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THE STABILITY OF $YBa_2Cu_3O_x$ IN DIFFERENT ATMOSPHERES, BY TGA

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ABSTRACT

It has been generally accepted that oxygen exchange in $YBa_2Cu_3O_x$ is rapid and reversible above about 400°C for $6<x<7$. On the other hand, for $x<6$ and at temperatures above about 950°C, irreversible changes take place. This is especially true in the presence of reducing agents, even at temperatures as low as 100°C.

Since it is often desirable to use organic solvents or reagents for the processing of this superconducting material, we have investigated the influence of inert (nitrogen and helium), oxidizing (oxygen and air), and reducing (organic vapors) atmospheres on producing irreversible products. The starting material was characterized by the hysteresis-free TGA curve in oxygen between room temperature and 900°C, obtained after annealing the sample in oxygen above 400°C. Reduction by organic vapors was followed as weight loss by isothermal TGA. Similarly, the release of oxygen under inert atmospheres was determined by dynamic thermogravimetry. The reversibility of oxygen loss was evaluated by cycling the reduced products in the thermobalance under pure oxygen. In addition, x-ray diffraction and visual inspection of the solid was helpful to interpret the results.

INTRODUCTION

The importance of oxygen content of $YBa_2Cu_3O_x$ (1,2,3 compound) has been demonstrated (1). While x-ray crystallography allows the determination of various crystalline species present in preparations of this superconducting material, thermogravimetry in different atmospheres can also detect changes in amorphous constituents. By observing weight changes of the 1,2,3 compound under oxidizing and reducing conditions between ambient temperature and 950°C we have been able to detect impurities and to evaluate the stability of the material.

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EXPERIMENTAL

The 1,2,3 compound was prepared as shown in Figure 1. Themogravimetry was carried out with a DuPont 1090 Thermal Analyzer and a 951 Thermal Balance. Other experimental conditions are recorded on the respective figures.

RESULTS

On exposure to the laboratory environment, the 1,2,3 compound adsorbs small amounts of water, combined with a small loss in oxygen content (figure 2). This process is completely reversible by annealing in oxygen. Heating the fully oxidized material in air results in oxygen loss, particularly for high cooling rates (figure 3). For this slightly reduced sample, recovery is complete by heating in pure oxygen (figure 4).

The dependence of oxygen content on both the partial oxygen pressure above the sample and the temperature is demonstrated by isothermal TGA in helium, containing a small amount of oxygen impurity (figure 5). The temperature ranges were 140 minutes each at 600 and 850°C. The final weight loss of 1.2% corresponds to an oxygen stoichiometry of about 6.5. In oxygen-free helium (figure 6), the oxygen content drops to about O_6. This loss is completely recovered by heating in oxygen atmosphere (figures 7 and 8). Figure 9 again represents an environment low in oxygen. As shown for slightly impure helium above, here also the 1,2,3 compound acts as a fast and efficient oxygen getter. Between 800 and 900°C a separate reaction is apparent. It may be due to the presence of one of the phases reported to be stable in this temperature range (3 - 4) possibly involving a peroxide reaction with barium and complicated by any carbonate

$Y_2O_3 + 4\ BaCO_3 + 6\ CuO$

BALLMILLED (ZIRCONIA MEDIUM)

CALCINED AT 875°C FOR 24 HOURS (AIR)
IN ALUMINA CRUCIBLE

CRUSHED

CALCINED AT 875°C FOR 12 HOURS (AIR)

CRUSHED & PRESSED (10.000 PSI)

SINTERED AT 950°C FOR 8 HOURS (OXYGEN)

ANNEALED AT 950°C FOR 3 HOURS (OXYGEN)

PREPARATION OF $Y\ Ba_2\ Cu_3\ O_x$

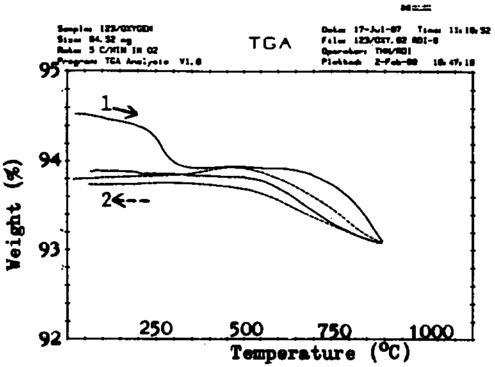

FIGURE 2:

1,2,3 COMPOUND IN OXYGEN

—— 1st CYCLE
---- 2nd CYCLE

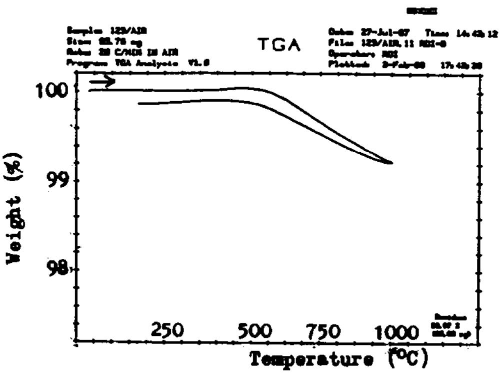

FIGURE 3:

