*Journal of Thermal Analysis and Calorimetry, Vol. 76 (2004) 633–638*

# KINETIC STUDY ON THERMAL DECOMPOSITION OF THE HIGH-TEMPERATURE SUPERCONDUCTOR IN VACUUM MICROBALANCE

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## Abstract

In this paper the theoretical approach and applications of Cahn ultramicrobalance to kinetic study on the thermal decomposition of the high-temperature $Y_1Ba_2Cu_3O_{7-x}$ superconductor are presented. Thermogravimetric in situ measurements of oxygen loss from $Y_1Ba_2Cu_3O_6$ samples heated isothermally in a relatively high dynamic vacuum were performed with a Cahn RG electrobalance. Single-phase orthorhombic samples of composition $Y_1Ba_2Cu_3O_{7-x}$ (highest oxygen content) were synthesized from stoichiometric (1:2:3) mixtures of high-purity $Y_2O_3$, $BaCO_3$ and CuO. The original 1:2:3 mixture was prepared by the two-stage procedure described earlier. The crystal structure of the sample in the original orthorhombic phase was controlled by the X-ray powder method ($CuK_\alpha$ radiation) using a Stadi P Stoe diffractometer with a position-sensitive detector. Activation energy is estimated from appropriate Arrhenius plots.

**Keywords:** kinetics, solid-state reaction, superconductor, thermogravimetry

## Introduction

Cryogenic electronics is a fast growing branch of modern electronics especially since the discovery of high-temperature superconductors (HTS) [1].

It is well established that the surface resistance of the HTS materials below critical temperature, at microwave frequency regions, is lower than that of normal metals by one to three orders of magnitude. The quality of HTS films at microwave frequencies is assessed on the basis of surface resistance of the material. Because of the low microwave surface resistance ($R_s$), ranged from 20 to 50 mΩ (at 75 K, 14.5 GHz), $Y_1Ba_2Cu_3O_7$ thin films on low dielectric loss substrates ($LaAlO_3$, MgO, sapphire) have been successfully used for fabricating microwave devices.

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*1388–6150/2004/ $ 20.00*

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A conducting ground plane on the rear of the substrate is needed to improve performance for some devices. For decreasing the insertion loss using a superconducting material as ground plane, rather than metal, is more effective. Thus the double-sided HTS thin film is preferred in device fabrication. To obtain better performance, some microwave devices, like high order multipole filters for wireless communications (satellite [2–5] or cellular [6–8]) need to be fabricated on large size HTS thin films. For large double-sided HTS films, both the in-plane homogeneity and the equality of the two sides are important for fabricating devices.

The oxygen stoichiometry in high-$T_c$ superconductors is a crucial physical-chemical problem because all these compounds are oxides and moreover because the superconducting properties are closely related to the mixed-valency states contained in these compounds, mixed-valency states which are controlled by the oxygen stoichiometry.

The atmospheric contaminants such as $CO_2$ and $H_2O$ can have strong effects on superconducting transition temperature, the critical current density and the width superconducting transition of the superconductors [9].

The microgravimetric method is very useful in analysis of oxide superconductors, because it enables investigations in vacuum and controlled environments [10] in applications: thermogravimetric analysis for the study of solid state reactions, kinetic and thermodynamic of reactions, determination of oxygen content in redox reactions [11], adsorption and surface properties these materials [12], as well as combined measurement mass and additional parameters, for example evolved gas analysis (EGA). Investigations of the thermal decomposition of the $Y_1Ba_2Cu_3O_7$ superconductor in dynamic vacuum are valuable, particularly in view of the high oxygen diffusion coefficient in this cuprate [13]. Dynamic vacuum protects against the readsorption of oxygen from environment.

Investigations of the influence of the oxygen isotope substitution on the properties of the high-$T_c$ oxide superconductors [14] is very important in understanding the mechanism of superconductivity [15]. The observation of an oxygen isotope effect provides supporting evidence that phonons play a role in the electron pairing mechanism [16]. Knowledge of the chemistry and thermodynamics of the superconducting oxides is essential not only for prediction of the optimum processing conditions for the different forms of the materials, but also for an understanding of the origins of the defects. In this paper the theoretical approach and applications of Cahn ulramicrobalance to study of high-temperature $Y_1Ba_2Cu_3O_{7-x}$ superconductor are presented [9, 10].

