Journal of Thermal Analysis, Vol. 41 (1994) 995-1005

$Ba_2Cu_3O_{5+\delta}$ AS AN INTERMEDIATE PHASE DURING THE SYNTHESIS OF $YBa_2Cu_4O_8$

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(Received June 10, 1993)

Abstract

We propose a reaction model for the synthesis of $YBa_2Cu_4O_8$ under normal pressure conditions, which contains 4 partial reaction steps. In a first step bariumnitrate and copperoxide react to $Ba_2Cu_3O_{5+\delta}$. This substance will be formed for each mixtures Ba:Cu = 2:3...3:2. The following two partial reaction steps are connected to $Ba_2Cu_3O_{5+\delta}$, which reacts with Y_2O_3 and CuO to $YBa_2Cu_4O_8$ or decomposes to $BaCuO_2$ and CuO. In a last step parts of $BaCuO_2$ reacts with Y_2O_3 and CuO to $YBa_2Cu_4O_8$.

Keywords: reaction model for the synthesis, superconductors, $YBa_2Cu_4O_8$

Introduction

Ba–Cu–O-phases were obtained during the synthesis of $YBa_2Cu_4O_8$ (124) under normal oxygen partial pressure.

Zhang [1] published a phase diagram for the system BaO-CuO at air for temperatures above 730°C. The crystalline phases Ba_2CuO_{3+x} and $BaCuO_2$ occur in addition to BaO and CuO. Ba_2CuO_{3+x} exists with an oxygen excess of $0.09<x<0.45$. These substance has a rhombic structure at low temperatures and appears above 810°C in their tetragonal modification [2]. The melting point in air is about 920°C.

Kipka [3] gave a detailed structure description of the cubic $BaCuO_2$ (a = 1.82855 nm). $BaCuO_2$ is producible in air at temperatures between 750 and 1000°C. The melting point in air is in the range 1000–1016°C [4, 5]. The substance has a variable oxygen content [5, 6].

Several authors find out the existence of a phase with BaO:CuO < 1:1 at temperatures below 800°C. De Leeuw [7] described a substance with a composition 'near' $Ba_3Cu_5O_{8+x}$, but he was not able to produce it in a crystallographic

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pure form. Thompson [8] and Halasz [9] found the substance $Ba_2Cu_3O_{5+\delta}$. $Ba_2Cu_3O_{5+\delta}$ has a rhombic structure and exists in two modifications: modification 'low' with $x = 0.6...1.0$ and modification 'high'. Thompson [8] investigated the synthesis procedure and found, that an oxygen overpressure is necessary for synthesis of $Ba_2Cu_3O_{5+\delta}$. Furthermore he pointed out, that $Ba_2Cu_3O_{5+\delta}$ was earlier obtained, but not recognised, by Arjomand [6]. In that publication the substance was indicated as $BaCuO_{2+x}$ with $x = 0.50...0.63$.

In the present paper we describe experiments to point out the role of Ba–Cu-oxides during the synthesis of $YBa_2Cu_4O_8$ and we give a reaction model for the synthesis of $YBa_2Cu_4O_8$.

Results and discussion

Ba–Cu–O-system

Mixtures with relations between Ba:Cu = 2:3 and 3:2 were used for investigations.

Table 1 shows the reaction conditions for three experiments. The experiments 1 and 2 differ in composite relations of starting materials. X-ray investigations show that $Ba_2Cu_3O_{5+\delta}$ forms in both cases. Sample 1 is the monophase $Ba_2Cu_3O_{5+\delta}$. Figure 1a shows the X-ray diffraction patterns of sample 1. The surplus barium in sample 2 excretes as BaO_2. Thermogravimetric investigations show, that BaO_2 is thermodynamical stable under oxygen normal pressure at temperatures below 600°C. It will be reduced at higher temperatures to BaO.

