

Note

A THERMOGRAVIMETRIC STUDY OF THE UPTAKE OF OXYGEN BY $\text{YBa}_2\text{Cu}_3\text{O}_x$

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INTRODUCTION

The T_c value and related properties of high- T_c superconductive ceramic materials are strongly dependent on the oxygen content. Therefore the reaction of oxygen and these superconductive materials has been the subject of a number of investigations [1–5]. However, at this moment no general accepted interpretation of the experimental data has been given. The main reason for this is the lack of reproducibility of the measurements owing to the heterogeneous composition of the material. In this study the reaction of $\text{YBa}_2\text{Cu}_3\text{O}_x$ and O_2 is investigated on cooling from 920°C to room temperature. The first aim of this study was to obtain reproducible thermograms by trying different ways of preparing the precursor and altering the pretreatment of this precursor. In this note a number of experiments are described which may contribute to a better understanding of the reaction between oxygen and $\text{YBa}_2\text{Cu}_3\text{O}_x$.

EXPERIMENTAL

The $\text{YBa}_2\text{Cu}_3\text{O}_x$ was prepared by the oxalate [6] and the hydroxycarbonate routes [7]. The starting materials for the first synthesis were Y_2O_3 (Janssen Chemica, 99.99%), BaCO_3 (Janssen Chemica, PA) and $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (Aldrich Chemie, 98%). For the hydroxycarbonate route $(\text{CH}_3)_4\text{NHOH}$ (Aldrich Chemie, 99%), $\text{Y}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Merck, PA), $\text{Ba}(\text{NO}_3)_2$ (Merck, PA) and $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (Aldrich Chemie, 98%) were used.

The thermogravimetric measurements were performed with a Du Pont thermogravimetric analyzer 951 controlled by a Du Pont 1090B analysis system. The prepared precursor was heated in a muffle furnace up to 900°C and kept at this temperature for 36 h. The by then black material was ground in an agate mortar, and pressed into a pellet by employing a pressure of 8 ton.

Annealing was done in pure O₂ in the thermogravimetric analyzer. The oxygen content of the different samples was determined by iodometric titration as described elsewhere [8,9].

RESULTS AND DISCUSSION

In the first experiment a piece of the pellet (119.03 mg) was heated up to 920 °C, at a speed of 20 °C min⁻¹, kept at this temperature for 4 h, cooled down at a rate of 2 °C min⁻¹ to 500 °C, again kept at constant temperature for 4 h and then cooled down further to room temperature again at a speed of 2 °C min⁻¹. All this was done in an O₂ stream of 30 ml O₂ min⁻¹ at a pressure of 1 atm.

The TG-diagram of this experiment is given in Fig. 1. On heating up to 920 °C there is a weight loss. On cooling down there is an uptake of oxygen. If the temperature is held constant there is no change in weight even after a few minutes; the uptake of oxygen proceeds only after cooling is restarted.

It seems that during the isothermal period the thermodynamic equilibrium O₂(gas) ⇌ O₂(solid) is reached. In the second experiment (Fig. 2), done in the quartz tube of the TGA analyzer, a table was mounted on which different samples of the same precursor pellets were placed. This table was constructed with small quartz bars so that the oxygen stream could reach each sample uniformly. The pellets were placed in such a way that the

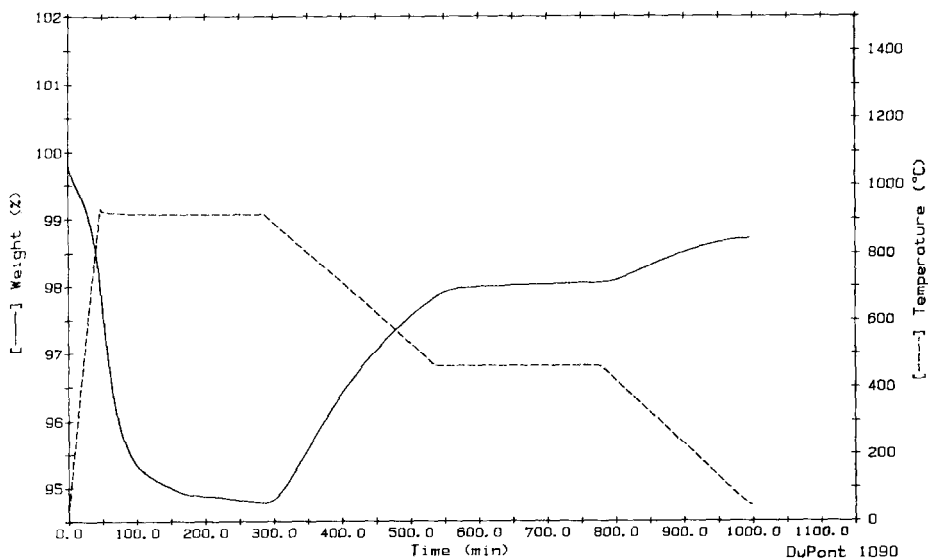


Fig. 1. TG-diagram of the first experiment. Full line, change in weight; broken line, change in temperature.

