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THERMOGRAVIMETRIC STUDY OF THE TRANSITION COPPER VALENCY IN THE SUPERCONDUCTIVE SYSTEM Y–Ba–Cu–O

F. HANIC, I. HORVÁTH and L. GÁLIKOVÁ

Institute of Inorganic Chemistry, Centre for Chemical Research, Slovak Academy of Sciences, Dúbravská cesta, 84236 Bratislava (Czechoslovakia)

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ABSTRACT

The transition copper valency in the Y–Ba–Cu–O superconductive system was studied with respect to its dependence on the sample processing, doping, the heating and cooling conditions, and on the atmosphere. Significant differences existed in the oxidation reaction between the reduced phases $Y(Ce)Ba_2Cu_3O_{5.9}$ and $YBa_2Cu_3O_{5.9}$ in the temperature interval 430–550 °C. The presence of Ce^{3+} accelerated the oxidation reaction.

INTRODUCTION

The superconducting properties of perovskite-like yttrium barium copper oxide, $YBa_2Cu_3O_{6.5+x}$, strongly depend on the processing of the sample, especially upon the annealing temperature, the surrounding atmosphere and the cooling rate, because they affect the oxygen stoichiometry of the compound [1]. The material shows a great ability to reversibly intercalate oxygen during annealing under surrounding atmosphere.

The coefficient x in the formula depends directly on the ratio Cu(III)/Cu(II), as $\mathrm{Cu(III)/Cu(II)} = 2x/(3-2x)$ and the formal valency of the copper ion is $n=(6+2x)/3$. Any phase, $YBa_2Cu_3O_{6.5+x}$, with $x<0$ contains Cu(I). The superconducting transition temperature T_c increases with the increasing nominal value of Cu(III)/Cu(II) [1].

The importance of the cooling rate during synthesis of the material can be correlated to the variable oxygen content connected with the reversible polymorphic transition from the high temperature tetragonal form to the superconductive low temperature orthorhombic form in the interval 830–890 K [2–7]. The non-superconductive tetragonal form ($P4/mmm$ [8] or $P\bar{4}m2$ [9]) can be rapidly quenched to room temperature without being converted to the orthorhombic form ($Pmmm$). Depending on the rate of cooling, different phase ratios of the orthorhombic to tetragonal form can be achieved. The orthorhombic form exceeds the tetragonal modification in its oxygen content: $0 < x \leq 0.5$ for the orthorhombic phase and $-0.5 < x < 0$ for the tetragonal form [6,8,9]. T_c regularity decreases with decreasing x; samples of the tetragonal form with $x < -0.2$ do not show superconductivity, even at liquid helium temperatures [8,9].

The aim of this work was to investigate the thermal behaviour of samples prepared in two ways: by direct reaction of the oxides; or by sol–gel procedure. Special attention was paid to the low temperature re-oxidation of the phase $YBa_2Cu_3O_6$.

EXPERIMENTAL

Samples of $YBa_2Cu_3O_{6.5+x}$ were prepared in two ways.

Direct synthesis from oxides

Stoichiometric amounts of Y_2O_3, CuO and $BaCO_3$, all 99.99% pure, doped with 1.27 wt.% (Ce_2O_3 + 2CuO) were carefully ground, homogenized and pressed into pellets of 10 mm diameter approximately 2 mm thick. They were heated in a platinum boat in a cylindrical furnace for 6 h at 930 °C in air. The decarbonized product was again ground, homogenized and pressed into pellets which were heated in flowing oxygen at 930 °C for 24 h. Cooling to room temperature took 3 h. The measured densities of the ceramic samples were 4.6–4.9 Mg m^{-3}. They showed a critical temperature of superconductive transition T_c of 90–92K.