Table 1 Starting temperatures, treatment conditions and reaction products of same sintering experiments in the system BaO–CuO

Cationrelation (Ba:Cu)	2:3	1:1	1:1
Starting materials	$Ba(NO_3)_2$	$Ba(NO_3)_2$	BaO_2
	CuO	CuO	$Cu(NO_3)_2 \cdot 3.7H_2O$
Temperature	580°C	580°C	580°C
Tempertime	24	24	24
Pressure	normal	normal	normal
Atmosphere	O_2	O_2	air
Result of X-ray analysis	$Ba_2Cu_3O_{5+\delta}$	$Ba_2Cu_3O_{5+\delta}$	$Ba_2Cu_3O_{5+\delta}$
	CuO (<3%)	BaO	$BaCO_3$
			CuO (< 3%)

The in [6] described starting materials and preparation conditions were used for synthesis of sample 3. The content of crystal water of $Cu(NO_3)_2$ was determined by thermogravimetry. The reaction product consists of $Ba_2Cu_3O_{5+\delta}$, $BaCO_3$ and small amounts of CuO. Our experiments confirm with the result of Thompson [8] that in [6] was not prepared $BaCuO_{2.5}$ but a mixture of $Ba_2Cu_3O_{5+\delta}$ and $BaCO_3$.

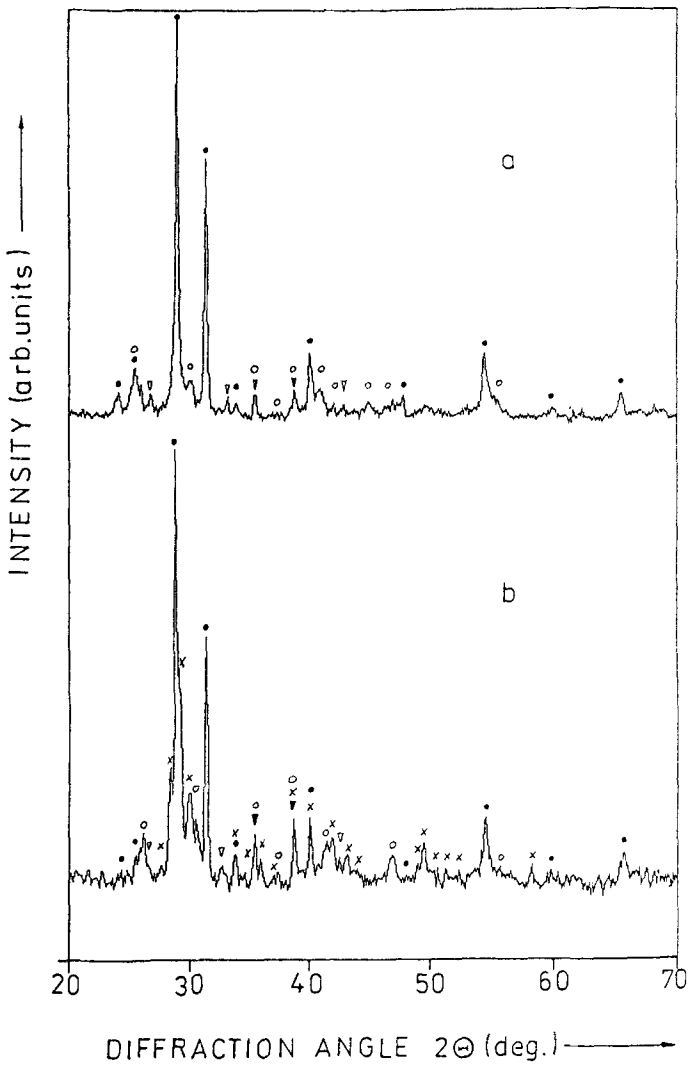

Fig. 1 X-ray diffraction patterns of $Ba_2Cu_3O_{5+\delta}$ sintered: a. in O_2 atmosphere, b. in N_2 atmosphere; symbols: • $Ba_2Cu_3O_{5+\delta}$ 'average' cell reflections; o $Ba_2Cu_3O_{5+\delta}$ satellite reflections, x $BaCuO_2$, ∇ BaO_2, ▼ CuO

