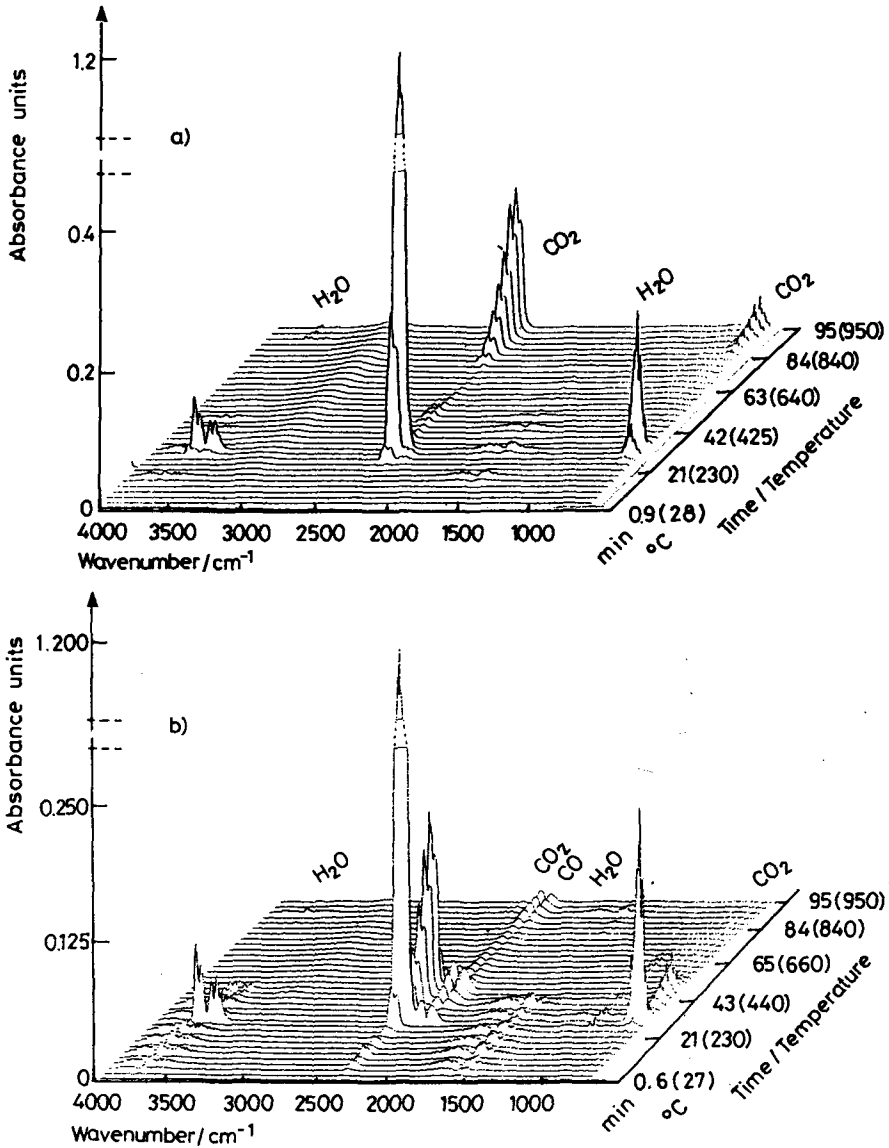


Fig. 2 FTIR plot of the gases evolved during heating of $Y_2(C_2O_4)_3\cdot4BaC_2O_4\cdot8CuC_2O_4\cdot xH_2O$ under $O_2$ (Fig. 2a) and Ar (Fig. 2b)
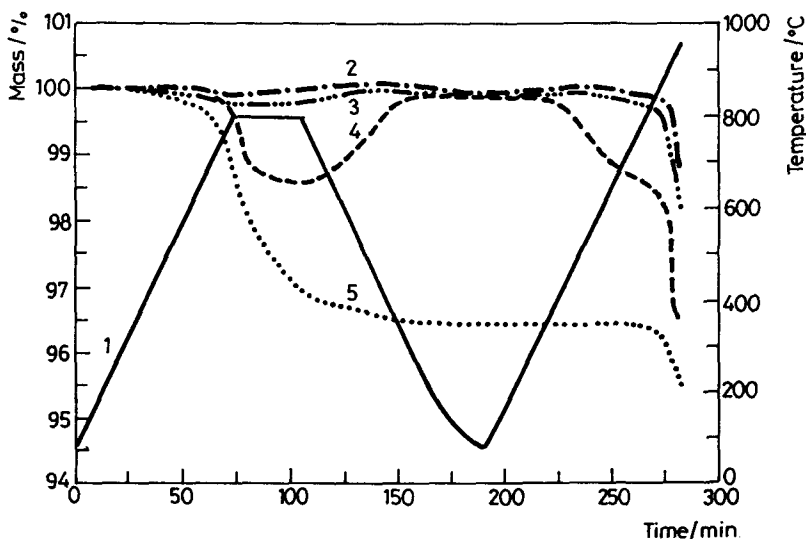
**Fig. 3** Thermal stability of YBa$_2$Cu$_4$O$_8$ in different atmospheres: 1. Temperature program: heating (10 deg·min$^{-1}$), isothermal period, cooling, heating in a gas flow of 60 ml·min$^{-1}$, 2. 50.305 mg YBa$_2$Cu$_4$O$_8$ in O$_2$, 3. 50.122 mg YBa$_2$Cu$_4$O$_8$ in air, 4. 50.813 mg YBa$_2$Cu$_4$O$_8$ in 1 vol% O$_2$- 99 vol% N$_2$, 5. 51.161 mg YBa$_2$Cu$_4$O$_8$ in N$_2$

In view of the small weight changes of the superconductor (see ordinate in Fig. 3), special attention was paid to the effect of buoyancy. Each experiment was compensated by a blank run on inert mixtures of Al$_2$O$_3$ and Pt with the same weight and volume as the superconductor. Appropriate software was used to subtract the data file with the weight values obtained for the inert samples from the data file obtained for the superconductor experiments during the same temperature program in the same gas atmosphere.

In O$_2$ (line 2 in Fig. 3) and in air (line 3 in Fig. 3) there is no significant weight change of the 124 superconductor YBa$_2$Cu$_4$O$_8$ during heating provided that the temperature does not exceed 800°C. At higher temperatures in the second heating the 124 product decomposes sharply from 890°C in O$_2$ and 830°C in air to YBa$_2$Cu$_3$O$_x$ and CuO.

Depending on the value of $x$ ($\leq 7$) for the 123 product, several weight percentages can be calculated; for example

