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Influence of calcium substitution on the formation and thermal stability of the $YBa_2Cu_4O_8$ superconductor

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Abstract

In order to study the influence of calcium substitution on the thermal stability and phase composition of the $YBa_2Cu_4O_8$ (Y-124) superconductor, precursor powders with composition $Y:Ca:Ba:Cu = 1-x:x:2:4$ ($x = 0.0$–0.1) are prepared using an acetate–tartrate based sol–gel method. The phase composition of the products formed after different stages of heat treatment at 800°C and under 1 atm oxygen pressure is examined by X-ray powder diffraction (XRD) and thermogravimetric analysis (TGA). We found that in the first stage of the heat treatment, among stable mixed oxides and carbonate, mainly $Y_2Ba_4Cu_7O_y$ (Y-247) and CuO are formed. Upon further heating Y-247 can react with CuO to form Y-124, but can also decompose into Y-124 and $YBa_2Cu_3O_{7-y}$ (Y-123). The formation of Y-123 is favoured by an increasing amount of calcium substitution. We also demonstrate that the TGA technique makes it possible to detect and distinguish between the presence of the Y-123, Y-124 and Y-247 when they are simultaneously present in a sample, while this is less obvious using only XRD.

Keywords: $YBa_2Cu_4O_8$ superconductor; X-ray powder diffraction; Thermogravimetric analysis; Calcium substitution

1. Introduction

Since the discovery of the $YBa_2Cu_3O_{7-y}$ (Y-123) superconductor by Wu et al. [1] two other members of the $Y_2Ba_4Cu_{6+n}O_{14+n\pm x}$ family, namely the $YBa_2Cu_4O_8$ (Y-124, $n = 2$) [2] and $Y_2Ba_4Cu_7O_{15-y}$ (Y-247, $n = 1$) [3] phases have been discovered.

Among layers of Ba–O, Y and Cu–O_2 planes perpendicular to the *c*-axis, the Y-123 structure contains single layers of Cu–O chains parallel to the *b*-axis between two barium oxide layers. The oxygen in the Cu–O chains is not stable and therefore the oxygen stoichiometry of the Y-123 phase is variable. Dependent on the oxygen content, the Y-123 phase can be [4] orthorhombic ($0 < y \leq 0.6$) and superconducting or tetragonal ($0.6 \leq y < 1$) and not superconducting. The transition temperature (T_c) in the orthorhombic region depends on the oxygen content. In the optimally doped phase ($y \approx 0.1$) T_c reaches a maximum value of 92 K. In an oxidizing atmosphere the tetragonal Y-123 phase starts to take up oxygen at about 200°C forming the orthorhombic Y-123 phase which reaches a maximum oxygen content at about 300–400°C. The orthorhombic Y-123 phase is stable up to 300°C à 400°C. From that temperature on it starts loosing the Cu–O chain oxygen until the tetragonal

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Y-123 phase is formed. This oxygen loss is reversible which means that upon cooling the sample will take up its oxygen to form the oxygen rich orthorhombic Y-123 phase again [5,6].

The structure of the Y-124 phase differs from that of the Y-123 phase by the replacement of the single layers of linear Cu–O by double layers of Cu–O chains with edge-sharing square planar coordination. An important consequence is that the copper coordination of the oxygen in the double chains increases and so does the stability of the oxygen in the double Cu–O chains [7]. As a result, the Y-124 has a stable oxygen content of eight oxygen atoms per unit cell and no orthorhombic to tetragonal phase transition. The stability of the oxygen in the double layers is proved by the fact that the Y-124 phase remains stable up to its decomposition temperature, above 800°C in an oxidizing atmosphere [8]. Then it decomposes into Y-123 and CuO with the release of oxygen. The critical temperature of the Y-124 phase is 81 K.

The Y-247 compound is not so widely studied as the Y-123 and the Y-124. Its structure consists of Y-123 and Y-124 blocks alternating along the *c*-axis. Since the Y-247 contains Y-123 unit cells, its oxygen content is also variable but to a lesser extent than for the Y-123. T_c values of Y-247 are reported from 14 K [9] to 92 K [10]. When the Y-247 phase is heated in an oxidizing atmosphere, it shows a reversible weight loss [11] between 570°C and 850°C due to the release of oxygen from the single Cu–O chains in the Y-123 blocks. At higher temperatures, about 880°C the Y-247 structure decomposes into Y-123, CuO and oxygen [12].

In 1989 Miyatake et al. discovered that the T_c of Y-124 increases to 90 K by 10% calcium doping for samples synthesized by the hot isostatic pressing technique [13]. This effect was also confirmed and examined for products synthesized under ambient pressure [14–19]. The enhancement of the T_c is explained by the increase in electron hole concentration per Cu–O unit due to the replacement of the trivalent Y^{3+} ion by a divalent Ca^{2+} ion [20–22].

