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Thermoanalytical features of $YBa_2Cu_3O_{7-x}$

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Abstract

This paper presents thermoanalytical features (DTA and TG) for $YBa_2Cu_3O_{7-x}$. It was shown that deoxidation occurred from about 400°C for the pure substance and that at 1020°C it was decomposed peritectically, forming Y_2BaCuO_5, which then decomposed similarly at 1247°C to Y_2O_3. Both reactions were accompanied by endothermic effects and a jump-type decrease in weight. Occurrences of additional effects, especially different DTA and TG courses, were caused by the presence of strange phases. This inconvenience was mostly due to secondary reactions, for instance, if the stable tetragonal type was cooled slowly.

Keywords: Ceramic; DTA; HTS; Superconductor

1. Introduction

A ceramic superconductor with chemical composition $YBa_2Cu_3O_{7-x}$ belongs to the cuprate family, i.e. substances which do not exist naturally and must be produced artificially. The superconducting cuprates are complex non-stoichiometric oxides with a perovskite-related structure. The first reports of their synthesis are about 150 years old [1]. Yet only in 1986 was a superconductive representative found at about 30 K [2]. One year later a high temperature superconductor of composition $YBa_2Cu_3O_{7-x}$ was synthesized, named 123, the ratio of the Y:Ba:Cu atoms [3]. This compound ($T_c = 90$ K) is currently treated as a model substance in

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superconductivity. In general, superconductive cuprates are characterized by oxygen non-stoichiometry and structural defects. The first simple cuprates were synthesized by means of a wet method, by oxidizing bivalent copper to trivalent copper in a strongly alkaline medium; therefore the sediments obtained contained water of crystallization [1]. At present, complex superconductive cuprates are made by the solid state reaction of oxide mixtures. The reactions between the initial oxides in the formation of cuprates can be observed by means of thermal analysis. Numerous experimental tests have analysed not only the synthesis of cuprates but also the conditions of their stability. Applying the DTA/TG technique, the oxygenation kinetics of cuprates [4,5] has been analysed, and the temperatures of melting and thermal decomposition [6,7] have been determined together with the oxygen content [8]. By means of such investigations the thermoanalytical characterization was also obtained, which may be used as the basis for the identification of, for example, minerals [9]. Such a thermoanalytical characterization in the preparation of cuprates is especially useful for determining their quality. Numerous literature references [10-16] contain valuable information concerning these materials which must be, however, critically evaluated. The courses of the TG and DTA curves for $YBa_2Cu_3O_{7-x}$ presented in the literature differ from one another. This is usually caused by impurity phases. The numerous endothermic peaks occurring in the temperature range 900-1100°C are, on the one hand, due to impure material and, on the other, caused by the instability of $YBa_2Cu_3O_{7-x}$. There is a lot of information in the literature on the origin and occurrence of respective phases in the system $YO_{1.5}$-BaO-CuO. It was, for instance, observed experimentally that the "blue phase" ($Y_2Cu_2O_5$) was the first stable intermediate phase, followed by the "green" phase (Y_2BaCuO_5) [10]. The decomposition of $BaCO_3$ is accelerated by reactions with other components [11] whereas $BaCuO_2$ was found in intermediate products [8,12]. The most important fact, however, is that the orthorhombic superconducting pure phase of $YBa_2Cu_3O_{7-x}$ is metastable.

Only the tetragonal non-superconducting phase is thermodynamically stable, although only at high temperatures. In air atmosphere, the stability area of $YBa_2Cu_3O_{7-x}$ is between about 850 and 1020°C [18]. The slow cooling of the preparation usually synthesized at 950°C leads to its partial oxidation and pollution by the green phase [18] or also by the blue phase (in the presence of CO_2) [19]. Only a very fast cooling from about 950°C to about 500°C of the tetragonal phase of $YBa_2Cu_3O_{7-x}$ and its subsequent saturation with oxygen, e.g. at 450°C (oxidation reaction) [4], can prevent the separation of these colourful impurities. However, it was observed that some preparations of $YBa_2Cu_3O_{7-x}$ are already decomposed above about 800°C and therefore $BaCuO_2$ [20] was found in the products. Metals like Al and Fe introduced during preparation, or CO_2 adsorbed on the sample surface, can continue to react and partially replace copper in the crystal lattice [21]. In this way a surplus of copper oxide is formed and the structure is changed from orthorhombic to pseudo-tetragonal [22]. When the amounts of such impurities grow, other complex oxides appear, for instance aluminates, ferrites [23], or barium carbonate. The influence of such impurities as CO_2 on $YBa_2Cu_3O_{7-x}$ is accelerated by the presence of moisture which is known as a process of ageing of samples [24]. From differential thermal and thermogravimetric analyses of cuprates, the precise thermal characterization of these compounds has been attempted. To do so, we have considered the results obtained for several of our preparations and compared them with other preparations of $YBa_2Cu_3O_{7-x}$.

