THE DECOMPOSITION OF THE OXALATE PRECURSOR
AND THE STABILITY AND REDUCTION OF THE
YBa$_2$Cu$_4$O$_8$ SUPERCONDUCTOR STUDIED BY TG
COUPLED WITH FTIR AND BY XRD

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The 124 superconductor YBa$_2$Cu$_4$O$_8$ was prepared from the oxalate precursor Y$_2$(C$_2$O$_4$)$_3$
4BaC$_2$O$_4$-8CuC$_2$O$_4$-xH$_2$O at one atmosphere oxygen pressure. In O$_2$ the precursor decomposes in
one step at 300°C and more gradually (300–600°C) in Ar. The stability of the superconductor is
strongly dependent on the gas atmosphere: in O$_2$ and in air there is no significant weight change as
long as the temperature does not exceed 800°C, whereas in a 1% O$_2$-99% N$_2$ mixture decomposi-
tion starts at about 670°C with the formation of CuO and YBa$_2$Cu$_3$O$_x$ with x<7. The reduction of
YBa$_2$Cu$_4$O$_8$ in a 5% H$_2$-95% Ar mixture takes place in at least four major steps with formation of
products such as Y$_2$O$_3$, BaO, Cu$_2$O, Cu, BaY$_2$O$_5$ and Ba$_4$Y$_2$O$_7$.

Keywords: oxalate, precursor, superconductor

Introduction

Recently the oxalate coprecipitation technique has been used for preparation
of the ‘124’ superconductor at one atmosphere oxygen pressure [1]. A general
method for computing the starting concentrations for preparing the precursor in
the correct proportions has been described previously [2].

TG coupled with FTIR gives information about the decomposition products
and the evolved gases.
An important characteristic of the YBa$_2$Cu$_4$O$_8$ superconductor is its thermally stable oxygen content.

Several methods, such as TG in H$_2$/Ar [3, 4], spectroscopic analysis, coulometric determination [5, 6] and potentiometric titrations [7, 8, 9], have been developed to determine the oxygen content of a superconducting material. In this paper, the following experiments carried out with TG coupled with FTIR, are described: the decomposition of the oxalate precursor Y$_2$(C$_2$O$_4$)$_3$·4BaC$_2$O$_4$·8CuC$_2$O$_4$·xH$_2$O in O$_2$ and Ar; the stability of the YBa$_2$Cu$_4$O$_8$ superconductor in different gas atmospheres with various oxygen contents (O$_2$; air; 1% O$_2$-99% N$_2$; N$_2$); and the reduction of YBa$_2$Cu$_4$O$_8$ in 5% H$_2$-95% Ar.

XRD is used to obtain information on the intermediate formed products.

**Experimental**

**Materials**

The oxalate precursor was made by adding a solution of the metal nitrates to a solution of H$_2$C$_2$O$_4$ and (NH$_4$)$_2$C$_2$O$_4$. Sintering of the oxalate took place in an oxygen flow at 800°C [1].

For investigation of the individual oxides, the following products were used: CuO (Merck, extra pure), BaO (Matthey reagent 95%), and Y$_2$O$_3$ (made at 900°C from a Y$_2$(C$_2$O$_4$)$_3$·9H$_2$O precursor).

**Methods**

Thermal analysis measurements were carried out with a TA Instruments 2000-951 (former DuPont), coupled with a Bruker IFS 48 FTIR spectrometer [10, 11] working at a resolution of 8 cm$^{-1}$.

A Siemens D5000 diffractometer was used to record XRD spectra. This diffractometer was equipped with a high-temperature unit HTK10 for measurements up to 1600°C.

Oxygen content and copper valence state were determined by iodometric titrations as described elsewhere [7–9].

**Results and discussion**

**Decomposition of the oxalate precursor** Y$_2$(C$_2$O$_4$)$_3$·4BaC$_2$O$_4$·8CuC$_2$O$_4$·xH$_2$O

Figure 1 shows TG plots of the oxalate recorded in O$_2$ and Ar. FTIR spectra of the evolved gases are given in Figs 2a and 2b.