$$\begin{array}{llll}
\text{YBa}_2\text{Cu}_4\text{O}_8 & = \text{YBa}_2\text{Cu}_3\text{O}_x & +\text{CuO} +(7-x)/2\ \text{O}_2 \\
100\% & x = 7 & \text{weight \%} = & 100\% \\
& x = 6.5 & & 98.93\% \\
& x = 6 & & 97.86\%
\end{array}$$
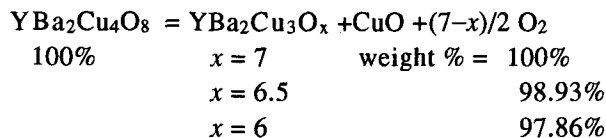
XRD experiments with the high-temperature unit were carried out in air to prove the existence of this reaction; CuO peaks clearly increase during heating the 124 product from 800° to 1000°C. The remainder of the XRD spectrum was too complex to prove eventual formation of intermediates, such as $YBa_2Cu_{3.5}O_{7.5}$ or $YBa_2Cu_4O_{7.5}$, and this aspect requires further investigation.

**In an atmosphere** with lower oxygen content such as a mixture of 1 vol% $O_2$– 99 vol% $N_2$ (line 4 in Fig. 3), decomposition starts as soon as 670°C. This weight loss is due to the formation of $YBa_2Cu_3O_x$ and CuO with $x < 7$. Weight percentages corresponding to $x$ values between 7 and 6 are obtained during the first heating period until 800°C.

The 123 product takes up oxygen during subsequent cooling. This reversibility has been shown previously for the pure 123 product [12]. During the second heating in the 1 vol% $O_2$–99 vol% $N_2$ mixture the first weight loss begins as low as 350°C instead of 670°C due to the fact that the 123 product is less stable than the 124. The weight loss increases sharply from 800°C due to further decomposition, which is comparable with the weight loss detected in pure oxygen and in air at higher temperatures.