## Experimental

Single-phase orthorhombic samples of composition $Y_1Ba_2Cu_3O_7$ (highest oxygen content) were synthesised from stoichiometric (1:2:3) mixtures of high purity $Y_2O_3$, $BaCO_3$ and CuO. Original 1:2:3 mixture was prepared in a two-stage procedure. Firstly, $BaCO_3$ and CuO in molar ratio of 2:3 were thoroughly mixed and ground in an agate mortar. Next, the appropriate quantity of $Y_2O_3$ was added and the whole was mixed and ground again. This mixture in the form of loose powder in alumina boat, was heated at 950°C in flowing oxygen during 4 h. After slow cooling to room temperature, the sample was reground and heated under the same conditions during a further 4 h. Subsequently, the temperature was lowered to about 400°C, and the sample was kept at this temperature during 15 h (still in oxygen) and then slowly cooled to room temperature. X-ray examinations revealed that the synthesis was virtually complete after the first heating. The in situ measurements of the oxygen loss, were performed in a Cahn RG ultramicrobalance system [17] permitting the decomposition to be followed in dynamic vacuum of $10^{-6}$ torr. The samples were heated up to the temperature of the experiment at a constant rate of 10°C $\text{min}^{-1}$. The initial mass of the samples was ca 80 mg and the fall in mass caused by the loss of one oxygen atom per chemical formula [18]

$$Y_1Ba_2Cu_3O_7 \rightarrow Y_1Ba_2Cu_3O_6 + 1/2O_2$$

corresponded to 2 mg. In order to determine disturbances which affect the accuracy of weighing in vacuum or in controlled atmosphere [19–21], blank runs were used to correct the data obtained during kinetic runs. The apparent mass changes did not exceed ±20 μg. As the accuracy of the measurements was better than ±20 μg our estimate of the oxygen content in the sample was at the level of at least ±0.01 atom per chemical formula. Loose-powder $Y_1Ba_2Cu_3O_7$ samples were placed in a small quartz crucible in the vicinity of a NiCr–Ni thermocouple. The system was first evacuated down to $10^{-4}$ torr and the sample was annealed at 120°C during 20 h to remove adsorbed gases and moisture. It was then heated up to temperature of the measurement at a constant rate of 10°C $\text{min}^{-1}$.

To ensure a constant grain size distribution, the small samples used in the measurements were always taken from a larger portion of an original $Y_1Ba_2Cu_3O_7$ preparation. In most instances, the measurement duration was long enough (sometimes up to 200 h) for equilibrium to be aproached.

The crystal structures of the samples in the original orthorhombic phase were controlled by the X-ray powder method ($CuK_\alpha$ radiation), using a Stadi P Stoe diffractometer with a position-sensitive detector.

## Results and discussion

Oxygen loss measurements were performed on $Y_1Ba_2Cu_3O_6$ preparation isothermally heated in range 700–850°C. Pertinent oxygen loss curves are exemplified in Fig. 1 for sample studied. Prior to further analysis, the oxygen loss data ($x_t$ values) were normalised. In this case desorbing oxygen is associated with total decomposition of tetragonal structure of compound into nonidentify products, where in the final stage cooper is monovalent. The final oxygen content in the formula should always be equal to 5, independently of the thermal decomposition.

Decomposition of the type

$$Y_1Ba_2Cu_3O_6 \rightarrow \text{‘}Y_1Ba_2Cu_3O_5\text{’} + 1/2O_2\uparrow$$

$$\text{'}Y_1Ba_2Cu_3O_5\text{'} = 1/2Y_2O_3{\cdot}2BaO{\cdot}3/2Cu_2O$$

at constant temperature should follow a simple exponential relation (a first-order process) if all grains of the preparation are of the same size. The bonding of the oxygen atoms was investigated by means of gas evolution measurement and interpreted in terms of a first-order desorption model for the evolution process [22]. As our samples consisted of grains of different sizes, which decomposed at different rates, we anticipated that the overall oxygen loss may be described by the sum of an appropriate number of exponential terms, depending on the grain size distribution. It has been found that for our powdered samples the number of such exponents can be limited to two terms, corresponding to high and low decomposition rates, in which small and large grains are involved:

$$(1-x_t) = A\exp(-k_1t)+B\exp(-k_2t) \tag{1}$$

where $x_t$ is the value reached after time $t$, while $k_1$ and $k_2$ are the rate constants.

The solid lines in Fig. 1 were calculated by using above equation and appropriate constants. It should be emphasized that the agreement between the calculated and experimental results is quite good.

For curves 1 and 2 in Fig. 1 the process is characterized by two stages:

$$1)\ 0 < \tau \le \tau_\lambda;$$

$$2)\ \tau_\lambda < \tau \le \tau_\mu;$$

where $\tau_\lambda$ – the time of system memory and $\tau$ – the time of Debye's relaxation.