When studying the effects of substitution on the properties of a superconductor, it is important that the phases that are responsible for the measured properties are identified as reliably as possible. For example, in the case of calcium substitution in the Y-124 phase it is necessary to prove that the enhancement of T_c is manifested by the substituted Y-124 phase and not due to the presence of substantial amounts of the 92 K Y-123 phase in the sample. In this work, we aim to study the formation of calcium substituted Y-124 from an acetate–tartrate gel precursor powder and its thermal stability. Therefore precursors for Y-124 phases with various amounts of calcium are prepared via an acetate–tartrate sol–gel technique. The phases that are formed during and after the different steps of the heat treatment are identified with X-ray powder diffraction (XRD) measurements. However, since the Y-123, Y-124 and Y-247 have very similar structures, we found that it is rather difficult to distinguish between their diffraction patterns, in particular when a mixture of the phases is present in a sample. We demonstrate that TGA can be used to identify the different YBaCu-based phases on the basis of their difference in thermal stability, even if the three phases are simultaneously present in the sample.

2. Experimental

The samples are prepared [14] by an acetate–tartrate sol–gel method developed previously for the synthesis of pure $YBa_2Cu_4O_8$ [23,24]. Gels with an elemental composition of $Y : Ca : Ba : Cu = 1 - x : x : 2 : 4$ and x ranging from 0 to 0.1 ($x = 0.00$, 0.025, 0.05, 0.075, 0.09), are prepared using stoichiometric amounts of Y_2O_3, $Cu(CH_3COO)_2{\cdot}H_2O$, $Ba(CH_3COO)_2$ and $Ca(CH_3COO)_2$, all of them analytical grade. First, Y_2O_3 is dissolved in 0.2 M acetic acid at 55–60°C. Consequently solutions of respectively 0.5 M $Ca(CH_3COO)_2$, 0.5 M $Ba(CH_3COO)_2$ and 0.5 M $Cu(CH_3COO)_2{\cdot}H_2O$ are added with intermediate stirring during several hours at the same temperature. A solution of tartaric acid in water is added to adjust the pH to 5.6, thus preventing crystallization of copper acetate during gelation [25]. The obtained solution is concentrated during about 8 h at 65°C in an open beaker and under continuous stirring until it becomes a clear blue gel. After further drying in an oven at 80°C a fine grained blue precursor powder is obtained. The precursor powder is then dried and calcined for 10 h at 800°C in flowing oxygen, reground in an agate mortar and heated for 20 h at 800°C. After another grinding, the powders are annealed during 40 h at 800°C in a flowing oxygen atmosphere. The entire heat treatment is carried out under atmospheric pressure. After each stage of the heat treatment (i.e., after a total heating time of 10, 30 and 70 h respectively), the products are slowly cooled to room temperature inside the furnace and samples are taken for characterization via XRD and TGA measurements. A schematic presentation of the processing steps involved in the preparation of the calcium-substituted Y-124 samples is shown in Fig. 1.

The stoichiometry of the precursor powders and the final products, dissolved in diluted nitric acid, is controlled by inductively coupled plasma atomic emission spectrometry (ICP-AES) on a Perkin-Elmer Optima 3000DV. XRD measurements are performed on a Siemens D-5000 powder diffractometer using Cu K_{α} radiation with a θ–2θ configuration. The phases that are present in the diffraction patterns are identified by comparison of the diffraction peaks with spectra from JCPDS-ICDD © 1991 and 1996 reference data. The thermal behavior of the samples is examined by means of a TA-Instruments HiRes 2950 thermogravimetric analyser in an oxidizing atmosphere (50 ml min^{-1}). Sample powders with a mass between 10 and 15 mg are spread onto platina sample pans. Before the measurement the samples are heated up to 250°C and cooled in order to avoid weight loss due to adsorbed gases or water. To obtain an as good as possible separation between the different decomposition steps, the TGA curves are recorded in the high resolution mode [26] using a maximum heating rate of 10°C min^{-1} from ambient to 900°C. After heating, the samples are slowly (maximum 10°C min^{-1}) cooled inside the apparatus and than the heating and cooling cycle is repeated.