Sol–gel synthesis

Stoichiometric amounts of Y_2O_3, CuO and $BaCO_3$ were reacted with concentrated nitric acid. Citric acid was then added to the nitrate solution. The solution was neutralized with ammonia (26% NH_3) until pH 7. The clear, deep blue solution was evaporated under an infrared lamp just until onset of the autocatalytic reaction in the residue. A spongy product was formed consisting of oxides of the constituent cations, but with all the barium present as $BaCO_3$. The product was then ground in an agate mortar, pressed into pellets and then heated for 6 h in an atmosphere of oxygen. The sintered pellets had densities in the range 5.2–5.4 Mg m^{-3}. The critical temperature T_c of the superconductive transition determined by A.C. susceptibility measurements, was 92–93 K [10].

Thermoanalytical measurements

Measurements were carried out on a 990 DuPont Thermoanalyzer, module TGA 951 using 30–40 mg powder samples of $YBa_2Ca_3O_{6.5+x}$ and working at heating and cooling rates of 10 °C min^{-} in flowing nitrogen (1 $\mathrm{cm}^3\ \mathrm{s}^{-1}$) or in static air. The maximum heating temperatures used in the experiments were 1000 °C. The low temperature re-oxidation reaction with isothermal conditions was performed in the interval 327–358 °C.

X-ray powder diffractometric measurements

The phase purity of the Y–Ba–Cu–O samples was monitored by X-ray powder diffraction using a Philips powder diffractometer with Cu *Kα* radiation.

Superconductive material characteristics

The critical temperature T_c of the superconductive transition was determined from the transport current measurements as well as from the A.C. susceptibility data [10]. The T_c values and the other superconductive material characteristics (critical current density, shielding current density, temperature dependence of both real and imaginary parts of the A.C. susceptibility data, and EPR characteristics) will be published elsewhere [11].

RESULTS AND DISCUSSION

Crystallographic characteristics

The products after heating in air at 930 °C, have tetragonal symmetry with a space group *P4/mmm* and unit cell parameters: $a = 0.3866(2)$ nm; $c = 1.1875(5)$ nm; $V = 0.17748\ \mathrm{nm}^3$; $D_x = 6.157\ \mathrm{Mg\ m}^{-3}$; and MW = 658.2.

The phase identified by X-ray powder diffraction after heating in the oxygen atmosphere at 930 °C was the orthorhombic form, space group symmetry *Pmmm* and unit cell parameters: $a = 0.3819(1)$ nm; $b = 0.3885(1)$ nm; $c = 1.1687(2)$ nm; $Z = 1$; $V = 0.1734\ \mathrm{nm}^3$; $D_x = 6.388\ \mathrm{Mg\ m}^{-3}$; MW = 666.2; and $T_c = 92$–93 K.

Thermogravimetric studies of $YBa_2Cu_3O_{6.5+x}$ under dynamic conditions

Figure 1 shows the TG and DTG curves of $\mathrm{YBa_2Cu_3O_{6.5+x}}$ prepared from the oxide powders by solid state reaction. The phase was doped with 1.27 wt.% ($\mathrm{Ce_2O_3} + 2\mathrm{CuO}$). Heating in $\mathrm{O_2}$ took 24 h.

Dynamic heating in flowing $\mathrm{N_2}$ (Fig. 1(a)) shows a total mass loss of 2.69 wt.% in the temperature range 800–1000 °C (state 1). This mass loss is related to the reaction scheme

$$\mathrm{YBa_2Cu_3^{2.33}O_7} \xrightarrow{-1/2\mathrm{O_2}} \mathrm{YBa_2O_3^{1.67}O_6} \qquad (1)$$

