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THERMAL ANALYSIS IN THE FIELD OF HIGH TEMPERATURE SUPERCONDUCTORS

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ABSTRACT

Thermoanalytical methods were used to study the preparation, oxygen stoichiometry and phase transitions of superconductors of the type (Y, Eu)$Ba_2Cu_3O_7$. A considerable increase in density during the sintering process for the starting oxide-carbonate powder mixture was achieved by rate controlled sintering in the dilatometer. The oxygen content and the reversibility of oxygen gain and loss between O_6 and O_7 was investigated with a symmetric thermo-microbalance.

INTRODUCTION

The ceramic technology used for manufacturing sintered bodies from specially prepared powders allows dilatometric, thermogravimetric and DSC/DTA measurements.

Mixtures of oxides, carbonates and oxalates were heated in air and in oxygen atmosphere to follow the reactions during the preparation of superconducting 1-2-3 oxides. The starting powders were stoichiometrical mixtures (by weight) from the fine grinded oxides of Ytterbium or Europium and CuO and $BaCO_3$; the resulting superconductors had critical temperatures at 90 K to 95 K.

EXPERIMENTAL

The sintering of powder compacts was followed by linear shrinkage measurements in a single pushrod dilatometer. The carbonate precursor for $YBa_2Cu_3O_7$ was compressed to small rods (diameter 6 mm, length 7-8mm, pressure 150-200 N/mm^2) and heated in oxygen atmosphere. The temperature increase was programmed linear at the rate of 10 K/min up to 975°C. For rate controlled sintering the temperature raise was programmed in the quasi isothermal or stepwise isothermal mode to hold the linear shrinkage at the desired rate level.

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Thermogravimetric tests were performed in a newly developed symmetrical thermo-microbalance. The symmetrical design of this instrument allows determination of very small mass changes over a wide range of temperature under a high vacuum or in a static or dynamic gas atmosphere. Powders of Eu_2O_3, CuO and $BaCO_3$ (stoichiometrical mixture) were heated in PtRh crucibles in dynamic oxygen atmosphere, the resulting product was tempered in oxygen, reduced in a helium-hydrogen (97% He, 3% H_2) atmosphere and afterwards again reoxidized.

RESULTS AND DISCUSSION

Dilatometry is used for a long time in ceramic technology to determine sintering temperatures, shrinkage in firing, mineral reactions and structural changes. Also in the field of high temperature superconductors, which are prepared according to a "ceramic technology", dilatometry provides useful information on the reactivity of the raw materials and on structural changes of the sintered product (ref 1).

Fig. 1 shows a comparison of sintering curves for powder compacts of the carbonate precursor for $YBa_2Cu_3O_7$. The main sintering process starts at 780°C when heated in oxygen at 10 K/min (curve 2). Minor shrinkage steps are recorded at 340°C and 610°C. The shrinkage is not completed at the final temperature shown in fig. 1. Rate controlled sintering leads to a 50% higher linear shrinkage for the same material (curve 1), thus providing higher mechanical strength and chemical stability of the sintered body.

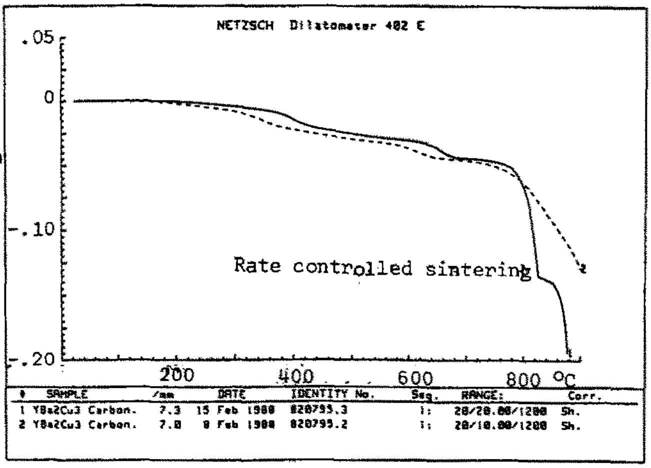


Fig. 1 Sintering of $YBa_2Cu_3O_7$ - carbonate precursors with linear heating rate (curve 2) or stepwise isothermal mode (rate controlled sintering, curve 1) in oxygen atmosphere

The sintering temperature 780°C corresponds to the main TG step (start of weight loss for the CO_2 evolution) for the same powder mixture. The smaller changes in the expansion curve at 340°C and 610°C have not been further investigated up to now. The stepwise isothermal mode resolves two shrinkage ranges with an intercept at 820°C, further tests are necessary to show whether different mechanisms are controlling the sintering in these ranges (e.g. stepwise isothermal heating in thermogravimetry and coupled evolved gas analysis).