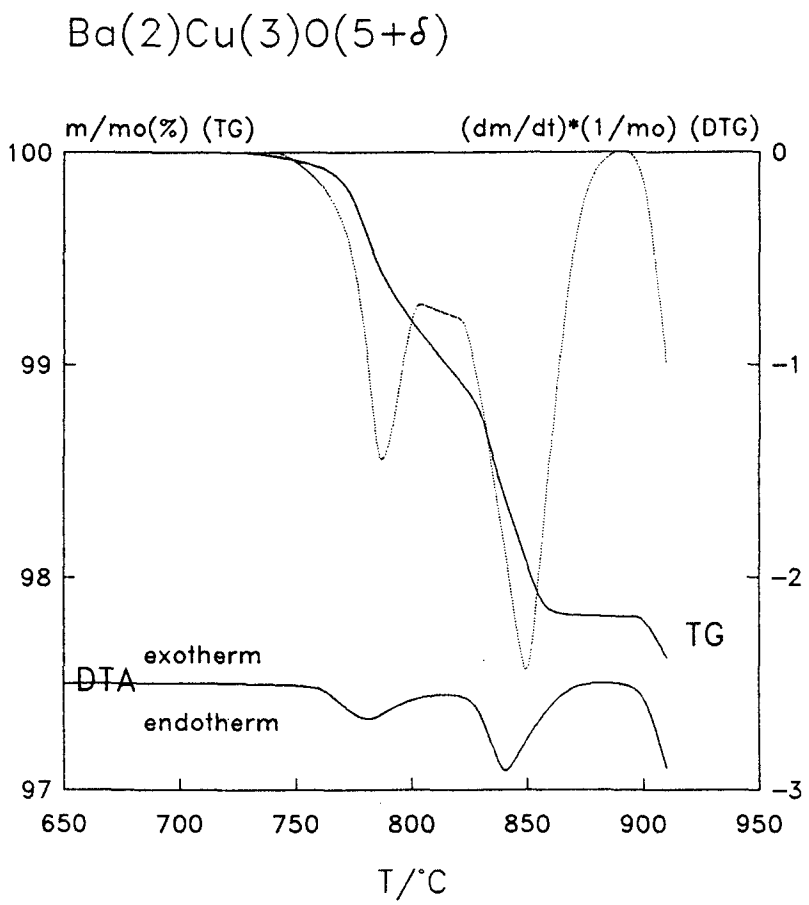

Fig. 2 TG, DTG and DTA curves of $Ba_2Cu_3O_{5+\delta}$ in air in the temperature interval 650–950°C; heating rate 5 deg·min^{-1}; atmosphere: air; m_o = 219.55 mg

Figure 2 shows a part of a TG, DTG and DTA curves of $Ba_2Cu_3O_{5+\delta}$ (sample 1) in air. There was no change in mass up to 735°C. Above this temperature two endotherm processes occur. The first one is the transformation of 'low' $Ba_2Cu_3O_{5+\delta}$ to 'high' $Ba_2Cu_3O_{5+\delta}$ which connected with a decrease of oxygen content. The second one is the reaction to $BaCuO_2$ and CuO. The second process starts before the first process was finished. So we can only give the equation for the whole reaction process between 730 and 865°C:

$$Ba_2Cu_3O_{5+\delta} \rightarrow 2BaCuO_2 + CuO + \frac{\delta}{2} O_2 \qquad (1)$$

δ was thermogravimetric determined with $\delta = 0.76 \pm 0.03$. This equation and the oxygen content of $Ba_2Cu_3O_{5+\delta}$ conforms with the results of X-ray investigations.

In further experiments $Ba(NO_3)_2$ and CuO were mixed in the composite relation Ba:Cu = 1:1 and heated in O_2, air or N_2 atmosphere. Figure 3 shows the heating thermogram of the oxygen treatment. From this thermogram and from X-ray investigations at room temperature of samples heated before in the thermobalance up to mass equilibrium we conclude the following reaction steps: $Ba(NO_3)_2$ starts to melt at 575°C. The following decrease of mass is connected with the decomposition of the Ba-containing melt. At 760°C the most part of starting components exists in form of $Ba_2Cu_3O_{5+\delta}$. At higher temperatures $Ba_2Cu_3O_{5+\delta}$ decomposes to $BaCuO_2$ and CuO, where the copperoxide reacts

