Journal of Thermal Analysis, Vol. 38 (1992) 2067-2075

THERMOGRAVIMETRIC STUDY OF THE NONSTOICHIOMETRIC REGIONS IN THE Y–Ba–Cu–O SYSTEM

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The paper presents the results of studies on thermal reduction and oxidation of the nonstoichiometric phases from the Y–Ba–Cu–O in air.

The thermogravimetric (TG, DTA) experiments were performed in air in order to establish the ranges of stoichiometry and temperature of oxidation and reduction of $YBa_2Cu_3O_x$, $YBa_4Cu_3O_x$, $YBa_5Cu_2O_x$ and $Y_3Ba_8Cu_5O_x$.

It has been found, that at 950°C in air there are four oxygen deficient ternary cuprates: $YBa_2Cu_3O_{6.02}$, $YBa_4Cu_3O_{8.01}$, $YBa_5Cu_2O_{8.35}$, $Y_3Ba_8Cu_5O_{16.45}$ and stoichiometric Y_2BaCuO_5. When these nonstoichiometric cuprates are cooled slowly to room temperature in air they oxidize to the following compositions: $YBa_2Cu_3O_{6.98}$, $YBa_4Cu_3O_{8.97}$, $Y_3Ba_8Cu_5O_{18}$ and $YBa_5Cu_2O_{8.97}$.

Keywords: high temperature reactions, superconductors, Y–Ba–Cu–O system

Introduction

The problem of nonstoichiometry is a central one in solid state chemistry [1]. Indeed, within the wider contex of Material Science, the possibility of modifying the properties of a solid by varying its composition is a goal much sought for. Very recently, with the discovery of the high temperature superconductors based on the Ba–Y–Cu–O system [2], where the oxidation state of copper seems to play a major role in modifying the superconducting transition temperature T_c, the study of compositional variations in these types of solids has gained a lot of interest.

As recently shown [3], $YBa_2Cu_3O_7$-x has a structure based on perovskite structure, so that in view of recent experiences with perovskite and perovskite related materials [4, 5], any modification in the oxygen content may be accompanied by an ordering phenomenon. In the case of Y–Ba–Cu–O system, since the barium and yttrium atoms

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should have a fixed oxidation state, the change in the copper oxidation state necessarily affects the oxygen stoichiometry and vice-versa.

According to Kanno *et al.* [6] the nonstoichiometry of Y_{123} changes with temperature. The oxygen content, x in the $YBa_2Cu_3O_x$ fired in air changes with temperature in the range from $x = 5.86$ at 1000°C to $x = 7.14$ at 200°C. Apparently there are two kinds of mixed valence states: Cu^{+1}/Cu^{+2} and Cu^{+2}/Cu^{+3}.

We also found noticeable changes of the oxygen content due to the partial reduction or oxidation of copper in air for several other cuprates from the Y–Ba–Cu–O system.

It is clear that the information on the phase relations around the superconducting phase is urgently necessary for preparing superconducting materials by solid-state sintering. The future applications of Y_{123} will depend partly on its thermodynamic stability over the range of temperatures and oxygen pressures to which the superconductor is exposed during its fabrication and use. While the high temperature superconductivity of materials has stimulated enormous interest, there has been a concern regarding the stability of these materials and their properties.

Experimental

For most experiments the individual compounds were prepared by high temperature synthesis in air at 950°C from the calculated amounts of the necessary chemicals: $BaCO_3$, Y_2O_3 and CuO.

Accurately calculated and weighed amounts of chemicals were ground thoroughly together in a mortar under absolute alcohol and dried. Then after firing the products were either cooled down to room temperature in the furnace or quenched in liquid nitrogen.

Identification of these compounds was carried with an X-ray diffractometer ($Fe_{K\alpha}$–radiation) in a closed sample holder.

Oxygen content, x in the single-phase samples was determined by thermogravimetry from the weight loss while heating the furnace-cooled samples in air or from the weight gain for the nitrogen-quenched samples. The XRD patterns revealed that the samples were devoid of unreacted compounds, which can give a false x–value.

Thermal analysis measurements were performed with the Derivatograph 1000°–1500°C thermal analyzer. Samples were placed in a Pt crucible on separate Pt–Pt/13 Rh thermocouples; heated up to 1000°C at 5 deg/min. Measurements were made in air with α–Al_2O_3 as a reference material. The oxygen content, 'x' in the furnace-cooled samples was determined by iodometric titration [7].