2. Materials

The investigations were performed on $YBa_2Cu_3O_{7-x}$ preparations, both synthesized according to generally known techniques and also of commercial origin (Solvay, Fluka and Hoechst). $YBa_2Cu_3O_{7-x}$ was prepared by means of solid state reactions between metal oxides and carbonates in the temperature range 850–950°C. Proper stoichiometric mixtures were prepared both by means of the dry method (mixing and grinding) and by the solution routes (coprecipitation) [25]. A standard $YBa_2Cu_3O_{7-x}$ sample was synthesized by the dry method, according to the authors' own procedure [26].

The stoichiometric amounts of powders of Y_2O_3, $BaCO_3$ and CuO, which had been subjected to separate fine grinding (4 h in a ball mill), were ground again in the same mill for 2 h in the presence of acetone. The dried mixture was vacuum-pressed (7 ton thrust) into 500 mg tablets which were then calcined and sintered in four stages, i.e. 870, 930, 960 and 970°C for 10–15 h, and finally annealed at 470°C for 5 h.

The preparation of $YBa_2Cu_3O_{7-x}$ obtained in this way was characterized not only by high purity but also by high thermal stability. Other pure phases, Y_2BaCuO_5, $Y_2Cu_2O_5$ and $BaCuO_2$, were synthesized in the same way but with the application of different temperature ranges.

3. Equipment

All the preparations of $YBa_2Cu_3O_{7-x}$ were characterized by means of powder X-ray diffractometry (Stoe), thermoanalytical analysis (NETZSCH), and also optical microscopy in polarized light (Olympus). In addition, the oxygen content was determined by iodometric titration while the carbon impurities were analysed by the coulometric method [22]. The thermal investigations were carried out under the standard measurement conditions: heating rate, 10 K min^{-1}; weight, 100 mg; and alumina crucibles in synthetic air flowing at 150 ml min^{-1}.

4. Investigation results

4.1. *Evaluating the accuracy of the temperature measurements*

In order to test the accuracy of measurement of transformation temperatures by means of the Netzsch thermobalance (S-type thermoelements), recommended cali-

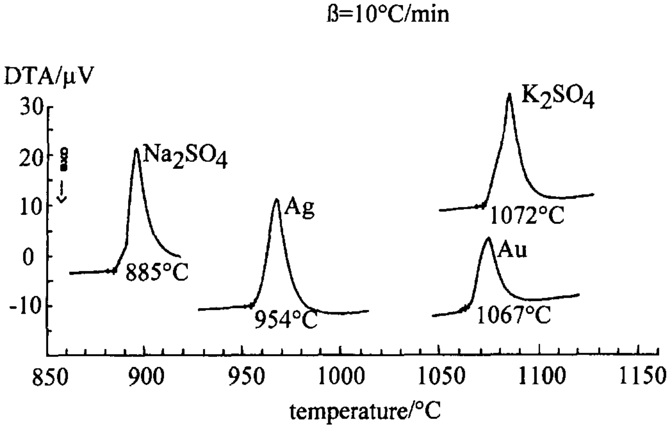


Fig. 1. DTA curves for calibration substances.

bration substances of known melting temperatures [27] were used. In the temperature range concerned, i.e. 800–1100°C, anhydrous sodium and potassium sulphates [28] were appropriate, as well as metallic silver and gold [27]. Satisfactory accuracy for the temperature measurement under the applied conditions was obtained, as illustrated in Fig. 1. The assignation between the temperatures determined experimentally as an extrapolated peak onset temperature and a true temperature is expressed by a difference of +2°C which is the overestimation of the measured temperatures.

4.2. Standard samples of $YBa_2Cu_3O_{7-x}$

Fig. 2 presents TG and DTA curves for two standard preparations in synthetic air, differing in oxygen content. The first was strongly saturated with oxygen ($x = 0.0566$) and, because of that, had an orthorhombic structure. This sample maintained its constant mass up to about 400°C before a slow decrease occurred. At 1020°C the mass decreased in a step (jump-type change) followed by a slow mass decrease between 1020 and 1245°C, and a second step at 1245°C (second jump-type change).

These two steps were accompanied by two endothermic effects which are a characteristic feature of $YBa_2Cu_3O_{7-x}$. According to the X-ray analysis (Fig. 3), it was observed that the perovskite-related structure of $YBa_2Cu_3O_{7-x}$ was stable in the temperature range up to 1020°C and only the oxygen content was changed, together with the crystallographic phase from orthorhombic to tetragonal. The orthorhombic symmetry of the initial sample can also be observed in the metallographic photographs (Fig. 4) in which twinned crystals of $YBa_2Cu_3O_{7-x}$ can be seen. The changes in sample masses during heating are connected with deoxidation and up to 1020°C it can be expressed by means of the reaction