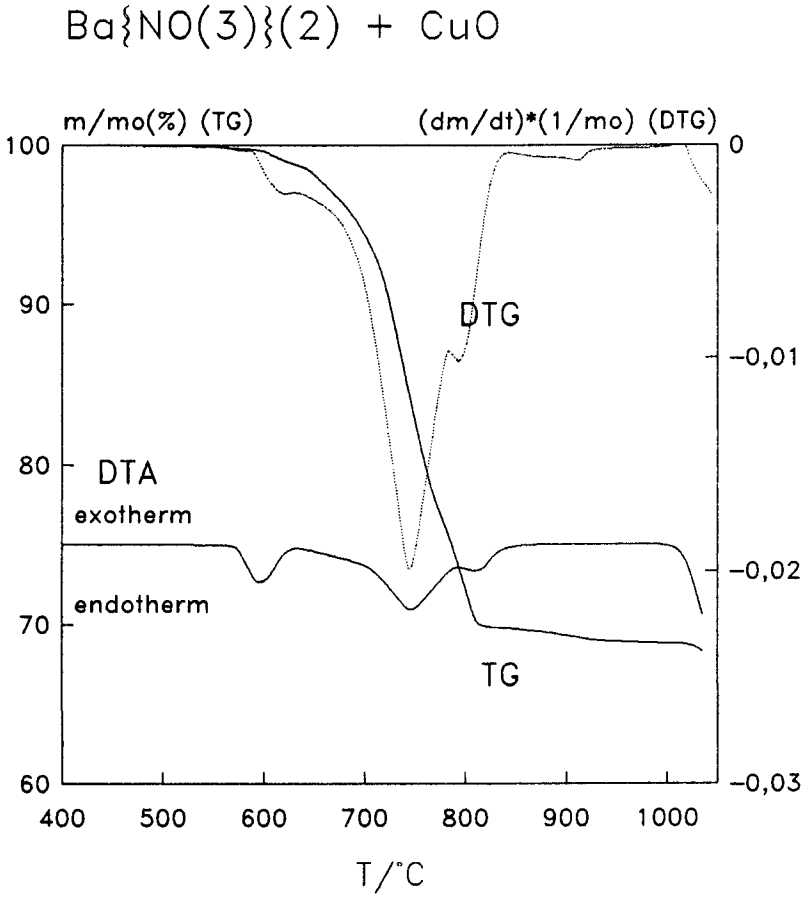

Fig. 3 TG, DTG and DTA curves of the mixture of $Ba(NO_3)_2$:CuO in the composition relation of 1:1 in oxygen; heating rate 5 deg·min^{-1}; atmosphere: oxygen; m_o = 287.75 mg

with the rest of the melt to $BaCuO_2$. After cooling down the sample from 950°C was found only $BaCuO_2$ by X-ray diffraction. The mass balance gives $BaCuO_x$ with $x = 1.98 \pm 0.06$.

When the treatment was performed in air a part of the intermediate existing BaO reacts with CO_2 of the air to $BaCO_3$. Under reducing atmosphere conditions (N_2) the decomposition of $Ba(NO_3)_2$ starts at lower temperature. At temperatures above 760°C a part of twovalent copper is reduced to monovalent copper and forms CuO_2. $BaCuO_2$ melts at 1010°C.

All experiments with composition relations in the region Ba:Cu = 3:2...2:3 show that the reaction product of heat treatment in the temperature range between the melting point of $Ba(NO_3)_2$ and 800°C has as main phase $Ba_2Cu_3O_{5+\delta}$. In difference with Thompson [8] we get monophase $Ba_2Cu_3O_{5+\delta}$ already under oxygen normal pressure conditions. In our experiments we used $Ba(NO_3)_2$. The decomposition of nitrogenoxid gives an excess of oxygen partial pressure during the preparation process; so $Ba_2Cu_3O_{5+\delta}$ was detected also during heat treatments of $Ba(NO_3)_2$ and CuO in nitrogen normal pressure atmosphere (Fig. 1b).

Thompson [8] pointed out that the structure of $Ba_2Cu_3O_{5+\delta}$ is incommensurately modulated. The XRD picture show reflections of the 'average' cell (•) and satellite reflections (o) due to the modulation. The position of the satellite reflections depends on the oxygen content; so it is possible to determine the oxygen content from the displacement of satellite reflections. The δ-value of $Ba_2Cu_3O_{5+\delta}$ prepared in oxygen atmosphere is 0.75; for the preparation in nitrogen atmosphere we get $\delta = 0.55$. The first value is in accordance with our thermogravimetric investigations.

Y–Ba–Cu–O-system

A mixture of oxides and nitrates with the composition relation (1/2) Y_2O_3:$Ba(NO_3)_2$:CuO = 1:2:4 was used to prepare quasiternary Y–Ba–Cu–O-phases. In the following the reaction processes in air and oxygen and the final reaction products were characterized.