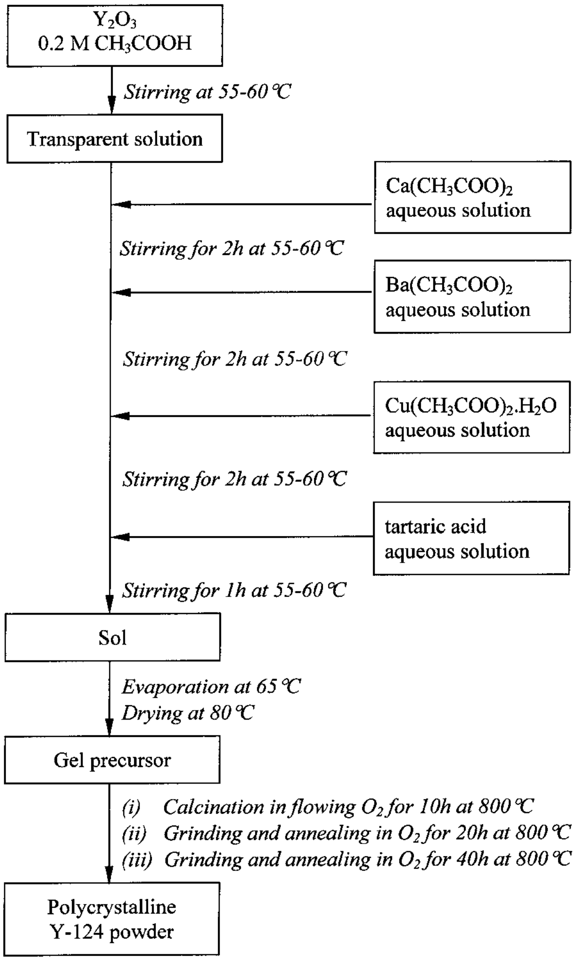

Fig. 1. Scheme of the steps involved in the sol–gel process used for the synthesis of the calcium-substituted $YBa_2Cu_4O_8$ superconductors.

3. Results and discussion

In Figs. 2–4 the XRD patterns of powders with calcium substitutions of $x = 0.0, 0.025, 0.075$ and 0.09 respectively are shown after 10 h (Fig. 2), 30 h (Fig. 3) and 70 h (Fig. 4) of total heat treatment at 800°C.

3.1. Results after 10 h heat treatment at 800°C

3.1.1. XRD measurements

After 10 h heat treatment the acetates have decomposed and oxidized into a mixture of Y_2O_3, $BaCO_3$, CuO and mixed oxides like $Y_2Ba_2O_5$ and also Y_2BaCuO_5 in the samples with higher calcium substitution. The phase that is predominantly present, i.e., with the most intense diffractions, has a perovskite structure. As was mentioned before, the greater part of X-ray diffractions of the Y-123, Y-124 and Y-247 phases coincide which makes them extremely difficult to distinguish on the basis of their XRD patterns alone. Fig. 5 shows a schematic representation of the XRD patterns of orthorhombic Y-123, Y-247 and Y-124. The tetragonal Y-123 phase is not likely to be present since the samples were slowly cooled in an oxygen

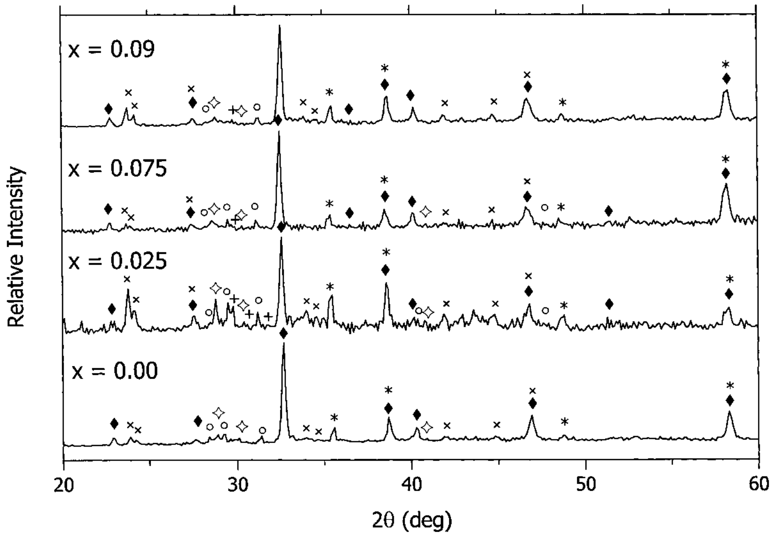

Fig. 2. XRD patterns of the acetate–tartrate precursors with different values of x after 10 h of heat treatment at 800°C in flowing oxygen at 1 atm ((◆) $YBa_2Cu_3O_{7-y}$ or $Y_2Ba_4Cu_7O_{15\pm y}$, (*) CuO, (o) Y_2O_3, (◇) $Y_2Ba_2O_5$, (×) $BaCO_3$, (+) Y_2BaCuO_5).