Preparation, tempering, reduction and oxidation of superconducting material of the type $EuBa_2Cu_3O_7$ was investigated in subsequent thermogravimetric experiments.
Fig. 2 shows the temperature program and TG-DTG curves for preparation and tempering, starting with the carbonate precursor.

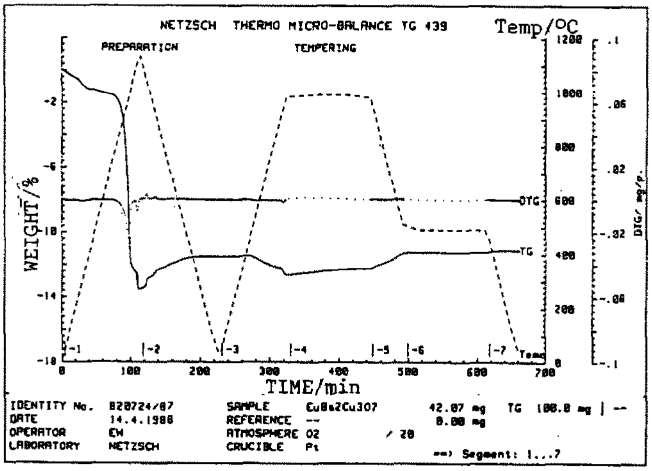


Fig. 2 Total graphic for preparation and tempering of $EuBa_2Cu_3O_7$ in a symmetrical thermobalance in flowing oxygen.

It can be seen from the one graph that the final weight of the sample after tempering is higher (+ 0.42%) compared to level after preparation, and the higher weight gain is achieved in the linear cooling segments compared to the isothermal segments of the selected tempering program.

The preparation was evaluated separately according to fig. 3.
The Eu_2O_3-CuO-$BaCO_3$ mixture shows an unexpected weight loss of 1.52 % at low temperature, most probable due to impurities in the starting powders. Therefore this weight step is not used for the further stoichiometric calculations.

The main weight loss starting at 760°C us evluated for the formation of $EuBa_2Cu_3O_{6.5}$ from the carbonate. The theoretical mass change of 10.88 % is exceeded in the experiment by impurities and inaccuracy in the stoichiometry of the starting mixture.

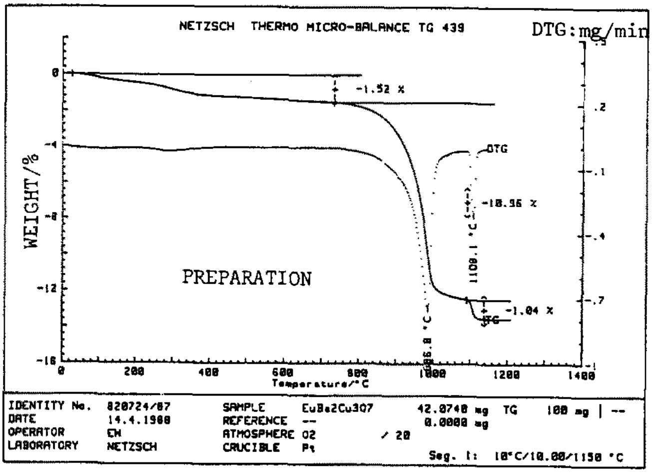
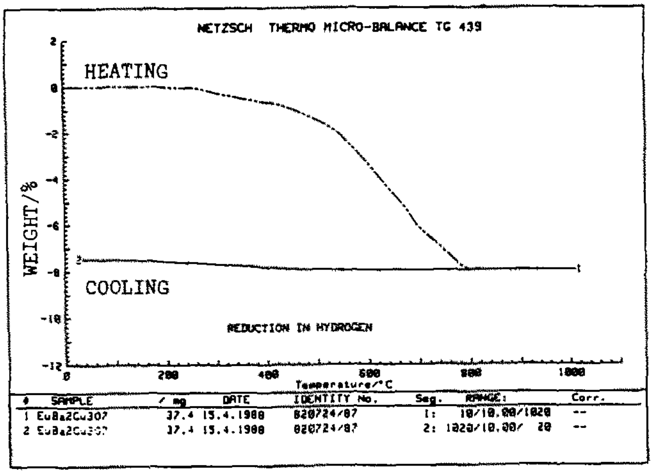


Fig. 3 Preparation of $EuBa_2Cu_3O_x$ (6 = x = 6.5) from the carbonate-oxide mixture.