Results and discussion

The thermal analysis was carried for the following nonstoichiometric ternary cuprates from Y–Ba–Cu–O system: $YBa_2Cu_3O_x$, $YBa_4Cu_3O_x$, $Y_3Ba_8Cu_5O_x$ and $YBa_5Cu_2O_x$.

Figures 1a, 2a, 3a, 4a show the DTA-TG curves for the furnace cooled samples annealed in air at 950°C.

Figures 1b, 2b, 3b, 4b show the DTA-TG curves for the nitrogen-quenched samples after annealing in air at 950°C.

The sample of $YBa_2Cu_3O_x$ which was heated to 950°C and cooled in air, exhibited a continuous weight loss from 340°C. The sample loses oxygen in three steps with accompany of three endothermic DTA peaks around 562°, 875° and 945°C, respectively.

More interesting results with respect to the reactivity of the nitrogen-quenched phase came from TG and DTA measurements in air. This is illustrated in Fig. 1b, which shows that upon heating of the sample oxygen uptake is observed in an exothermic

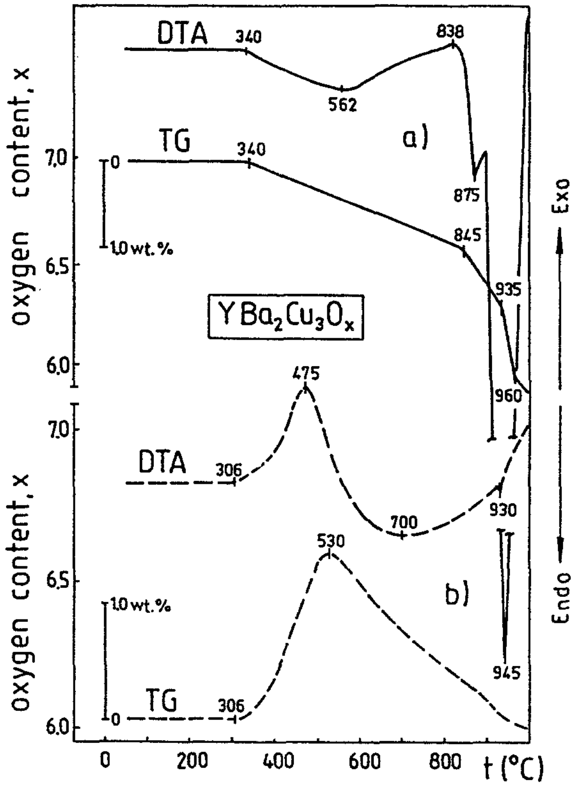

Fig. 1 DTA-TG curves of $YBa_2Cu_3O_x$ annealed in air at 950°C, a) furnace cooled sample, b) nitrogen-quenched sample

reaction at temperatures as low as 306°C. The O_2 uptake continues up to 530°C with a total gain in weight of 1.4%. Above 530°C a continuous loss in weight appears up to 1000°C, where the amount of O_2 consumed originally has been quantitatively released.

Through the TG curves shown in Fig. 1, the oxygen content 'x', can be read from the ordinate. It is apparent that there are two kinds of mixed-valence states of Cu^{+1}/Cu^{+2} and Cu^{+3}/Cu^{+2} stabilized at high and low temperatures, respectively.

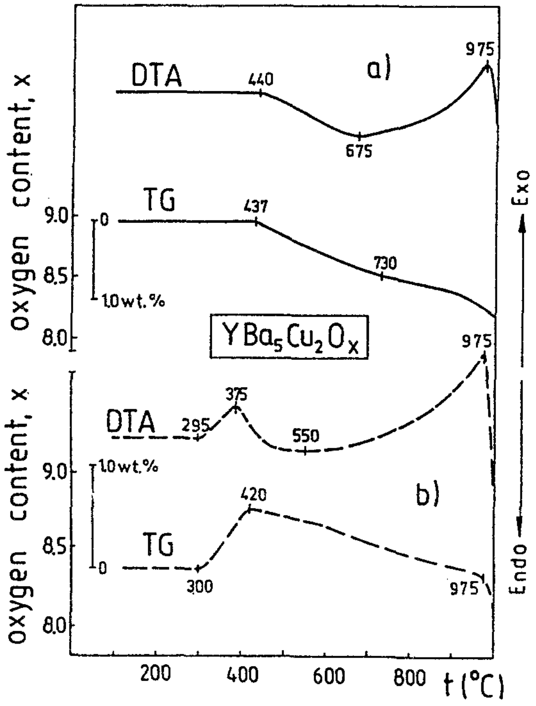

Fig. 2 DTA–TG curves of $YBa_5Cu_2O_x$ annealed in air at 950°C, a) furnace cooled sample, b) nitrogen-quenched sample

Figure 2 shows the DTA-TG curves for the samples of $YBa_5Cu_2O_x$ annealed in air at 950°C and cooled to room temperature in the furnace (Fig. 2a) or quenched in liquid nitrogen (Fig. 2b).