**In pure $N_2$** (line 5 in Fig. 3) a greater weight loss is found than with the mixture of 1 vol% $O_2$–99 vol% $N_2$ and no weight gain is possible during cooling due to the complete absence of oxygen. Small weight changes in the time interval 200 to 350 min are due to the fact that the TG equipment is being used on the limit of its sensitivity as shown by the scale used for the ordinate. The inert working conditions of the TG equipment have been carefully tested with the decomposition of copper oxalate as described elsewhere [13].

*Reduction of pure oxides*

A TG plot of the reduction of CuO in 5 vol% $H_2$–95 vol% Ar is shown in Fig. 4. Reduction of CuO to metallic Cu starts at 200°C and is complete at 600°C. The weight percentage of 89.9% at 350°C corresponds to the intermediate formation of $Cu_2O$. No weight loss, attributable to evaporation [14] of Cu is observed above 700°C.

BaO and $Y_2O_3$ show no weight change during heating to 1000°C in a reducing atmosphere. Due to the high sensitivity of BaO for $H_2O$ and $CO_2$, the reducing atmosphere has to be completely free from traces of these gases.

*Reduction of $YBa_2Cu_4O_8$*

The reduction experiments in $H_2$/Ar can be used to determine the oxygen content of the superconducting $YBa_2Cu_4O_8$. Before the 124 product was exposed to the $H_2$/Ar mixture, it was heated in $O_2$ to 800°C to ensure there was no $H_2O$ or $CO_2$ remained at the surface.
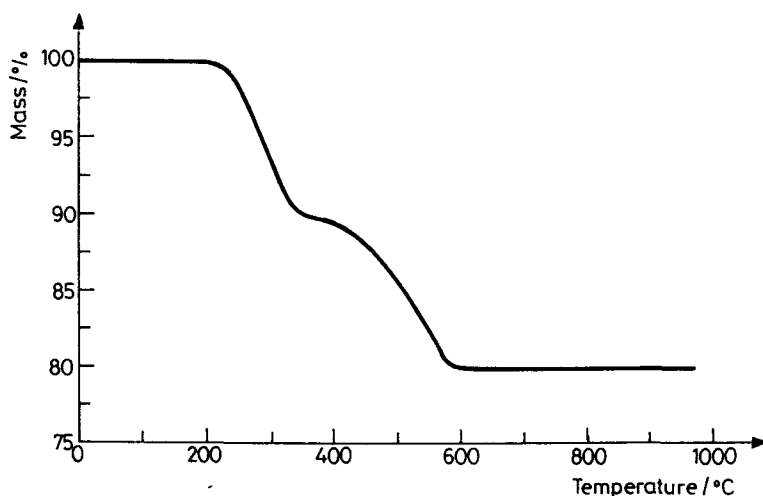
**Fig. 4** Reduction of 46.5150 mg CuO in 5 vol% $H_2$ - 95 vol% Ar; heating rate 20 deg·min$^{-1}$; gas flow 60 ml ·min$^{-1}$

There has been some discussions about the final temperature of the reduction experiment. Some authors have proposed 700°C as final temperature because above this Cu would evaporate [14], others [3, 4, 15, 16] determine the oxygen content at temperatures above 900°C because there is a final reduction step from 800°C.

As the reduction curve of CuO showed no weight loss above 700°C (Fig. 4) and the FTIR spectrum of the gases released by the reduction of $YBa_2Cu_4O_8$ still showed $H_2O$ bands above 800°C, the 124 product was heated to 950°C and the temperature kept constant for one hour.

A typical reduction curve is shown in Fig. 5, from which it is seen that reduction of the 124 product occurs in at least four major steps.

The first step, between 200°–450°C, can be further divided as DTG shows. To obtain information on the intermediate products, XRD and iodometric titration experiments were carried out on samples heated to between 25°–950°C and cooled to room temperature in $H_2$/Ar. XRD spectra of these samples were obtained in air. Iodometric titration of a sample, heated to 300°C under $H_2$/Ar, demonstrated the presence of $Cu^{2+}$ and $Cu^+$, but no $Cu^{3+}$. The XRD spectrum of this sample did not show peaks for metallic copper. This result is in agreement with previous findings for the $YBa_2Cu_3O_7$ superconductor [4] where samples with different oxygen content proved the loss of oxygen from the CuO chains below 420°C with formation of $YBa_2Cu_3O_6$.