$$YBa_2Cu_3O_{7-x} \rightarrow YBa_2Cu_3O_{7-y} + [(y-x)/2]O_2 \qquad (1)$$

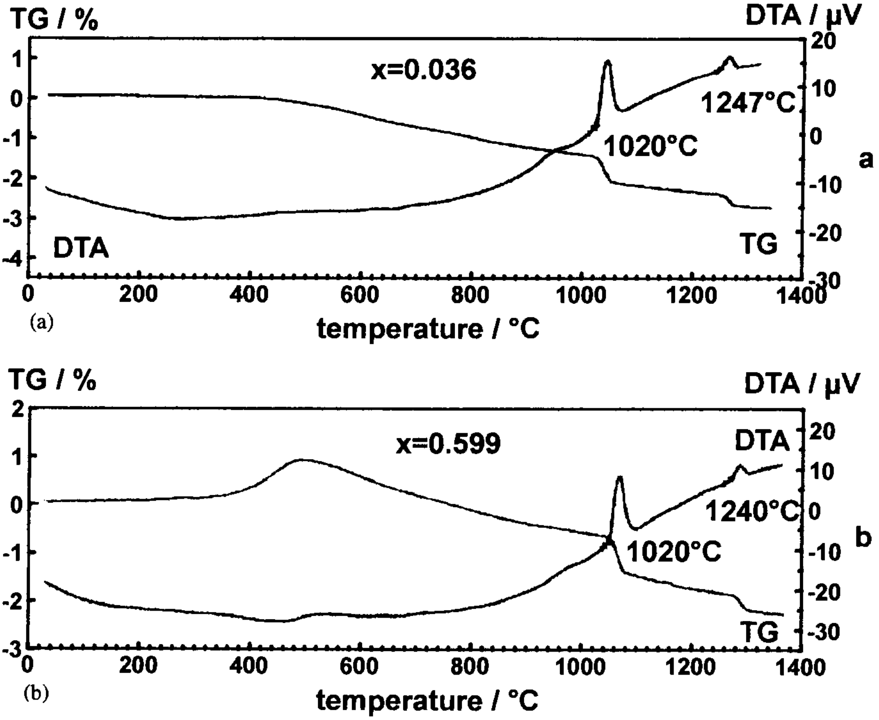


Fig. 2. Measured curves for standard $YBa_2Cu_3O_{7-x}$ samples (TG, mass change in %): (a) oxygen-rich sample; (b) oxygen-low sample.

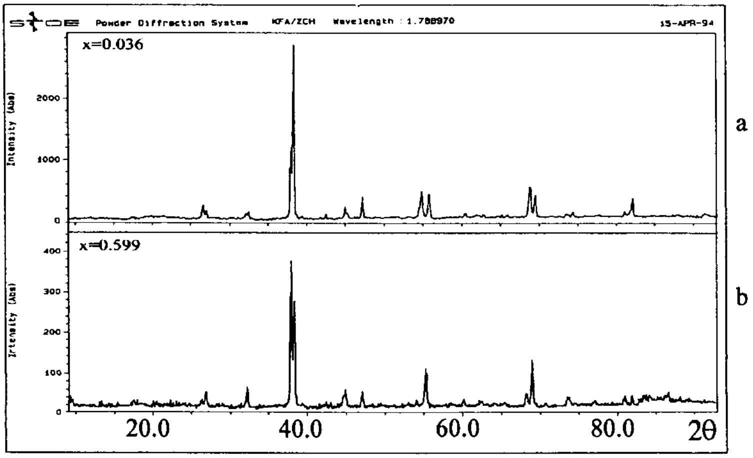


Fig. 3. X-ray photographs of standard $YBa_2Cu_3O_{7-x}$ sample: (a) orthorhombic structure for $x = 0.036$; (b) tetragonal structure for $x = 0.599$.

Fig. 4. Microstructures of the sintered sample of Fig. 2(a); original magnification × 1250.

At 1020°C, $YBa_2Cu_3O_{7-x}$ melts incongruently to Y_2BaCuO_5, i.e. a peritectic reaction takes place

$$YBa_2Cu_3O_{7-x} \rightarrow 0.5Y_2BaCuO_5 + [1.5BaO + (v/4)Cu_2O + [(10-2v)/4]CuO]_m + [(2-4y+v)/8]O_2 \qquad (2)$$

This results in the formation of a solid green phase and a liquid solution (m) of barium oxide and copper oxides in which only a small number of yttrium-containing compounds can be dissolved. A further decrease in mass between 1020 and 1245°C occurs as a result of a developing decomposition of CuO to Cu_2O ($v \rightarrow 5$). Finally, at 1245°C, the decomposition of Y_2BaCuO_5 to Y_2O_3 takes place but with the participation of a liquid phase

$$Y_2BaCuO_5 + L \rightarrow Y_2O_3 + L \qquad (3)$$

The pure green phase, Y_2BaCuO_5, is decomposed peritectically at 1275°C. All the mentioned reactions depend on the oxygen pressure in the atmosphere whereby the reaction temperature increases under growing pressure [6]. For a low-oxygen sample (Fig. 2b), the process of oxidation and weight increase takes place during its heating in air. Under these conditions, the above statement is true, as in the case of the oxygen-rich sample. But for $YBa_2Cu_3O_{7-x}$ impure substances, the thermoanalytical characterization changes.