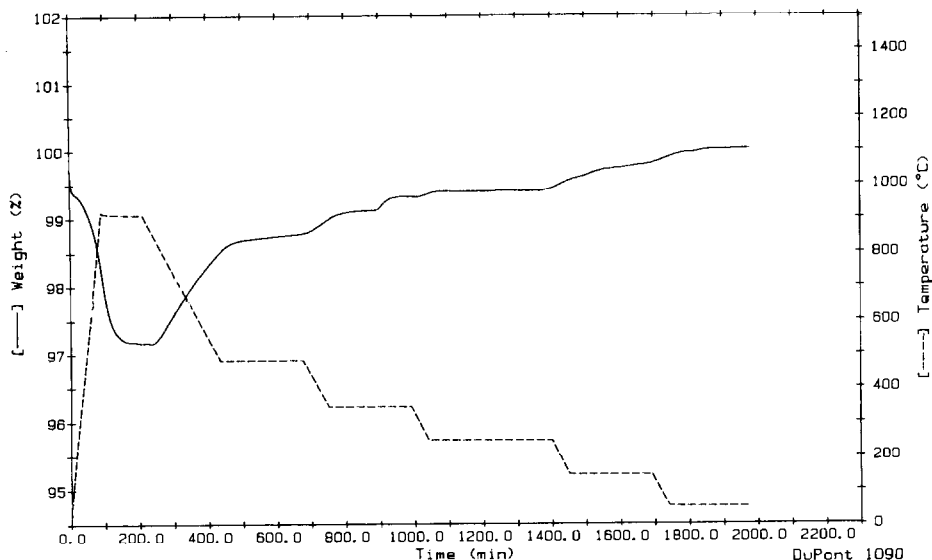


Fig. 2. TG-diagram of the second experiment. Full line, change in weight; broken line, change in temperature.

temperature gradient between them was acceptable. The weight of one sample (131.53 mg) of the precursor was followed continuously during the whole 2000 min run.

The following program was carried out: heating up to 920°C , at a speed of $10^{\circ}\text{C min}^{-1}$, isothermal period of 2 h, cooling down at a speed of $2^{\circ}\text{C min}^{-1}$, holding the temperature constant at 500°C , 350°C , 250°C , 150°C and 50°C each for a period of 4 h.

Again, oxygen uptake takes place mostly when cooling down, in contrast with the isothermal period. At 350°C an additional uptake of oxygen was found to occur. A possible explanation for this is the tetragonal-orthorhombic transition.

During each isothermal period a sample was taken from the quartz table and the oxygen level was measured by iodometric titration. The following results were obtained: $T = 900^{\circ}\text{C}$, $x = 5.8$; $T = 500^{\circ}\text{C}$, $x = 6.47$; $T = 350^{\circ}\text{C}$, $x = 6.7$; $T = 250^{\circ}\text{C}$, $x = 6.74$; $T = 150^{\circ}\text{C}$, $x = 6.89$; $T = 50^{\circ}\text{C}$, $x = 6.9$. The samples taken at 350°C , 250°C , 150°C and 50°C showed the Meissner effect.

Our ideas on the reaction between oxygen and $\text{YBa}_2\text{Cu}_3\text{O}_x$ can roughly be described as follows:

- (i) the reaction is reversible [3];
- (ii) there is a phase transition from tetragonal to orthorhombic at an oxygen stoichiometry of approximately 6.5 [10,12] and at a temperature of 500°C , depending on the O_2 pressure [5,10,11];

(iii) the activation energies of the uptake of oxygen of the tetragonal and orthorhombic phases do not differ very much, and this also seems to be the case for the difference in activation energies for the uptake and release of oxygen [5];

(iv) above 500 °C, reactions are fast and reach thermodynamic equilibrium, but below 400 °C the speed of the reaction is rather slow.

From the published preparation methods it can be deduced that some authors believe that the optimal temperature for preparing superconductive materials lies between 400 °C and 300 °C [3,4]. Our results show that over the whole range x is dependent on temperature, attaining a maximum value at a relatively low temperature of about 150 °C. This means that an equilibrium experiment at higher temperatures does not result in $x = 7$. This value can only be obtained by a slow cooling process after the equilibration period.

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