TG-curve of the furnace-cooled sample shows a weight loss from 437°C and rate of loss changes at about 730°C. A large endothermic DTA peak appears in this range of temperature. This effect is caused by reduction of copper ions $Cu^{+3} \rightarrow Cu^{+2}$ at the first step and $Cu^{+2} \rightarrow Cu^{+1}$ at the second step. TG-curve of the nitrogen-quenched sample shows a weight gain from 300°C and a weight loss from 420°C. On the DTA-curve an exothermic peak appears with a maximum at 375°C. The range of nonstoichiometry and thermal effects of $YBa_5Cu_2O_x$ samples were significantly lower than of the $YBa_2Cu_3O_x$ samples.

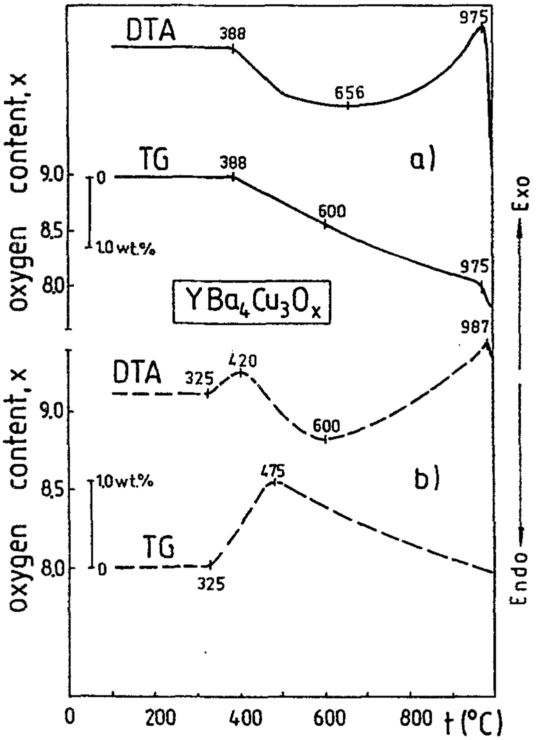

Fig. 3 DTA–TG curves of $YBa_4Cu_3O_x$ annealed in air at 950°C, a) furnace cooled sample, b) nitrogen-quenched sample

Figure 3 shows the DTA–TG curves for the samples of $YBa_4Cu_3O_x$ annealed in air at 950°C and cooled to room temperature in the furnace (Fig. 3a) or quenched in liquid nitrogen (Fig. 3b). The shape of curves is the same as for the samples of $YBa_5Cu_2O_x$ but the nonstoichiometric ranges and thermal effects are larger.

Figure 4 shows the DTA–TG curves for the samples of $Y_3Ba_8Cu_5O_x$ prepared as the samples described above. The nitrogen quenched sample of $Y_3Ba_8Cu_5O_x$ demonstrated the largest range of nonstoichiometry. Also the thermal effects accompanying reduction or oxidation of copper ions were the largest. Upon heating of the sample, oxygen uptake is observed in an exothermic reaction at temperatures as low as 200°C. This means that the nitrogen-quenched sample of $Y_3Ba_8Cu_5O_x$ is an unstable phase at low-temperature ranges.

In Table 1 the resulting oxygen contents of the investigated samples from Y–Ba–Cu–O system at temperatures of 25° and 950°C are listed.

Table 1 Composition of samples from Y–Ba–Cu–O system

Sample	Oxygen content	
	$x_{25°C}$	$x_{950°C}$
$YBa_2Cu_3O_x$	6.98	6.02
$YBa_5Cu_3O_x$	8.97	8.35
$YBa_4Cu_3O_x$	8.97	8.01
$Y_3Ba_8Cu_5O_x$	18.00	16.45

The quaternary system Y–Ba–Cu–O may conveniently be illustrated by a tetrahedron [7]. The compositions of Y_2O_3, BaO, CuO, Cu_2O, and 'Cu_2O_3' are indicated on the edges and are chosen as the components even though 'Cu_2O_3' does not exist as a stable phase. The choice of the 'Cu_2O_3' has been made in order to find the possibility for the presentation of the nonstoichiometry within the system after slow cooling in air to room temperature.