Slightly changed characterizations were obtained for the typical $YBa_2Cu_3O_{7-x}$ preparations as compared to the standard samples. This is caused by the occurrence of small amounts of strange phases which occur primarily as impurities or can be formed by partial decomposition from preparations having lower thermal stability, for instance

$$YBa_2Cu_3O_{7-x} \rightarrow 0.5Y_2BaCuO_5 + 1.5BaCuO_2 + CuO + [(1-2x)/4]O_2 \quad (4)$$

In this way an additional endothermic effect at 910°C (Fig. 5) was observed in the DTA curve, a characteristic feature of the ternary eutectic of the Y_2BaCuO_5–$BaCuO_2$–CuO system. A certain amount of the liquid phase formed in this way decreases the temperature of the peritectic transformation (2) from 1020 to 990°C.

4.3. Samples containing impurities

For the other typical preparations, the possibility of the occurrence of impurities, connected usually with the incomplete reaction of the initial substances ($BaCO_3$, surplus of CuO), the remains of intermediate products, e.g. $BaCuO_2$, or caused by secondary reactions, for instance with the atmosphere (reactions with carbon dioxide and moisture) or with the crucible material, e.g. Al_2O_3, should be considered. Fig. 6 gathers typical examples of the $YBa_2Cu_3O_{7-x}$ preparations with the identified impurities (<5% of weight). The presence of $BaCO_3$ in a sample is manifested on the DTA curve by an additional endothermic peak at 805°C and larger weight losses on the TG curve, Fig. 6a. A surplus of CuO in a sample is manifested by an additional endothermic effect at 941°C, originating from the $YBa_2Cu_3O_{7-x}$–CuO eutectic, Fig. 6b. The presence of the green phase and copper oxide leads to the occurrence of several endothermic effects in the temperature range 932–1040°C, Fig. 6c. The occurrence of $BaCuO_2$ also decreases the temperature of reaction (2) while over 900°C a characteristic "ridge" appears, typical for $BaCuO_2$ contaminated by CO_2, Fig. 6d. Typical strange impurities are due to the

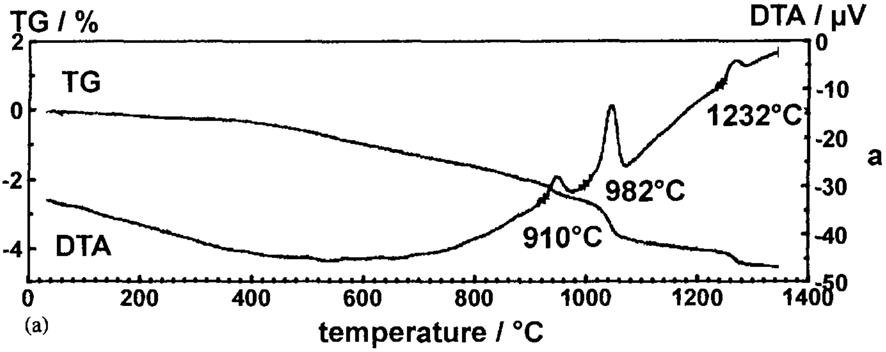


Fig. 5(a).

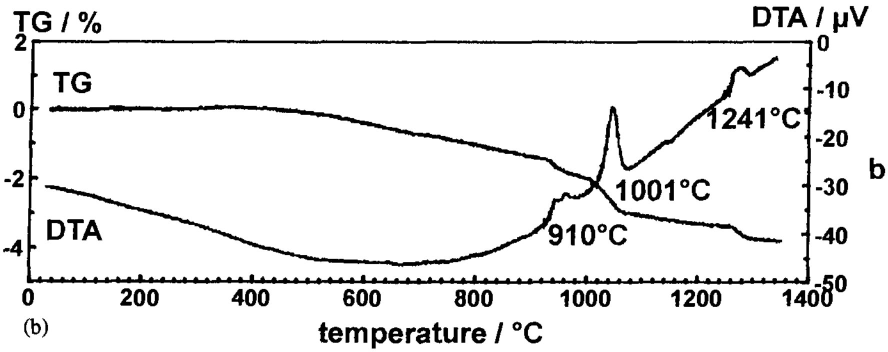


Fig. 5. Measured curves of an "X-ray pure" sample of $YBa_2Cu_3O_{7-x}$ revealing additional effects (TG, mass change in %): (a) Hoechist; (b) Fluka.

crucible material. Aluminium diffusing into the $YBa_2Cu_3O_{7-x}$ samples can partly replace copper and it also forms $BaAl_2O_4$ and CuO. This gives additional effects on the DTA curve, Fig. 6e. It can be added that all of the above reactions are connected with a step-like (jump type) weight change in the TG curve.