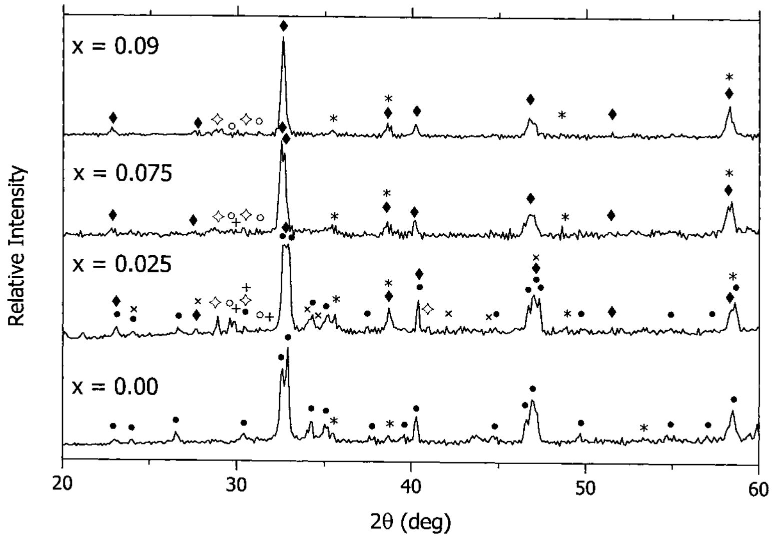

Fig. 3. XRD patterns of the acetate–tartrate precursors with different values of x after 30 h of heat treatment at 800°C in flowing oxygen at 1 atm ((●) $YBa_2Cu_4O_8$, (◆) $YBa_2Cu_3O_{7-y}$ or $Y_2Ba_4Cu_7O_{15\pm y}$, (*) CuO, (o) Y_2O_3, (◇) $Y_2Ba_2O_5$, (×) $BaCO_3$, (+) Y_2BaCuO_5).

flow. There is also no sign yet of the Y-124 phase, for the diffractions (113) and (108) at 2θ angles of 34.4° and 35.2°, typical for the Y-124 phase, are not present in the spectrum. The diffraction peaks of the perovskite phase agree most with those of the orthorhombic Y-123 phase or the Y-247 phase.

3.1.2. TGA measurements

In the TGA profiles an important weight loss starting at about 600°C is observed in all the samples after 10 h of calcination. As an example, the TGA profile of the calcium substituted sample with $x = 0.05$ is presented in Fig. 6. The weight loss at 600°C can be

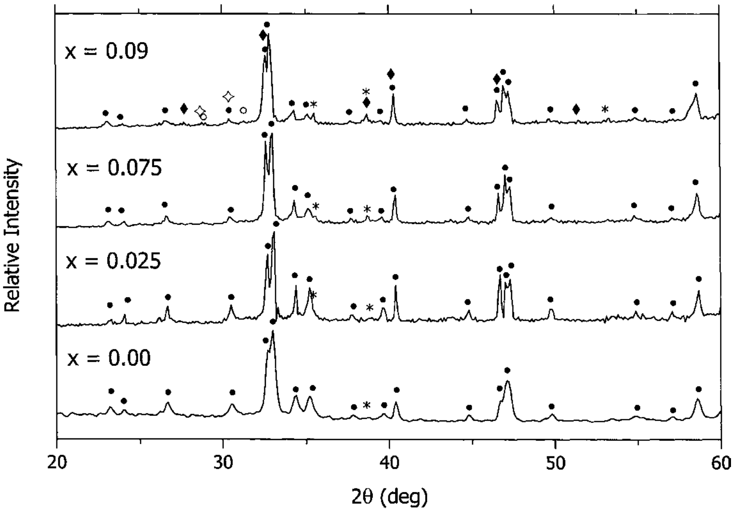

Fig. 4. XRD patterns of the acetate–tartrate precursors with different values of x after 70 h of heat treatment at 800°C in flowing oxygen at 1 atm ((●) $YBa_2Cu_4O_8$, (◆) $YBa_2Cu_3O_{7-y}$ or $Y_2Ba_4Cu_7O_{15\pm y}$, (*) CuO, (o) Y_2O_3, (◇) $Y_2Ba_2O_5$).