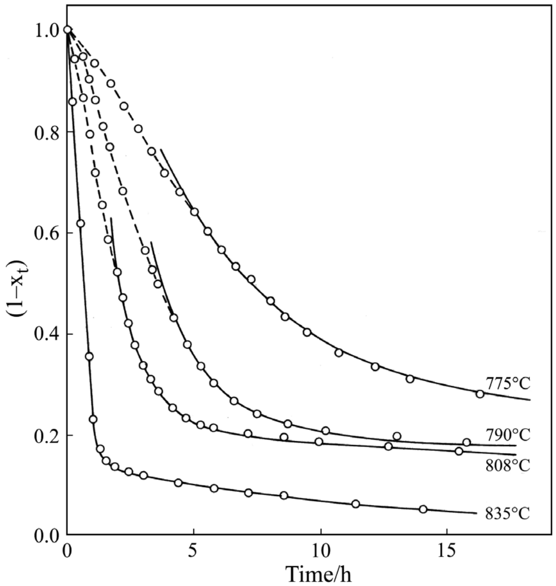

**Fig. 1** Plot ($1-x_t$) *vs*. time for yttrium preparation, curve 1 – 775°C; curve 2 – 790°C; curve 3 – 808°C and curve 4 – 835°C

In the general case for description of kinetic curves 1 and 2 there can be used the following equation:

$$(1-x_t) = (1+x)^* e^{-(1+x)\Gamma\tau} - x e^{-\lambda\tau} \tag{2}$$

where $x = \Gamma/\lambda$ – the medium pressure, $\lambda = 1/\tau_\lambda$ and $\Gamma = 1/\tau$ .

With the increase of temperature $T$, the memory time $\tau_\lambda$ decreases. The kinetic analysis of curves 3 and 4 showed that for $T = 808°C$ and $T = 835°C$ values of $x \to 0$, however the relaxation process deflects from the Debye's relaxation. In this case the kinetic relaxation is characterized by expanded exponential law:

$$(1-x_t) = \exp[-(\tau/\tau_p)^\alpha] \tag{3}$$

where $\tau_p = 0.435$ – the relaxation time and $\alpha = 0.33$ – the index showing deviation of the relaxation process from the Debye's relaxation law.

Equation (3) is also valid for curve 4. For process at $T = 808°C$ there is observed very quick relaxation of curve 3 as indicated by the relaxation algebraic equation:

$$(1-x_t) = a\tau^{-b} \tag{4}$$

where $a = 0.89$ and $b = 0.69$.

Utilizing the Arrhenius relationship, we plotted log$k$ ($k_1$ or $k_2$) *vs.* reciprocal temperature (Fig. 2).

The activation energy estimated for oxygen loss from $Y_1Ba_2Cu_3O_6$ was 3.0 eV.

The obtained results indicate that quantum chemistry calculation are extremely necessary for mechanism and theory of high-temperature superconductors. Presented data show that calculations can be fundamental for resolving high-temperature super-

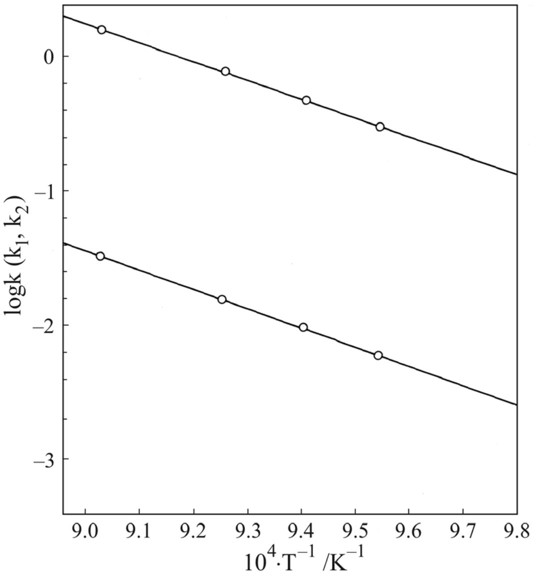

**Fig. 2** Arrhenius plots for yttrium preparation

conductivity phenomena. Using above equations is possible to study the kinetic and structural properties changes of samples in relation to temperature and time. Further basic knowledge of the high-temperature chemistry of cuprates for a wide range of rare earth, and with appropriate dopant additions is necessary for successful application of these materials in bulk and thin film form.

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