Figure 4 shows the thermal curves for a 1-2-4-mixture on air in the temperature range 500–925°C. The whole reaction is characterized by the equation:

$$1/2\ Y_2O_3 + 2Ba\ (NO_3)_2 + 4CuO \rightarrow$$

$$YBa_2Cu_3O_{6+x} + CuO + 4NO_2 + \frac{(2.5-x)}{2}\ O_2$$

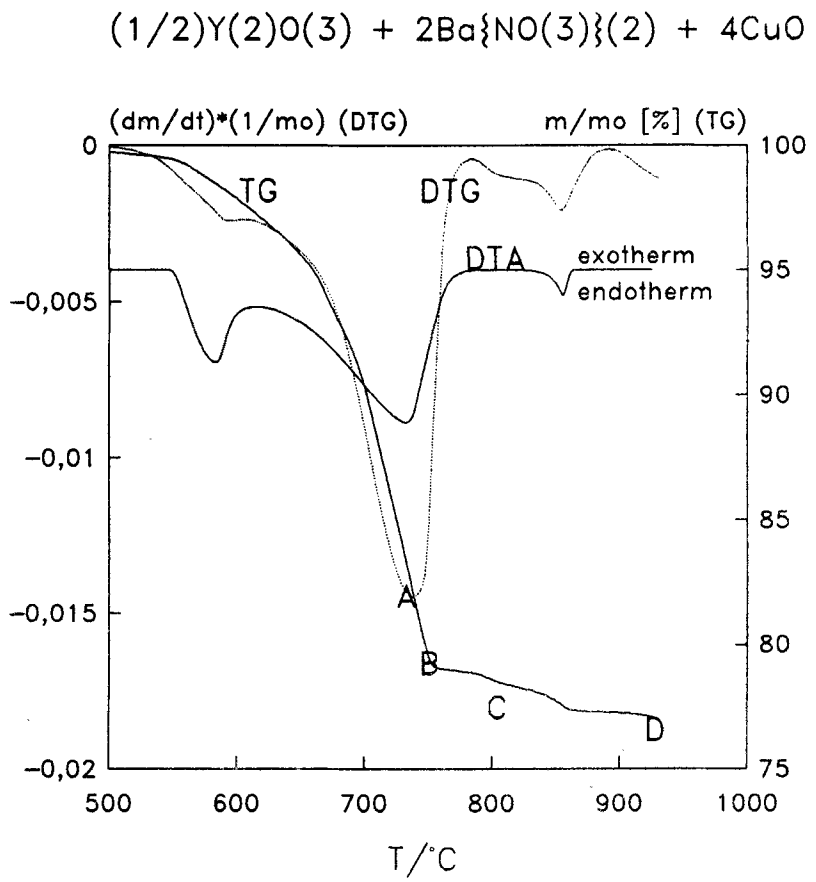

Fig. 4 TG, DTG and DTA curves of a 1-2-4-mixture in air in the temperature region 500–925°C. 4 Samples of this mixture were heated up to defined temperatures (corresponding to the points A, B, C and D) and annealed some hours at this temperatures to mass equilibr; heating rate 5 deg·min^{-1}; atmosphere: air; A–D: at this temperatures the samples were holded to constant mass

For detailed investigation of the reaction process samples of this mixture were heated up to defined temperatures and annealed some hours at this temperatures to mass equilibrium. These temperatures are shown in Fig. 4 by A, B, C and D. After cooling down the samples were characterized by X-ray diffraction. The results are summarized in Table 2.

The point A at 735°C corresponds with the maximum of the DTA-signal for the nitrate decomposition. The detected phases are: $Ba_2Cu_3O_{5+\delta}$, $BaCO_3$, CuO and Y_2O_3 and small amounts of a ternary Y–Ba–Cu–O-phase. A part of the bar-

iumoxide, formed during the nitrate decomposition, reacted with the CO_2 contained in air to $BaCO_3$.

Table 2 Conditions for thermal treatments of the sintering mixture $1/2Y_2O_3+2Ba(NO_3)_2$ + + 4CuO and the reaction products

Sample	Annealing-temperature	Atmosphere	Obtained phases
A	735°C	air	$Ba_2Cu_3O_{5+\delta}$, CuO, Y_2O_3, $BaCO_3$, 123/124
B	755°C	air	$YBa_2Cu_3O_{6+\delta}$, $Ba_2Cu_3O_{5+\delta}$, CuO, Y_2O_3
C	820°C	air	$YBa_2Cu_3O_{6+\delta}$, $BaCuO_2$, CuO, Y_2O_3, $Ba_2Cu_3O_{5+\delta}$, $BaCO_3$
D	925°C	air	$YBa_2Cu_3O_{6+\delta}$, CuO, Y_2BaCuO_5