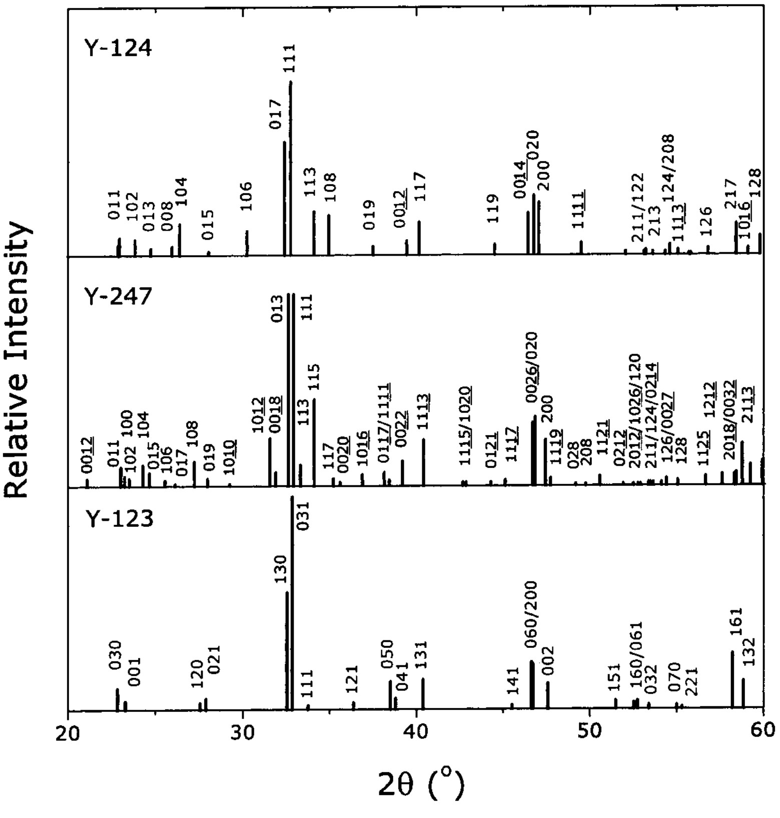

Fig. 5. Schematic presentation of the XRD patterns and Miller indices of Y-123, Y-247 en Y-124 phases from JCPDS-ICDD © 1991 and 1996 reference data.

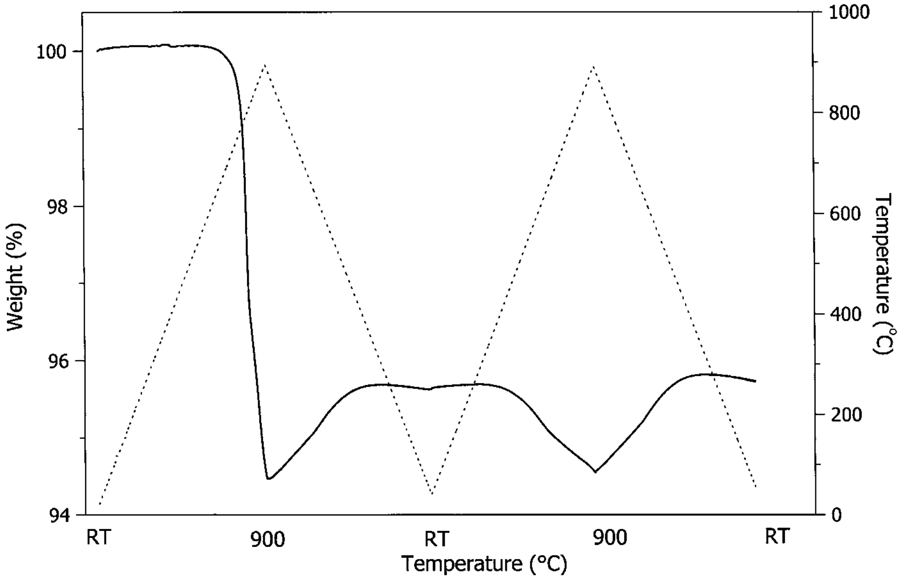

Fig. 6. TGA profile of an acetate–tartrate precursor with composition Y : Ca : Ba : Cu = 0.95 : 0.05 : 2.0 : 4.0 after 10 h heat treatment at 800°C in oxygen at 1 atm, recorded with a maximum heating rate of 10°C min^{-1} under 60 ml min^{-1} oxygen flow, (—) weight, (. . .) temperature. (RT = room temperature).

attributed to the Y-247 phase. At temperatures above 850°C, the Y-247 phase is known to decompose into the tetragonal Y-123 phase and copper oxide with the release of oxygen [12]. During cooling and reheating of the sample, the weight increases reversibly due to the oxygen uptake and release of the Y-123 phase.

3.2. Results after 30 h heat treatment at 800°C

3.2.1. XRD measurements

After 30 h of heat treatment at 800°C more differences can be observed in the XRD patterns depending on the calcium content of the sample. In the no calcium containing sample, already a substantial amount of Y-124 phase is formed, as can be seen in Fig. 3. Also in the sample with $x = 0.025$ (Fig. 3) diffraction peaks of the Y-124 phase start to develop. But, when more calcium is present in the sample, the Y-124 phase is not visible yet. In the XRD patterns of calcium containing samples we can see still, but to a lesser extent than after 10 h, various metal oxides, much less $BaCO_3$ and mainly the perovskite diffractions that can be attributed to either orthorhombic Y-123 or Y-247.