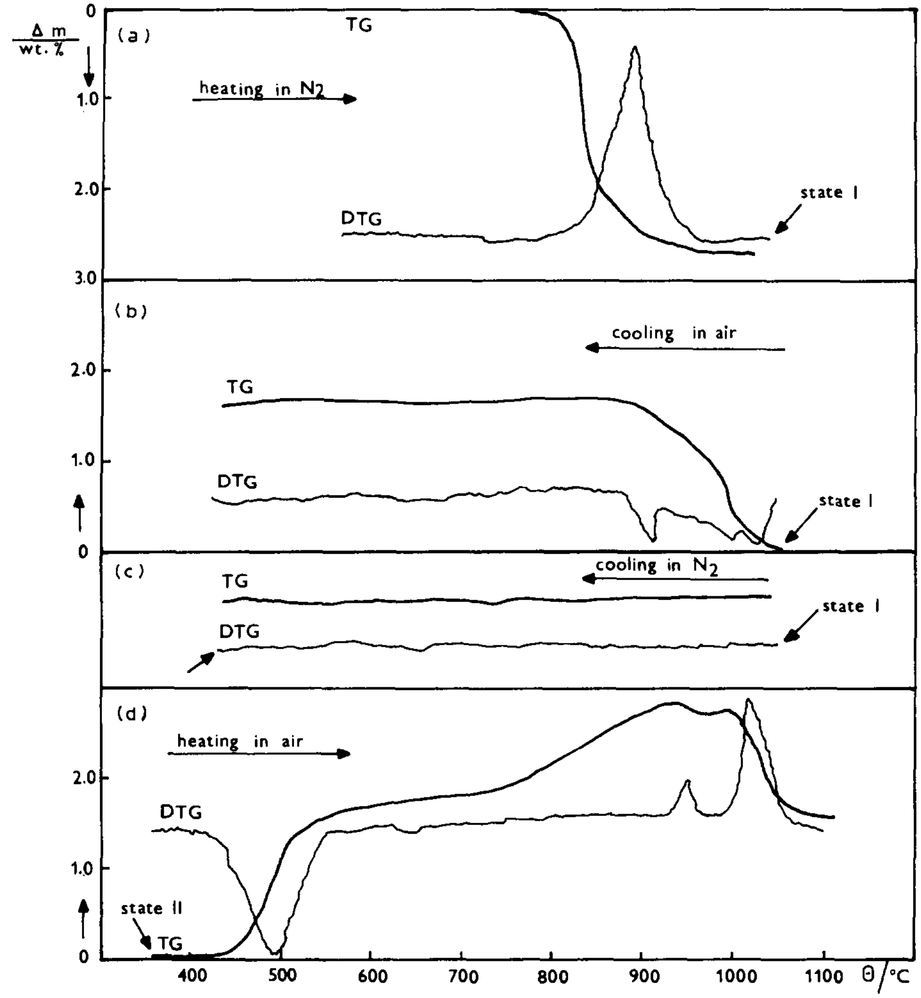

Fig. 1. TG and DTG heating and cooling curves of $Y(Ce)Ba_2Cu_3O_{6.5+x}$ (synthesis from oxides by solid state reaction) under various experimental conditions.

in which the theoretical mass decrease is 2.40 wt.%. The experimental result indicates formation of a reduction product $YBa_2Cu_3^{1.6}O_{5.9}$.

By cooling in a N_2 stream (Fig. 1(c)), the product retains its reduced composition.

The typical heating curve in static air (Fig. 1(d)) shows that re-oxidation of the product (state II) starts very rapidly at approximately 430 ° C, with the DTG maximum at 480 ° C. In the range 550–700 ° C, a retardation in the mass increase can be observed. The mass gain corresponding to the plateau on the TG curve is 1.50 wt.%, which represents a Δx value of 0.6 i.e. the following reaction takes place

$$YBa_2Cu_3^{1.6}O_{5.9} \xrightarrow{\sim 1/4 O_2} YBa_2Cu_3^{2.0}O_{6.5} \qquad (2)$$