Above 1090°C a sharp mass change is recorded for the oxygen loss from $O_{6.5}$ to O_6. This TG step is reversible for heating and cooling in oxygen to this temperature range (see Fig. 2). With starting powders of high purity and an exact stoichiometric mixture one could evaluate the oxygen stoichiometry only from this type of experiment shown in fig. 2. In above example the oxygen content after tempering results to $O_{6.92}$. But the better proof for oxygen stoichiometry seems to be the reduction of the superconductor in hydrogen containing atmosphere. The reaction temperatures in the reduction process are strongly depending on the hydrogen content of the atmosphere, therefore comparison between laboratories seem to be critical. Fig. 4 shows the total mass change during reduction, evaluated to 7.51 %. This corresponds to loss of oxygen in the amount of $O_{3.42}$. With the general assumption for the composition of the reduced material to be Eu_2Cu_3, BaO and Cu, the stoichiometry of the superconductor is calculated as $EuBa_2Cu_3O_{6.92}$ before the reduction experiment. This corresponds to the result shown above, after tempering.

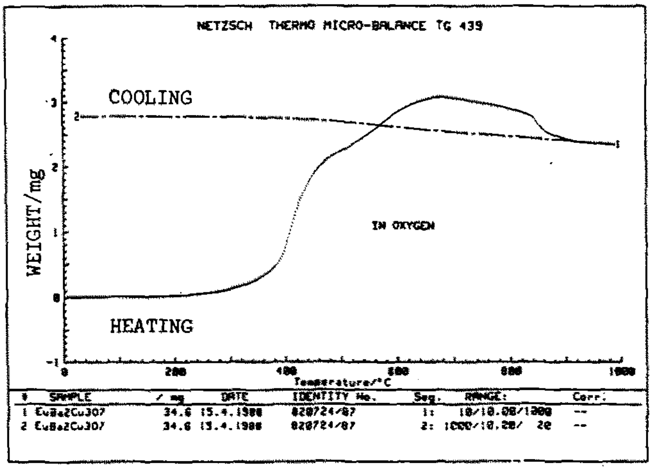


#	SAMPLE	/ mg	DATE	IDENTITY No.	Seg.	RANGE:	Corr.
1	EuBa2Cu3O7	37.4	15.4.1988	020724/87	1:	10/10.00/1020	--
2	EuBa2Cu3O7	37.4	15.4.1988	020724/87	2:	1020/10.00/ 20	--

Fig. 4 Reduction of $EuBa_2Cu_3O_x$ in hydrogen containing atmosphere.

The reduction covers a broad temperature range between 200°C and 800°C because of the relatively low hydrogen content in the atmosphere. Using pure hydrogen gas, sharp reduction mass changes are achieved around 400°C.

The reoxidation of the same material is shown in fig. 5. The oxygen content of the sample is calculated as $EuBa_2Cu_3O_{6.89}$ after this run, but there are intermediate stages with higher oxygen content (600°C to 800°C). Further tests are necessary for identification of these apparently unstable products.



#	SAMPLE	/ mg	DATE	IDENTITY No.	Seg.	RANGE:	Corr.
1	EuBa2Cu3O7	34.6	15.4.1988	020724/87	1:	10/10.00/1000	--
2	EuBa2Cu3O7	34.6	15.4.1988	020724/87	2:	1000/10.00/ 20	--

Fig. 5 Reoxidation of $EuBa_2Cu_3O_{3.5}$ in flowing cxygen.

The highest reaction rate for reoxidation is found at 410°C and a second maximum at 570°C. The latter corresponds to the temperature of the orthorhombic tetragonal transition described by Gallagher (ref. 2).

A newly developed software program will be used to study the reaction kinetics for reduction and reoxidation.

CONCLUSION

Densification during sintering of a powder compact from the carbonate precursor for $YBa_2Cu_3O_7$ can be improved by rate controlled sintering in dilatometers. Thermogravimetry is shown to be useful for the determination of oxygen stoichiometry from preparation, tempering, reduction and reoxidation experiments on $EuBa_2Cu_3O_7$-type superconductors. Impurities in starting powders and unstable intermediate products may influence the exact stoichiometric calculations.

REFERENCES

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