3.2.2. TGA measurements

Again, TGA measurements were performed to define which of the phases, Y-123, Y-124 or Y-247, is present in the 30 h treated powders. The TGA profile of the pure Y-124 sample shows a major weight loss at 800°C (Fig. 7), confirming the formation of mainly Y-124. As in the samples treated for 10 h, the TGA curves of the 30 h treated calcium containing samples (Fig. 8 shows the TGA profile of the $x = 0.09$ calcium substituted sample) show a rather important weight decrease at 600°C due to the Y-247 phase. The weight loss above 800°C is therefore mainly ascribed to the decomposition of Y-247. However, also a weight loss is observed at about 300°C, indicating that the orthorhombic Y-123 phase has been formed, which is hardly distinguishable in the XRD patterns. It seems therefore that the calcium substitution obstructs the formation of Y-124 during the heat treatment at 800°C but rather favours the formation of Y-123.

3.3. Results after 70 h heat treatment at 800°C

3.3.1. XRD measurements

The XRD patterns of the samples treated for 70 h at 800°C are shown in Fig. 4. In all the diffractograms,

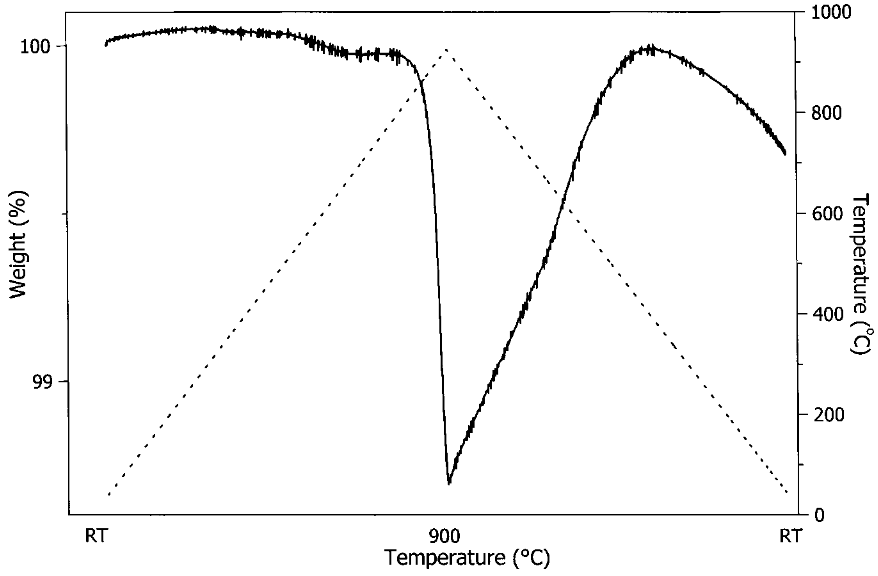

Fig. 7. TGA profile of a precursor with composition Y : Ca : Ba : Cu = 1.0 : 0.0 : 2.0 : 4.0 after 30 h heat treatment at 800°C in oxygen at 1 atm, recorded with a maximum heating rate of 10°C min^{-1} under 60 ml min^{-1} oxygen flow, (—) weight, (. . .) temperature.