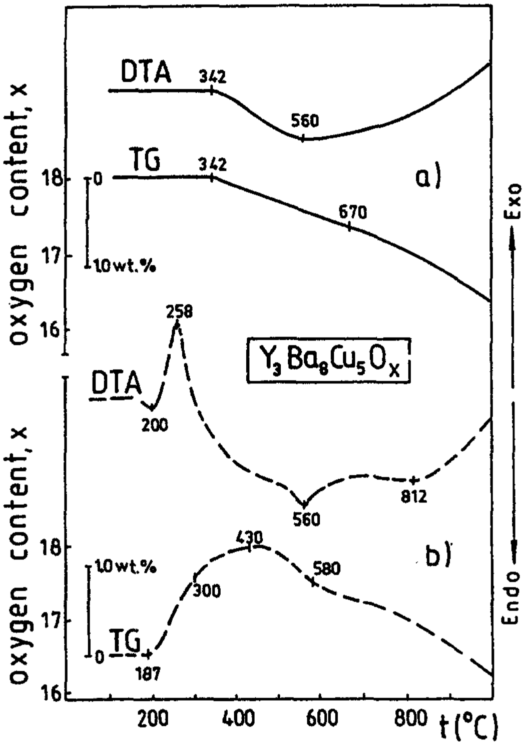

Fig. 4 DTA–TG curves of $Y_3Ba_8Cu_5O_x$ annealed in air at 950°C, a) furnace cooled sample, b) nitrogen-quenched sample

The nonstoichiometric cuprates, slowly cooled in air to room temperature, oxidized to the compositions: $YBa_2Cu_3O_{6.98}$, $YBa_4Cu_3O_{8.97}$, $Y_3Ba_8Cu_5O_{18}$, $YBa_5Cu_2O_{8.97}$, Y_2BaCuO_5 is the stoichiometric compound. Phase relations and phase compositions in the cooled samples can be illustrated in the ½(Y_2O_3)–CuO–BaO–½('Cu_2O_3') tetrahedron, Fig. 5.

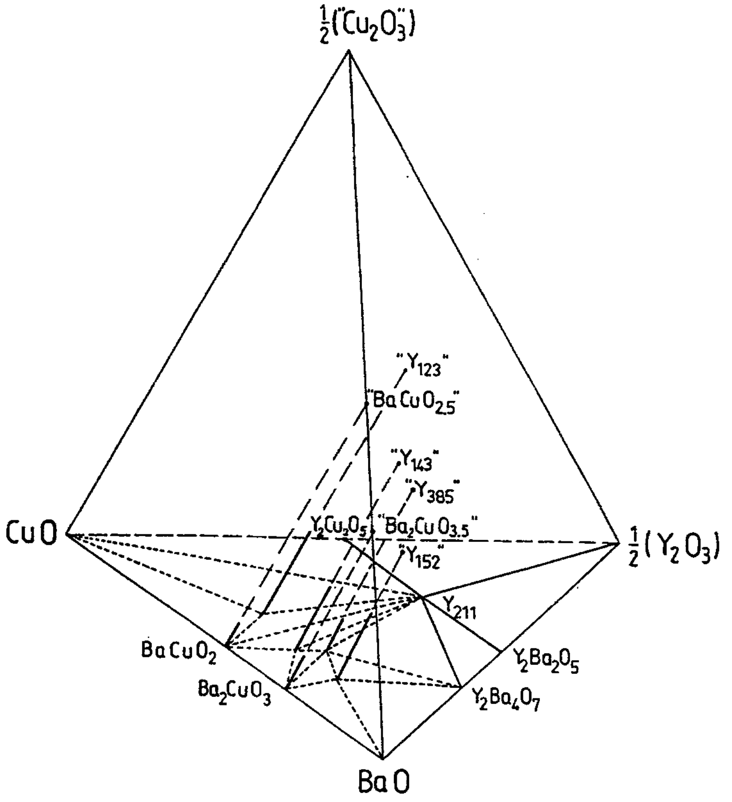

Fig. 5 The nonstoichiometry in the CuO–Y_2O_3–BaO–'Cu_2O_3' system cooled slowly in air to room temperature

Oxidation during cooling will move the compositions of the cuprates gradually along the lines which can be drawn through the points on the two planes. On the $YO_{1.5}$–BaO–'$CuO_{1.5}$' plane the hypothetical cuprates with Cu^{+3} have been indicated.