The point B at 755°C corresponds with the conclusion of nitrate decomposition. The X-ray analysis found 4 substances $YBa_2Cu_3O_{6+x}$, $Ba_2Cu_3O_{5+\delta}$, CuO and Y_2O_3. The amount of $BaCO_3$ was at the detection limit. On the assumption that the oxygen contents are known from other experiments ($x = 0.47$, $\delta = 0.7$) the mass balance of the reaction up to 755°C is described by:

$$1/2Y_2O_3 + 2Ba(NO_3)_2 + 4CuO \rightarrow$$

$$1/3YBa_2Cu_3O_{6+x}+1/3Y_2O_3 + CuO+2/3Ba_2Cu_3O_{5+\delta} +$$

$$+ 4NO_2 + \frac{(6.5-x-2\delta)}{6} O_2$$

The third sample (point C) was heated up to 820°C and annealed to the mass equilibrium. The X-ray diffraction analysis prove $YBa_2Cu_3O_{6+x}$, $BaCuO_2$, CuO and Y_2O_3 and also small amounts of $Ba_2Cu_3O_{5+\delta}$ and $BaCO_3$. The content of $YBa_2Cu_3O_{6+x}$ is a little bit bigger in sample 3 as in sample 2. In this temperature region the decomposition of $Ba_2Cu_3O_{5+\delta}$ to $BaCuO_2$ and CuO is the main reaction process.

A fourth sample (point D) was heated up to 925°C and annealed to the mass equilibrium. The final mass of this specimen get the same value as of specimen 3. The sample 4 was cooled slowly down. The by X-ray diffraction obtained phases were $YBa_2Cu_3O_{7-x}$, CuO and very small amounts of Y_2BaCuO_5 (detection limit). This experiments show that it is impossible to produce in air

the 124-phase ($YBa_2Cu_4O_8$), even though the 124-phase own the smaller free energy at the corresponding temperatures than the 123-phase.

Figure 5 shows the TG, DTG and DTA curves for the treatment of the starting mixture (1/2) $Y_2O_3+2Ba(NO_3)_2+4CuO$ under normal pressure oxygen atmosphere. The sample was heated up to 720°C and holded to the mass equilibrium. The X-ray analysis and the obtained mass difference allow to conclude the reaction equation:

$$1/2Y_2O_3 + 2Ba(NO_3)_2 + 4CuO \rightarrow$$

$$1/2Y_2O_3 + CuO + Ba_2Cu_3O_{5+\delta} + 4NO_2 + \frac{(2-\delta)}{2} O_2$$

(1/2)Y(2)O(3) + 2Ba{NO(3)}(2) + 4CuO

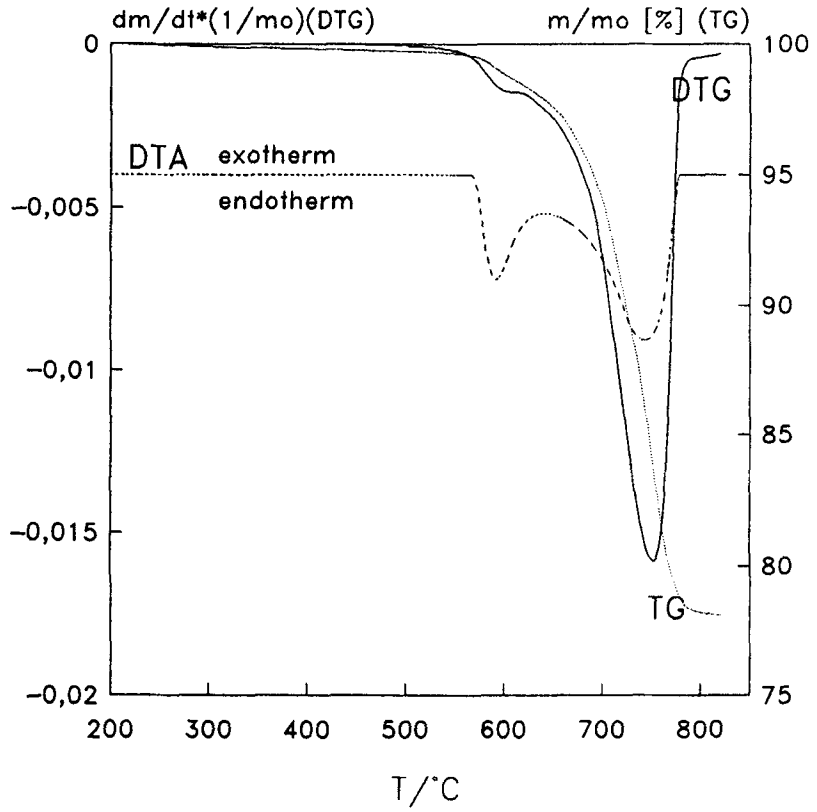

Fig. 5 TG, DTG and DTA curves of a 1-2-4-mixture under normal oxygen pressure conditions; heating rate 5 deg·min^{-1}; atmosphere: oxygen; m_o = 323.75 mg

In a further experiment a new sample of starting material 124-mixtures was annealed in oxygen atmosphere at 820°C for 3 h. After cooling down the annealing treatment was repeated several times with intermediate grinding the cooled powder and X-ray analysis. This experiment result in:

– The decrease of mass became smaller after each annealing, even the reaction process is not finished after 7 h annealing time.

– The content of $YBa_2Cu_4O_8$ increases.

– Y_2O_3 can not be detected after the second annealing.

– $Ba_2Cu_3O_{5+\delta}$ decomposes to $BaCuO_2$ and CuO.

Table 3 Reaction products of sintering the starting mixture $(1/2)Y_2O_3 + 2Ba(NO_3)_2 + 4CuO$ in oxygen atmosphere

Phases sample	$YBa_2Cu_4O_8$	CuO	Y_2O_3	$Ba_2Cu_3O_{5+\delta}$	$BaCuO_2$
I (3h)	+++	+	+	++	–
II (3h+2h)	++++	+	–	+	+
III (3h+2h+2h+2h)	++++	+	–	–	+

After 8 h annealing time the product consists $YBa_2Cu_4O_8$ with very small amounts of $BaCuO_2$ and CuO. The superconducting temperature T_c amounts 80 K detected by a SOUID-Magnetometer. By magnetic measurements a very small amount of $YBa_2Cu_3O_{7-x}$ was found, which can not be detected by X-ray diffraction measurements. The thermogravimetric and X-ray diffraction measurements summarize in the following reaction model for synthesis process of $YBa_2Cu_4O_8$ under the described conditions above:

Reaction model

Starting materials: $1/2Y_2O_3 + 2Ba(NO_3)_2 + 4CuO$

$$2Ba(NO_3)_2 + 3CuO \rightarrow Ba_2Cu_3O_{5+\delta} + 4NO_2 + \left(\frac{2-\delta}{2}\right)O_2 \qquad \text{(a)}$$

$$1/3Ba_2Cu_3O_{5+\delta} + 1/3CuO + 1/6Y_2O_3 \rightarrow$$

$$1/3YBa_2Cu_4O_8 + \left(\frac{\delta - 0.5}{6}\right) O_2 \qquad \text{(b)}$$

$$2/3Ba_2Cu_3O_{5+\delta} \rightarrow 4/3BaCuO_2 + 2/3CuO + (\delta/3)O_2 \qquad \text{(c)}$$

$$1/3Y_2O_3 + 4/3BaCuO_2 + 4/3CuO + 1/6O_2 \rightarrow 2/3YBa_2Cu_4O_8 \qquad \text{(d)}$$

Products of reaction: $YBa_2Cu_4O_8 + 4NO_2 + 3/4O_2$

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Zusammenfassung — Vorgeschlagen wird ein aus vier Teilschritten bestehendes Reaktionsmodell zur Synthese von $YBa_2Cu_4O_8$ unter Normaldruckbedingungen. In einem ersten Schritt reagieren Bariumnitrat und Kupferoxid zu $Ba_2Cu_3O_{5+\delta}$. Dieser Stoff bildet sich für alle Gemische mit Ba:Cu = 2:3 .... 3:2. An den anschließenden zwei Teilreaktionen ist $Ba_2Cu_3O_{5+\delta}$ beteiligt und reagiert entweder mit Y_2O_3 und CuO zu $YBa_2Cu_4O_8$ oder zersetzt sich zu $BaCuO_2$ und CuO. In einem letzten Teilschritt reagieren Teile von $BaCuO_2$ mit Y_2O_3 und CuO zu $YBa_2Cu_4O_8$.