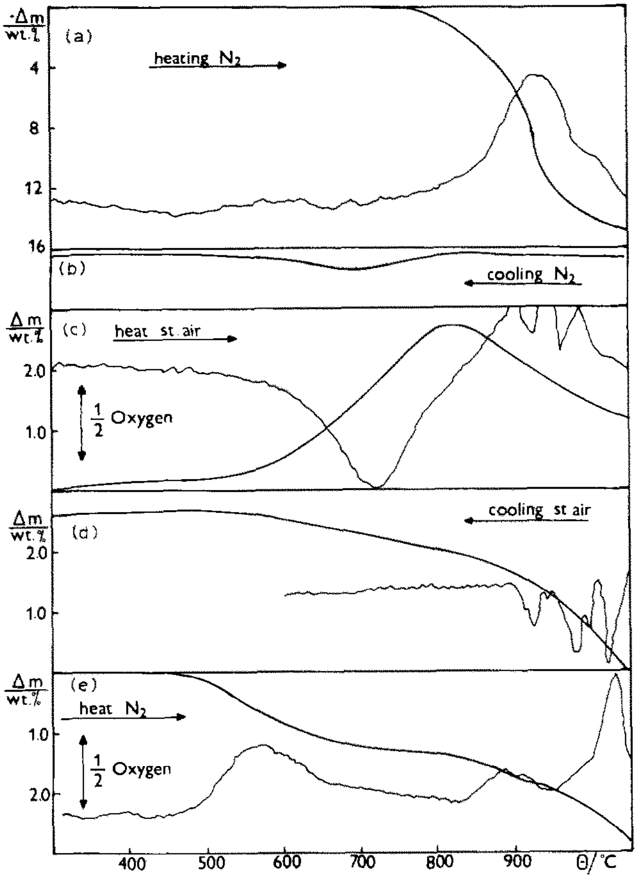

Fig. 2. TG and DTG curves of $YBa_2Cu_3O_{6.5+x}$ (sol–gel processing) under various experimental conditions.

A further increase in the oxygen content (1.25 wt.%) occurs in the interval 750–930 °C, which corresponds to the reaction

$$YBa_2Cu_3^{2+}O_{6.5} \xrightarrow{1/4O_2} YBa_2Cu_3^{2.33}O_7 \qquad (3)$$

Heating to 1000 °C results in a mass decrease which occurs in several steps (Fig. 1(d)). When cooling of the product from 1000 °C to room temperature takes place in air (Fig. 1(b)), re-oxidation results with a total mass gain of 1.6 wt.%. This increase corresponds approximately to model reaction (2).

Figure 2 represents the TG and DTG curves of the spongy product of the sol–gel procedure, consisting of Y_2O_3, CuO and $BaCO_3$.

Figure 2(a) shows the heating curves of the product. The total mass loss in the interval 700–950 °C is 13.1 wt.% which corresponds to the decarbonation reaction

$$4BaCO_3 + Y_2O_3 + 6CuO \rightarrow 2YBa_2Cu_3O_6 + 4CO_2 + \tfrac{1}{2}O_2 \qquad (4)$$

The calculated mass loss of reaction (4) is 12.87 wt.%. The experimental result indicates the formation of a reduction product $YBa_2Cu_3O_{5.9}$ (state I).

Figure 2(d) shows the cooling curves (TG and DTG) of the product from about 1000 °C (state I) to room temperature corresponding to a re-oxidation of the reduced product to the approximate composition $YBa_2Cu_3O_{6.68}$ ($\Delta m = 1.9$ wt.%, $x = 0.78$). However, cooling under N_2 atmosphere leaves the product unchanged (Fig. 2(b)).

When the product remaining after cooling in N_2 is reheated from state II in static air (with a heating rate of 10 °C min^{-1}), the increase of the sample mass caused by intercalation of oxygen, is steady up to a maximum at approximately 800 °C, showing no retardation of oxygen chemisorption in the interval 550–700 °C (Fig. 2(c)). This thermal alteration in comparison with the previous system $Y(Ce)Ba_2Cu_3O_{6.5+x}$ can be ascribed to the absence of the cerium ion in the structure.

Thermogravimetric studies of $Y(Ce)Ba_2Cu_3O_{6.5+x}$ under isothermal conditions

The oxidation rate of the reduced product after heating and cooling in N_2 i.e. $Y(Ce)Ba_2Cu_3O_{5.9}$, was investigated in the range 327–358 °C. This range is close to the temperature interval 430–550 °C in which a rapid oxidation of the system occurs according to reaction (2). The isothermal curves are shown in Fig. 3.