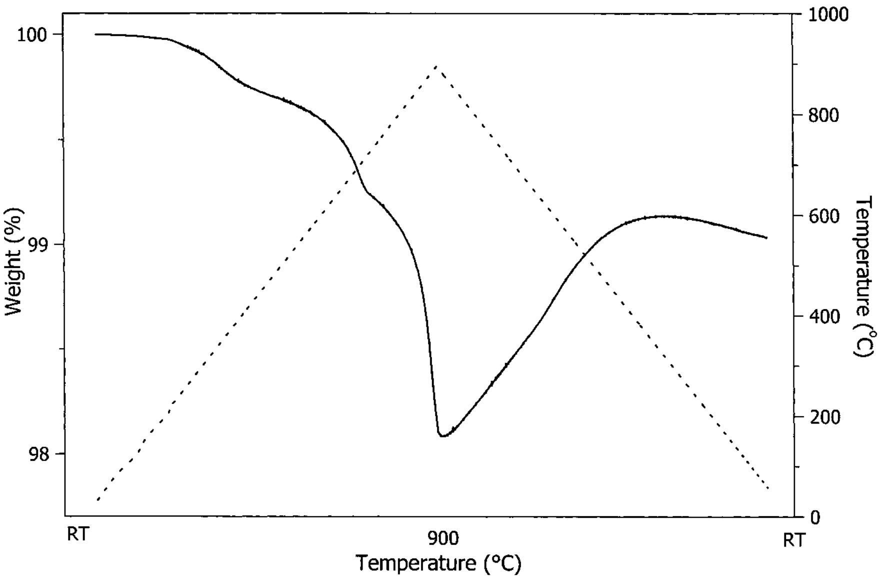

Fig. 8. TGA profile of a precursor with composition Y : Ca : Ba : Cu = 0.91 : 0.09 : 2.0 : 4.0 after 30 h heat treatment at 800°C in oxygen at 1 atm, recorded with a maximum heating rate of 10°C min^{-1} under 60 ml min^{-1} oxygen flow, (—) Weight, (. . .) temperature.

mainly the Y-124 phase can be seen. It is clear that as more calcium is introduced into the sample, more impurity phases have been formed besides the Y-124 phase. In the XRD pattern of the pure Y-124 sample as well as the calcium containing samples with x up to 0.075 only the Y-124 phase and some CuO

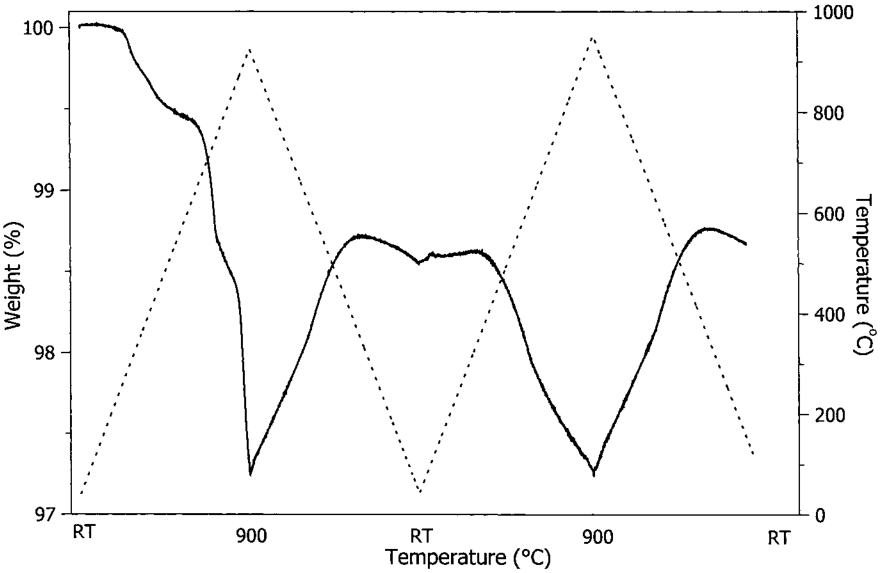

Fig. 9. TGA profile of a precursor with composition Y : Ca : Ba : Cu = 0.925 : 0.075 : 2.0 : 4.0 after 70 h heat treatment at 800°C in oxygen at 1 atm, recorded with a maximum heating rate of 10°C min^{-1} under 60 ml min^{-1} oxygen flow, (—) weight, (...) temperature.

impurity can be observed. The sample with $x = 0.09$ contains also other impurity phases like $Y_2Ba_2O_5$ and orthorhombic Y-123 or Y-247. These are the conclusions as they can be drawn from the XRD measurements. However, the TGA profiles of the 70 h treated samples provide more information.

3.3.2. TGA measurements

In all the thermograms, a major weight loss is present at about 800°C which, taking into account the XRD results, is attributed to the decomposition of Y-124 into Y-123 and CuO with the release of oxygen. But, even in the samples with $x = 0.025$–0.075 (Fig. 9) also a weight loss at 600°C occurs. This was not expected considering only the XRD patterns of the samples, but it indicates the presence of some Y-247 in the powders. In addition to the weight loss at 600°C, also a minor loss is observed at about 300°C in the samples containing calcium. The sample with the largest amount ($x = 0.09$) of calcium (Fig. 10) is characterized by a relatively large weight loss at 300°C, but no additional decrease of weight is observed at 600°C. It can be concluded therefore that this sample contains Y-124 and some Y-123, but no or almost no Y-247.

4. Discussion

Taking into account all the above described observations, one can propose the following reactions to happen during the heat treatment of acetate–tartrate gel precursors for calcium substituted Y-124 phases.