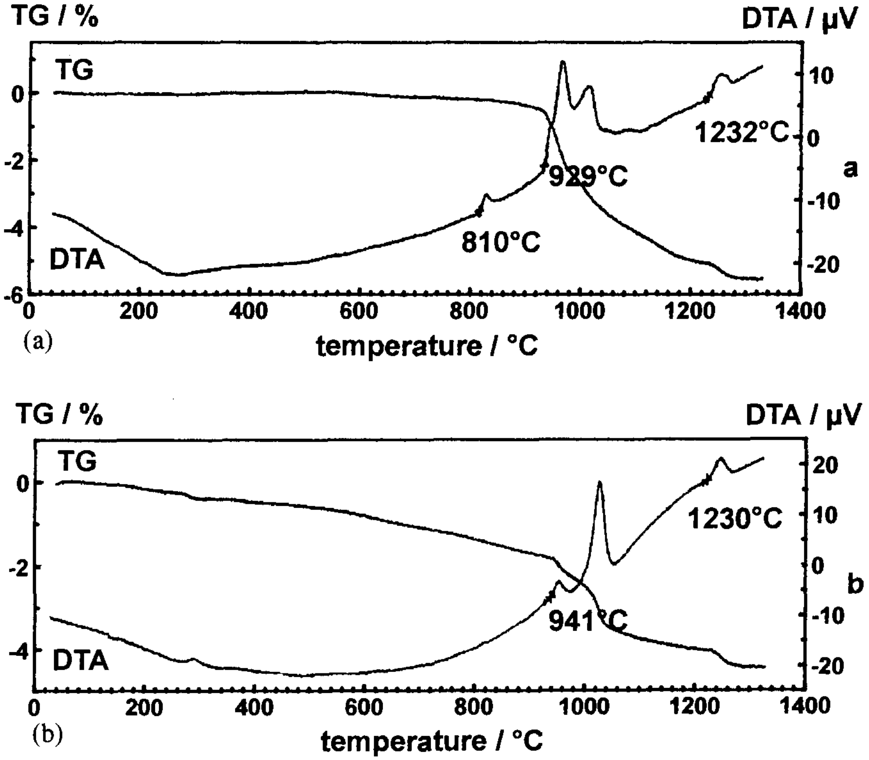
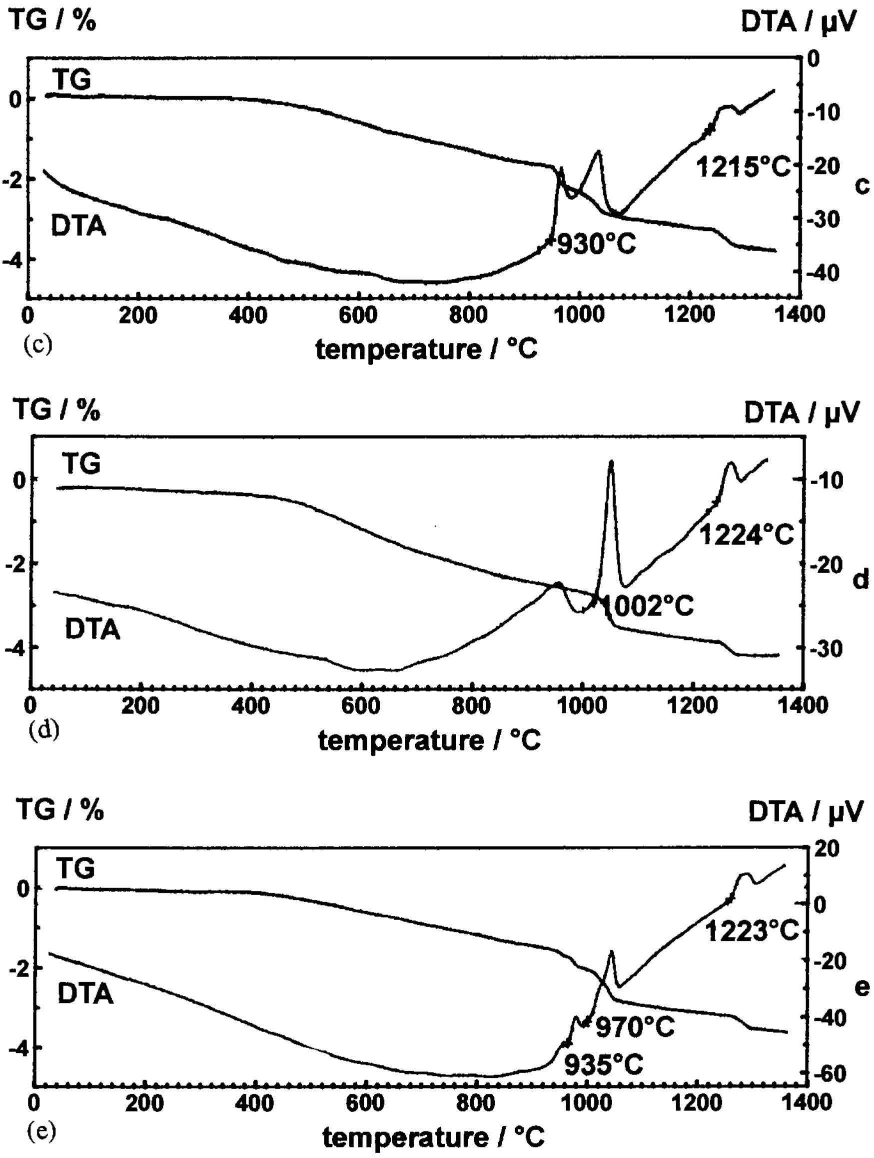


Fig. 6(a,b).