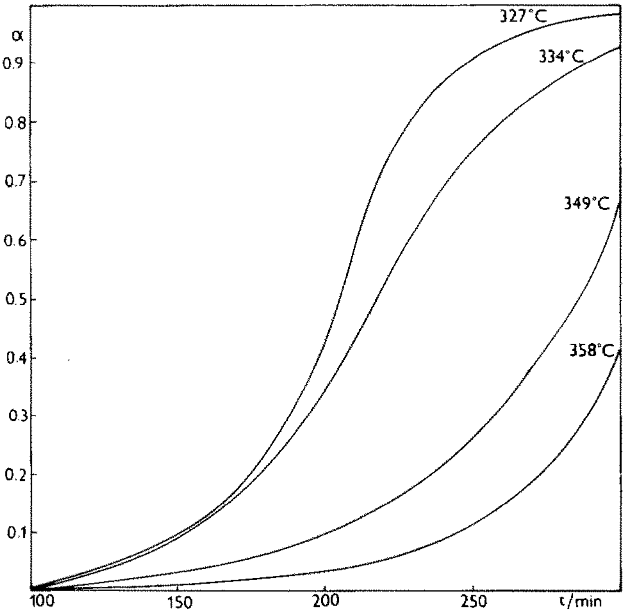

Fig. 3. Isotherms $\alpha = f(t)$ of the oxidation reaction of $Y(Ce)Ba_2Cu_3O_{5.9}$.

The isotherms exhibit pronounced long induction periods of 100–200 min, depending on temperature. The higher the heating temperature, the longer the inductive period because of the exothermic nature of the reversible reaction. The sigmoidal shape of the isotherms at 327 and 334° C indicates that the rate of oxidation is controlled by a nucleation process of the orthorhombic phase. A comparison of the experimental data with the kinetic model on a relative time scale $t/t_{0.5}$ (t is the time of reaction, $t_{0.5}$ is the half-time of reaction) suggests the Avrami–Jerofjejev's equation in its integrated form $[-\ln(1-\alpha)]^{1/2}$, where α is the conversion degree of reaction.

The isotherms at 349 and 358° C suggest an autocatalytic Prout–Tompkins reaction $\mathrm{d}\alpha/\mathrm{d}t = \alpha(1-\alpha)$, or in its integrated form $\ln \ln\{[\alpha/(1-\alpha)] + C\} = K + q \ln t$, where C is an integration constant, and K and q are reaction constants which depend on temperature θ. The induction period increases with temperature.

A correlated study of the DTA characteristics of $YBa_2Cu_3O_{6.5+x}$ processed from different feed materials is reported elswhere [12].

CONCLUSIONS

The re-oxidation of $Y(Ce)Ba_2Cu_3O_{5.9}$ (in air) prepared by a solid state reaction of oxides differs from the re-oxidation of $YBa_2Cu_3O_{5.9}$ prepared by the sol-gel process. The first shows a retardation of the oxygen intercalation in the range 550–700° C with a plateau corresponding to a composition $Y(Ce)Ba_2Cu_3O_{6.5}$. The second shows a continuous increase in the oxygen content with a maximum at 800° C. No intermediate plateau occurs in the oxidation process.

The isothermal oxidation of $Y(Ce)Ba_2Cu_3O_{5.9}$ indicates long induction periods in the range 327–358° C which increase with temperature. The intercalation of oxygen is an exothermal process. The sigmoidal shape of the isotherms $\alpha = f(t)$ at lower temperatures (327 and 334° C) indicates an Avrami–Jerofjejev-type of reaction governed by nucleation of the orthorhombic phase and by growth of nuclei. At higher temperatures, 349 and 358° C, a Prout–Tompkins autocatalytic oxidation reaction takes place.

The presence of the cerium ion in the phase $Y(Ce)Ba_2Cu_3O_{5.9}$ increases the rate of oxidation of the phase at lower temperatures 430–550° C, in comparison with the compound $YBa_2Cu_3O_{5.9}$, to a $YBa_2Cu_3O_{6.5}$ form.

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