Iodometric titration could only be carried out on samples heated below 450°C because the samples heated above this temperature where only partially soluble. Thus information on the average copper valence of samples heated above 450°C

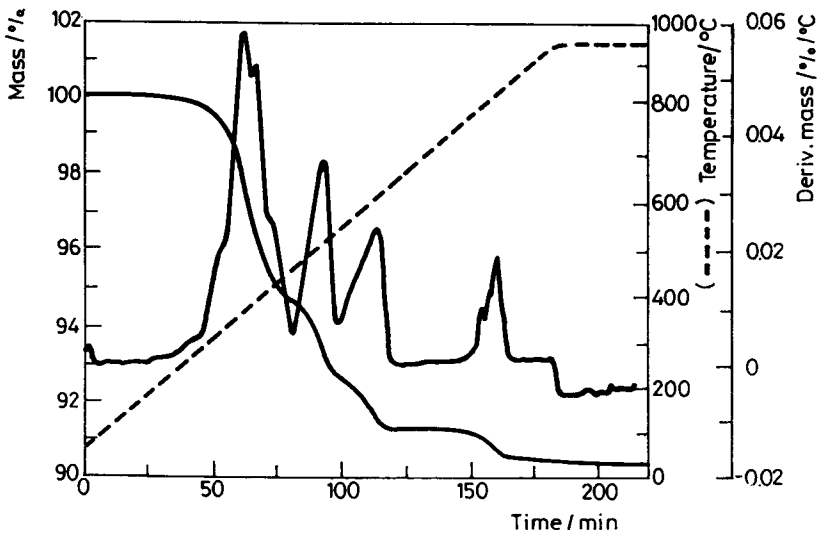could only be deduced from the weight percentages received from the TG experiments.



**Fig. 5** Reduction of 49.047 mg $YBa_2Cu_4O_8$ in 5 vol% $H_2$ –95 vol% Ar; heating rate: 5 $deg \cdot min^{-1}$; gas flow: 60 ml $\cdot min^{-1}$

A weight percentage of 94.60% at 450°C corresponds to the overall formula $YBa_2Cu_4O_{5.5}$, or an average copper valence of one. At this point, peaks for $Y_2O_3$, $Cu_2O$ and $BaCO_3$ (due to $CO_2$ absorption of BaO) are recognizable in a complex XRD spectrum. The global reaction during the first step can be given as:

$$YBa_2Cu_4O_{8-x} + (2.5-x)H_2 \rightarrow 0.5Y_2O_3 + 2BaO + 2Cu_2O + (2.5-x)H_2O$$
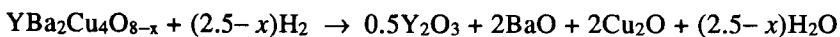
At 550°C the overall formula, calculated from the weight percentage, can be rewritten as $YBa_2Cu_4O_{4.7}$, which means that besides $Cu^+$ metallic copper also has to be present. XRD proves that the following reactions occur:

$$Cu_2O + H_2 \rightarrow 2Cu + H_2O$$

$$Y_2O_3 + BaO \rightarrow BaY_2O_4$$
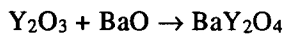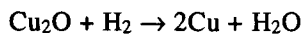
During the third reduction step (550°–630°C) the amount of metallic copper further increases: a $Cu^+$:Cu ratio of 1:3 corresponds to a weight percentage of 91.42%, or an overall formula of $YBa_2CuO_4$ and 3Cu.

The last reduction step starts at 775°C and results in a mixture of at least three compounds: Cu, $BaY_2O_4$ and $Ba_4Y_2O_7$ at 950°C.