(c)

(d)

(e)

Fig. 6. Comparison of the DTA curves for the preparations with the identified impurities (TG, mass change in %): (a) with $BaCO_3$; (b) surplus of CuO; (c) with Y_2BaCuO_5 and CuO; (d) with $BaCuO_2$; (e) with Al_2O_3.

4.4. Supplementary investigations and discussion

For many preparations, however, it is not possible to determine all of the strange phases by means of the X-ray analysis. They are pure within the limits of X-ray analysis (called X-ray pure). In this case by means of the elementary analysis it is possible both to determine the amount of impurities (ppm range) and to control the molar ratio of the yttrium to barium and copper. The amount of carbon impurities can also determine the preparation quality. It has however been observed experimentally that thermal analysis helps to describe the purity of preparations and, especially, the presence of strange phases. Figs. 7, 8 and 9 collect the DTA results for mixtures of $YBa_2Cu_3O_{7-x}$ with other known substances that can occur in the Y–Ba–Cu–O system.

Temperature changes for the peritectic transformation (2) occur for $YBa_2Cu_3O_{7-x}$ samples with the addition of other phases. The presence of each

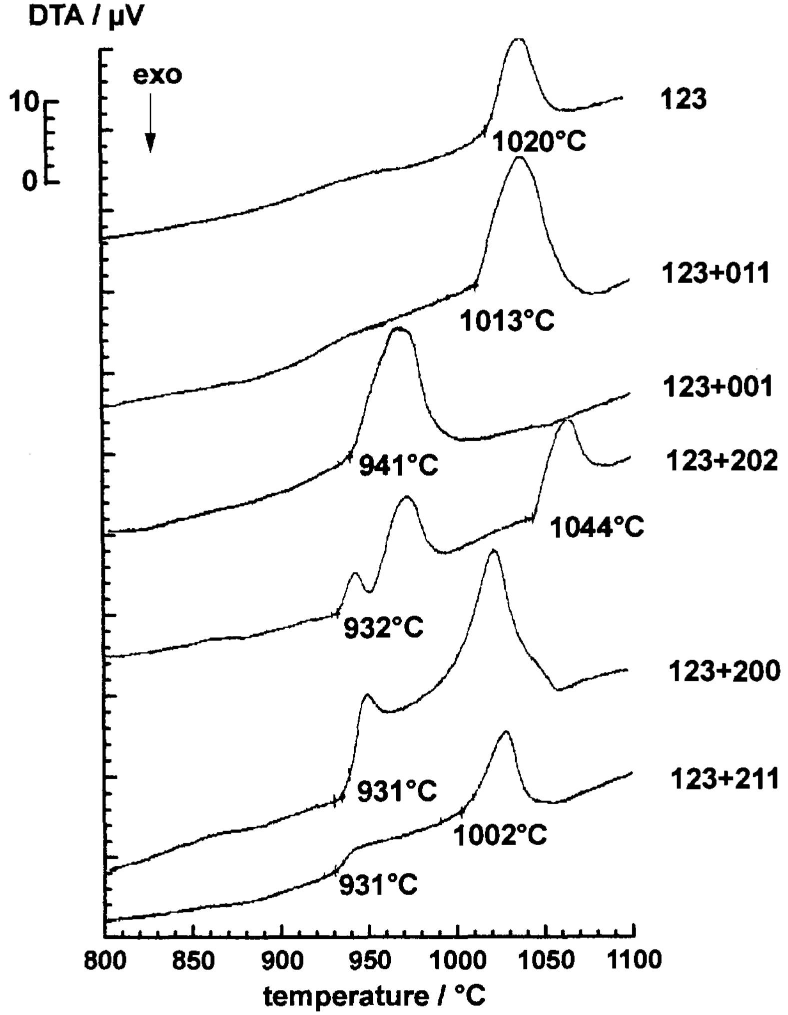


Fig. 7. The DTA curves for two-component mixtures of $YBa_2Cu_3O_{7-x}$.

addition changes the course of the DTA curve. Many of these effects are known as invariant points in the $YO_{1.5}$–BaO–CuO system [24]. The effects (123 + 202, Fig. 7; 123 + 211 + 202 and 123 + 211 + 001, Fig. 8; and the four-component mixtures, Fig. 9) were determined experimentally in the temperature range 932–939°C and could not be attributed to the known invariant points. This problem requires a separate treatment and investigation. It must also be remembered that $YBa_2Cu_3O_{7-x}$ is stable at high temperatures (Fig. 10) and during its slow cooling in air it enters the area of occurrence of strange phases, i.e. Y_2BaCuO_5, $BaCuO_2$ and