For the presentation of the nonstoichiometry among the cuprates in air at 950°C the ½(Y_2O_3)–CuO–BaO–½(Cu_2O) tetrahedron can be used. In Fig. 6 partial reduction of Cu^{+2} to Cu^{+1} in the different cuprates with a given Y : Ba : Cu ratio will move its compositions along lines which can be drawn through the points on the two ternary planes $YO_{1.5}$–BaO–CuO and $YO_{1.5}$–BaO–$CuO_{0.5}$.

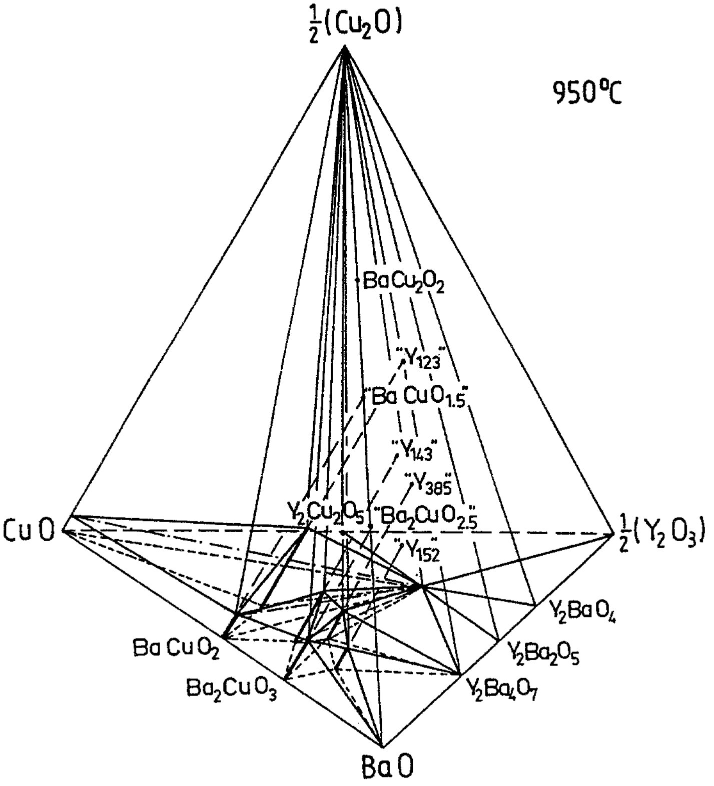

Fig. 6 The nonstoichiometry in the $CuO–Y_2O_3–BaO–Cu_2O$ system in air at 950°C

For complete reduction of Cu^{+2} to Cu^{+1} the composition would end up on the $YO_{1.5}$–BaO–$CuO_{0.5}$ plane, where the hypothetical cuprates have been indicated.

In conclusion we have found, that at 950°C in air there are four oxygen deficient ternary cuprates with the following compositions: $YBa_2Cu_3O_{6.02}$, $YBa_4Cu_3O_{8.01}$, $Y_3Ba_8Cu_5O_{16.45}$, $YBa_5Cu_2O_{8.36}$ and stoichiometric Y_2BaCuO_5.

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This work has been supported by the CPBR 6.6.64 research programme.

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Zusammenfassung — Es werden die Ergebnisse einer Untersuchung der thermischen Reduktion und Oxidation von nichtstöchiometrischen Phasen des Systemes Y–Ba–Cu–O in Luft beschrieben.

In Luftatmosphäre wurden thermogravimetrische Experimente (TG, DTG) durchgeführt, um die Bereiche von Stöchiometrie und Temperatur von Oxidation und Reduktion von $YBa_2Cu_3O_x$, $YBa_4Cu_3O_x$, $YBa_5Cu_2O_x$ und $Y_3Ba_8Cu_5O_x$ zu ermitteln.

Es wurde gefunden, daß bei 950°C in Luft vier verschiedene sauerstoffdefiziente ternäre Kuprate: $YBa_2Cu_3O_{6.02}$, $YBa_4Cu_3O_{8.01}$, $YBa_5Cu_2O_{8.35}$, $YBa_8Cu_5O_{16.45}$ sowie das stöchiometrische $YBaCuO_5$ existieren. Werden diese nichtstöchiometrischen Kuprate in Luft langsam auf Raumtemperatur abgekühlt, ergeben sich daraus folgende Oxidationsprodukte: $YBa_2Cu_3O_{6.98}$, $YBa_4Cu_3O_{8.97}$, $YBa_5Cu_2O_{8.97}$, $YBa_8Cu_5O_{18}$.