The global reduction reaction can be written as:

$$YBa_2Cu_4O_{8-x} + (4.5-x)H_2 \rightarrow YBa_2O_{3.5} + 4Cu + (4.5-x)H_2O$$
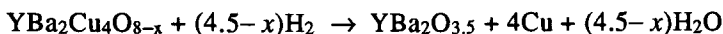
($YBa_2O_{3.5}$ stands for a mixture of at least $BaY_2O_4$ and $Ba_4Y_2O_7$).

The end percentage of 90.37% is in good agreement with the theoretical weight loss of 9.65% corresponding to this global reaction.


## References

1  A. Vos, J. Mullens, J. Yperman, J. Vanhees, L. C. Van Poucke, T. Krekels, G. Van Tendeloo, F. Persijn, I. Van Driessche and S. Hoste, Superconductivity, Ed. Raveau *et al.*, Technology Transfer Series I.I.T.T.-I.C.M.A.S., Paris 1991, p. 85.

2  A. Vos. R. Carleer, J. Mullens, J. Yperman, J. Vanhees and L. C. Van Poucke, Eur. J. Solid State Inorg. Chem., 28 (1991) 657.

3  P. K. Gallagher, H. M. O'Bryan and G. S. Grader, Thermochim. Acta, 137 (1989) 373.

4  H. Vlaeminck, D. Depla and S. Hoste, Proceedings ISTEC, Tokyo 1991, in press.

5  P. Podhájecky and F. P. Dousek, Physica C, 173 (1991) 99.

6  J.-H. Chloy, D. Y. Jung, S. J. Kim, Q. Won Choi and G. Demazeau, Physica C, 185–189 (1991) 763.

7  D. C. Harris and T. A. Hewston, J. Solid State Chem., 64 (1987) 182.

8  D. C. Harris, M. E. Hills and T. A. Hewston, J. Chem. Educ., 64 (1987) 847.

9  J. Yperman, A. De Backer, J. Mullens and L. C. Van Poucke, Book of Abstracts, ESEAC, Noordwijkerhout 1992, p. 123.

10  J. Mullens, R. Carleer, G. Reggers, J. Yperman, J. Vanhees and L. C. Van Poucke, Proceedings NATAS, Boston 1990, p. 155.

11  J. Mullens, R. Carleer, G. Reggers, M. Ruysen, J. Yperman and L. C. Van Poucke, Bull. Soc. Chim. Belges, 101 (1992) 267.

12  K. Leroy, J. Mullens, J. Yperman, J. Vanhees and L. C. Van Poucke, Thermochim. Acta, 136 (1988) 343.

13  J. Mullens, A. Vos, R. Carleer, J. Yperman and L. C. Van Poucke, Thermochim. Acta, 207 (1992) 337.

14  E. M. Vogel, G. W. Hull and J. M. Tarascon, Materials Letters, 6 (1988) 269.

15  D. C. Harris and T. A. Hewston, J. Solid State Chem., 69 (1987) 182.

16  R. J. Cava, B. Batlogg, R. B. van Dover, D. W. Murphy, S. Sunskine, T. Siegrist, J. P. Remeika, E. A. Rietman, S. Zahurak and G. P. Espinosa, Phys. Rev. Letters, 58 (1987) 1676.

**Zusammenfassung** — Aus dem Oxalatpräkursor $Y_2(C_2O_4)_34BaC_2O_48CuC_2O_4 \cdot xH_2O$ wurde der 124 Supraleiter $YBa_2Cu_4O_8$ hergestellt. In Sauerstoff zersetzt sich der Präkursor bei 300°C in einem Schritt, in Argon nach und nach (300°–600°C). Die Stabilität des Supraleiters hängt stark von der Atmosphärenzusammensetzung ab: in Sauerstoff und in Luft gibt es bis 800C keinen bemerkenswerten Gewichtsverlust, während in einem Gemisch aus 1 % $O_2$ und 99 % $N_2$ die Zersetzung bei etwa 670°C beginnt, wobei CuO und $YBa_2Cu_3O_x$ mit $x$ gebildet wird. Die Reduktion von $YBa_2Cu_4O_8$ in einem 5%$H_2$-95%Ar-Gemisch erfolgt in mindestens vier Hauptschritten, wobei Produkte wie $Y_2O_3$, BaO, $Cu_2O$, Cu, $BaY_2O_4$ und $Ba_4Y_2O_7$ gebildet werden.