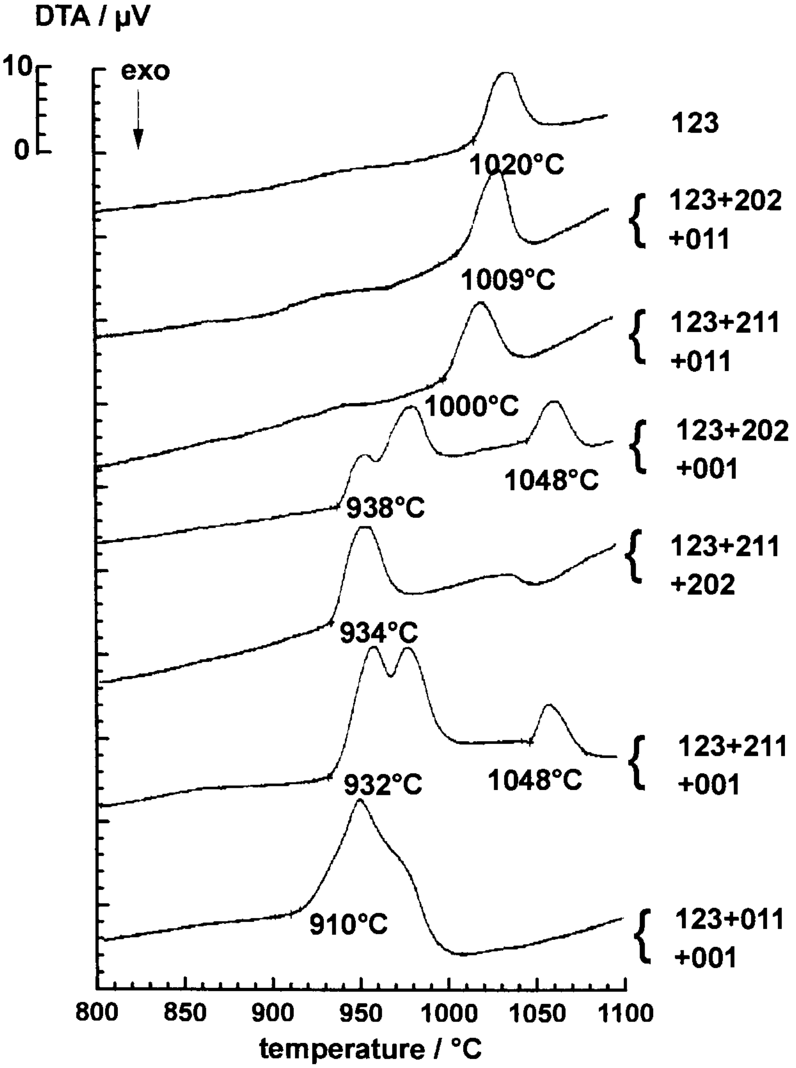


Fig. 8. The DTA curves for three-component mixtures of $YBa_2Cu_3O_{7-x}$.