During the calcination of the precursor powder (first 10 h at 800°C) the Y-247 phase is formed besides stable oxides and barium carbonate. In this stage of the heat treatment, no much differences exist whether calcium is present in the precursor or not. The formation of Y-247 proceeds upon further heat treatment, which makes the presence of stable oxides and barium carbonate decrease. The Y-247 in turn reacts further in two possible ways: It can combine with CuO to form the Y-124 phase (Eq. (1)):

$$Y_2Ba_4Cu_7O_{15-x} + CuO \xrightarrow{O_2} 2YBa_2Cu_4O_8 \quad (1)$$

This is what, we think, predominantly happens in the samples without substitution or with low calcium content. On the other hand, Y-247 could also transform into Y-124 and Y-123 (Eq. (2)):

$$Y_2Ba_4Cu_7O_{15-x} \xrightarrow{O_2} YBa_2Cu_4O_8 + YBa_2Cu_3O_{7-y} \quad (2)$$

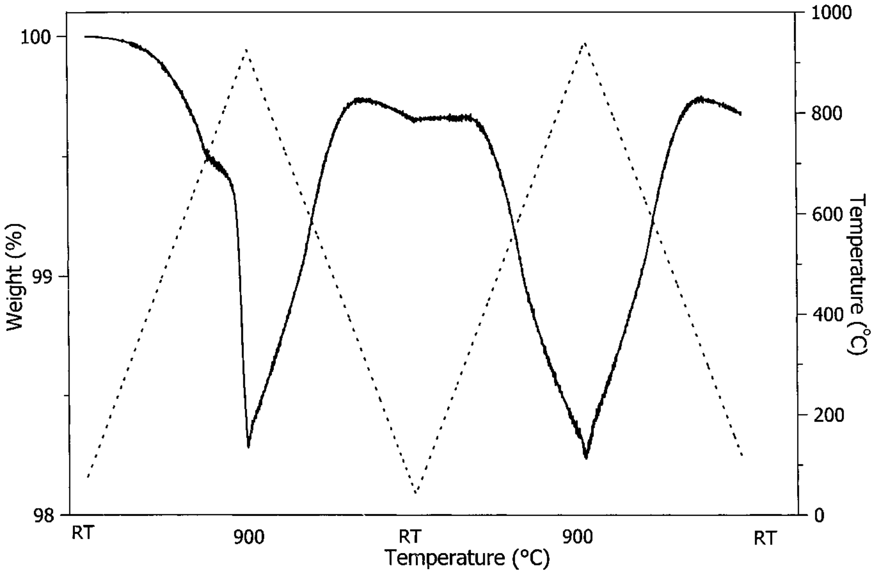

Fig. 10. TGA profile of a precursor with composition Y : Ca : Ba : Cu = 0.91 : 0.09 : 2 : 4 after 70 h heat treatment at 800°C in oxygen at 1 atm, recorded with a maximum heating rate of 10°C min^{-1} under 60 ml min^{-1} oxygen flow, (—) weight, (...) temperature.

The presence of calcium seems to favour the second reaction rather than the first (Eq. (1)) since the sample without calcium has after 30 h heat treatment already turned into almost pure Y-124 while in the samples with more calcium the Y-123 and Y-247 phases are detected rather than the Y-124.

The results of the TGA measurements after 70 h at 800°C confirm our supposition: The calcium substituted sample with $x = 0.09$ consists of mainly Y-123 and Y-124, the reaction products of (Eq. (2)). The samples with less calcium still contain Y-247 besides Y-123 and Y-124. The sample without calcium has undergone mainly the first reaction (Eq. (1)) since it contains only Y-124 and not Y-123 neither Y-247.

5. Conclusions

XRD is a very appropriate method to identify almost all the phases present in heat treated precursors for YBaCu-based superconductors. However, because of their structural similarity, the diffraction patterns of Y-123, Y-124 and Y-247 are hardly distinguishable, particularly when they are simultaneously present in a sample. Using TGA it is possible to identify Y-123, Y-124 and Y-247 individually on the basis of their different thermal stability, even if they are simultaneously present in a sample.

The combination of XRD and TGA data allows us to conclude that the formation of Y-124 and calcium substituted Y-124 from the acetate–tartrate gel precursor happens as follows: After the thermal decomposition of the acetate and tartrate ligands of the precursor, first, the Y-247 phase is formed, besides some thermally stable oxides and barium carbonate. In turn, the Y-247 phase can react with CuO to form Y-124. This is (possibly) what happens in the unsubstituted Y-124. But Y-247 could also decompose into Y-124 and Y-123, which is orthorhombic after cooling. It seems that the calcium substitution favours the second possibility, the formation of Y-123 and Y-124, rather than the reaction of Y-247 with CuO resulting in the formation of Y-124. The formation at 800°C of calcium substituted Y-124 phases from acetate–tartrate gels therefore possibly needs a modified heat treatment.

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