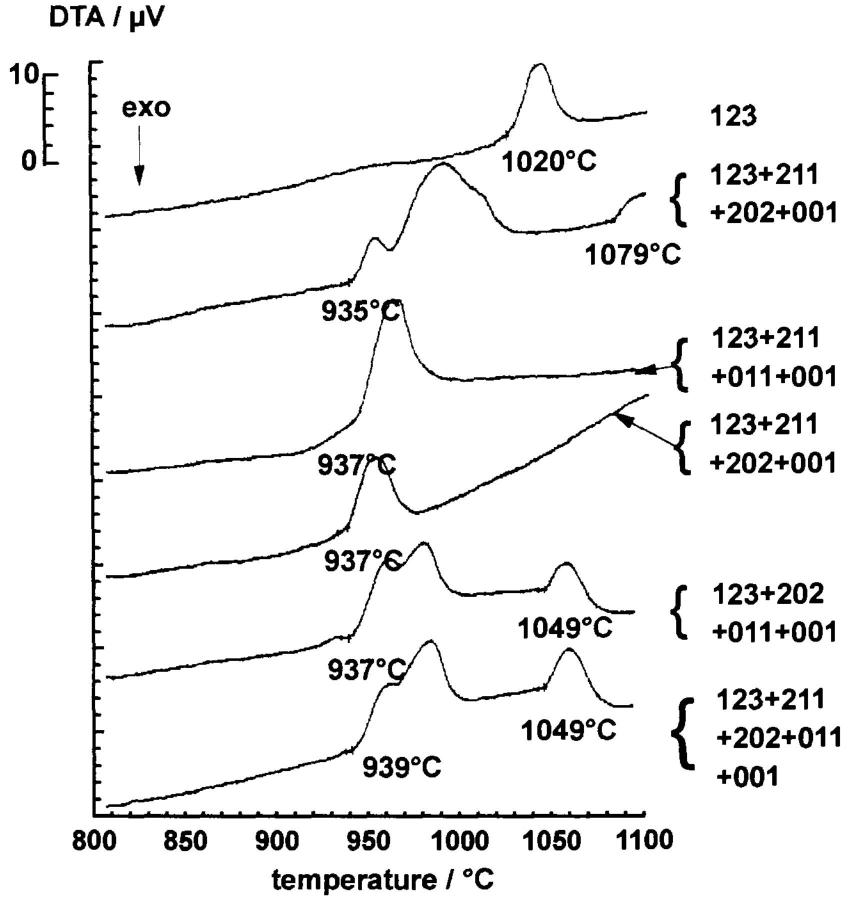


Fig. 9. The DTA curves for four- and five-component mixtures of $YBa_2Cu_3O_{7-x}$.

Table 1
Invariant points in the system $YO_{1.5}$–BaO–CuO [29]

Temperature	Invariant point	Reaction	Ref. [29]
910°C	e1	$123 + 011 + 001 \rightarrow L$	890°C
916°C	e2	$011 + 001 \rightarrow L$	920°C
941°C	p1	$123 + 001 \rightarrow 211 + L$	940°C
957°C	p2	$211 + 001 \rightarrow 202 + L$	975°C
1004°C	p3	$123 + 011 \rightarrow 211 + L$	1000°C
1010°C	e3	$211 + 011 \rightarrow L$	1000°C
1020°C	m1	$123 \rightarrow 211 + L$	1015°C
1015°C	m2	$011 \rightarrow L$	1015°C
1031°C		$CuO \rightarrow Cu_2O$	1026°C
1044°C	p4	$211 + 202 \rightarrow 200 + L$	
1274°C	m4	$211 \rightarrow 200 + L$	1270°C

Key: 123, $YBa_2Cu_3O_{7-x}$; 211, Y_2BaCuO_5; 202, $Y_2Cu_2O_5$; 200, Y_2O_3; 011, $BaCuO_2$; 001, CuO.

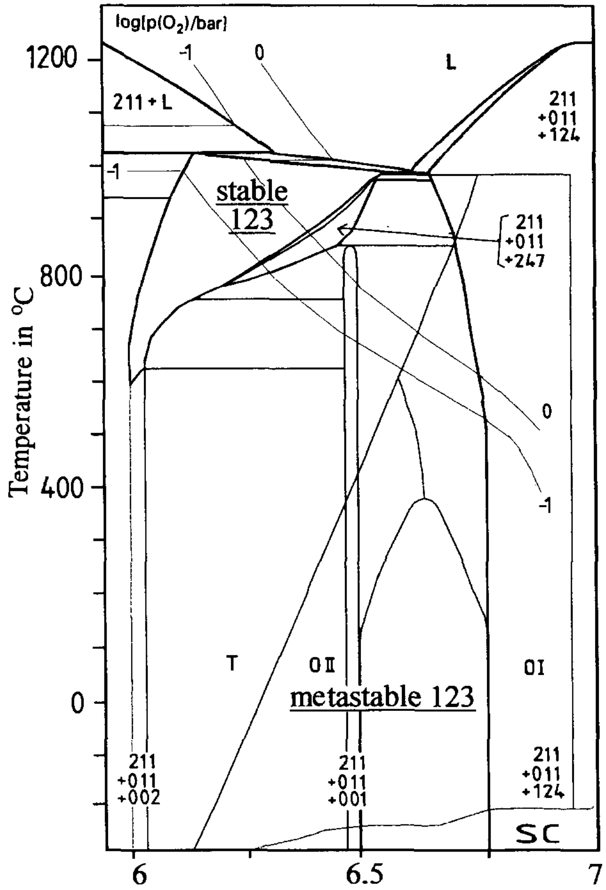


Fig. 10. A pseudo-binary phase diagram for $YBa_2Cu_3O_{7-x}$, stability area marked.

$Y_2Ba_4Cu_7O_x$ (area 211 + 011 + 247 in Fig. 10). Their presence changes the thermal features of $YBa_2Cu_3O_{7-x}$.

5. Summary

On the basis of the thermal investigations of $YBa_2Cu_3O_{7-x}$, it was found that this cuprate is stable up to 1020°C (±2°C) and has very characteristic DTA and TG patterns. The thermal characterization of $YBa_2Cu_3O_{7-x}$ reveals a weight decrease from about 400°C with two step-like (jump type) changes; the first one at 1020°C (±2°C) and the second at 1247°C (±2°C). These two steps in the TG curve are accompanied by endothermal effects which concern peritectic reactions. $YBa_2Cu_3O_{7-x}$ is first decomposed to the mixture of the green phase and the liquid phase; then the green phase in the presence of the liquid phase is decomposed to yttrium oxide and the restored liquid phase. Such model courses are changed by the presence of other phases which depends on the "sample biography."

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