1,2,3 COMPOUND IN AIR

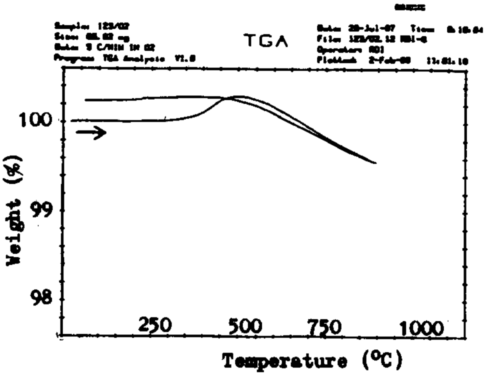

FIGURE 4:

SAMPLE FROM FIG. 3 IN OXYGEN

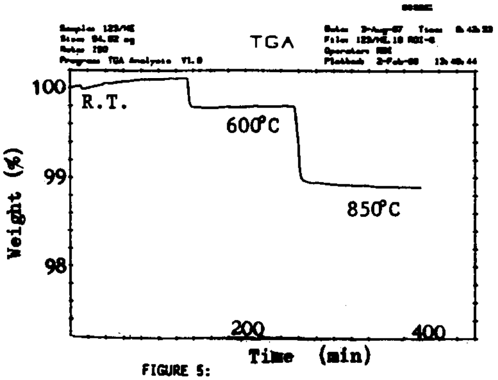

FIGURE 5:

1,2,3 COMPOUND HEATED STEPWISE
IN HELIUM

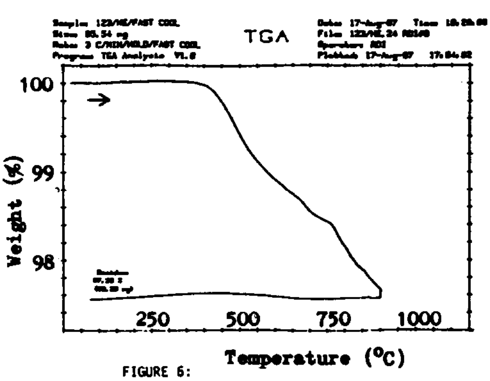

FIGURE 6:

1,2,3 COMPOUND HEATED AND
QUENCHED IN O_2-FREE He

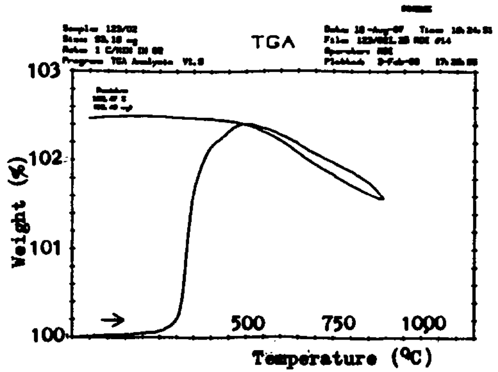

FIGURE 7:

SAMPLE FROM FIG. 6 IN OXYGEN

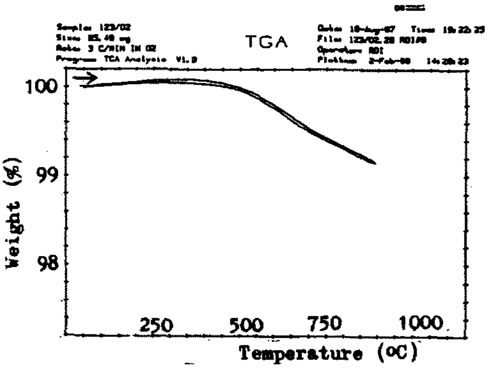

FIGURE 8:

SAMPLE FROM FIG. 7 IN OXYGEN

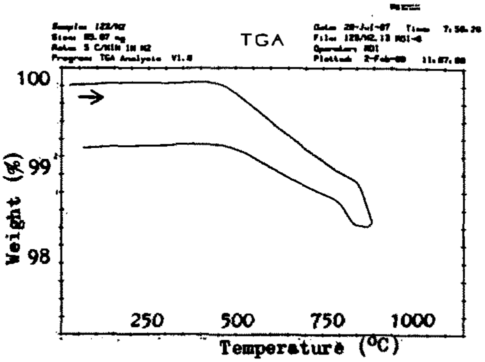

FIGURE 9:

1,2,3 COMPOUND IN NITROGEN

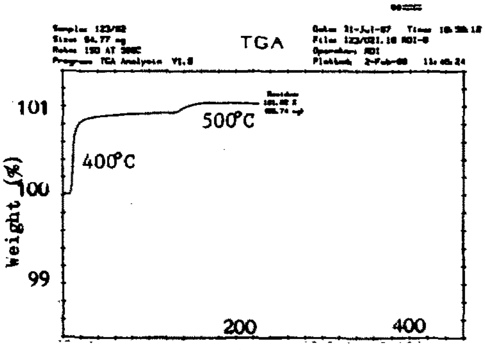

FIGURE 10:

SAMPLE FROM FIG. 5 STEPWISE
IN OXYGEN

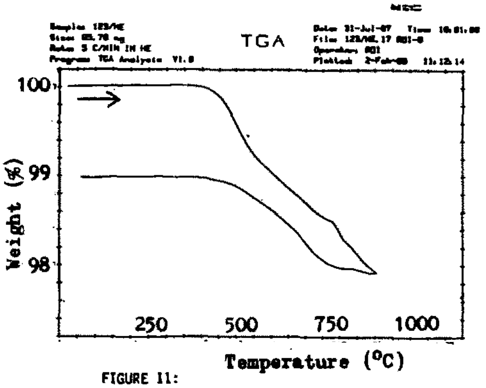

FIGURE 11:

SAMPLE FROM FIG. 10 IN HELIUM

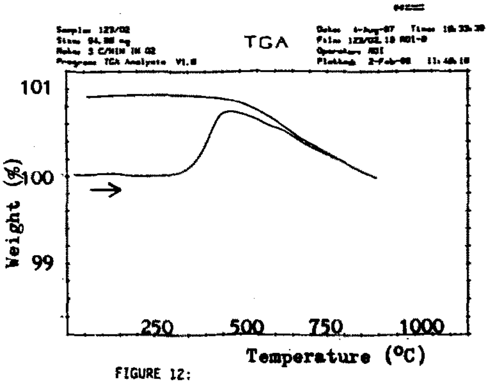

FIGURE 12:

SAMPLE FROM FIG. 11 in OXYGEN

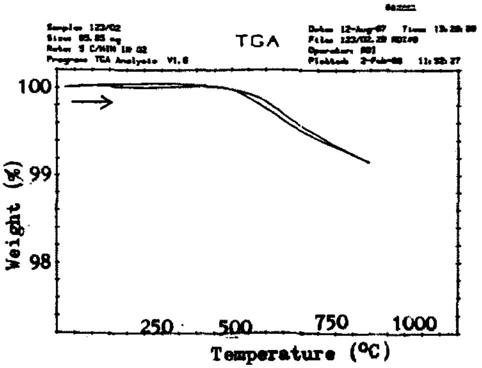

FIGURE 13:

SAMPLE FROM FIG. 12 IN OXYGEN

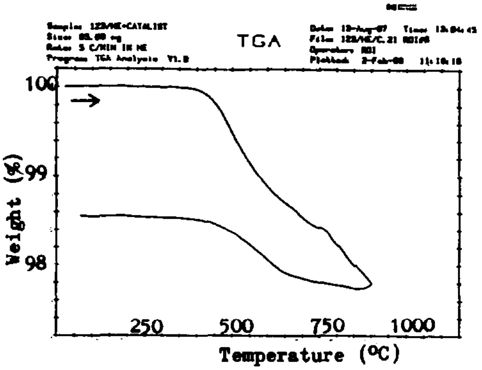

FIGURE 14:

SAMPLE FROM FIG. 13 IN O_2-FREE He

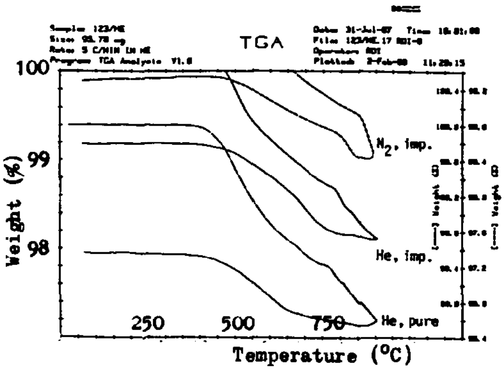

FIGURE 15:

COMPOSITE OF FIGS. 9, 11, 14

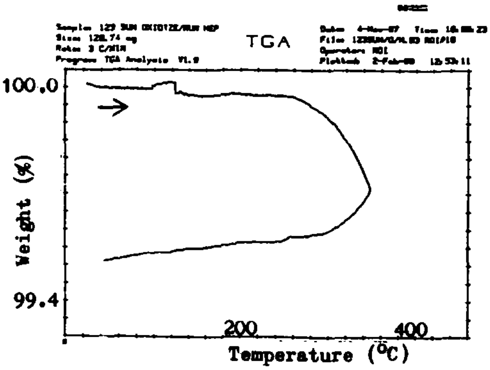

FIGURE 16:

1,2,3 COMPOUND IN HEPTANE ATMOSPHERE

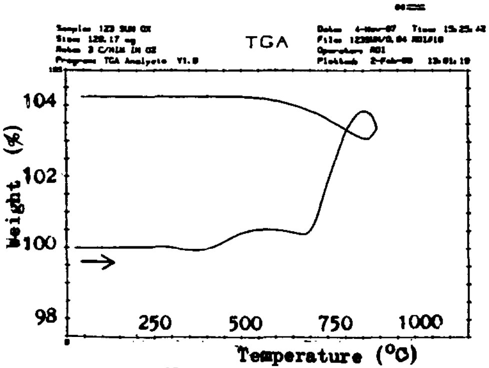

FIGURE 17:

SAMPLE FROM FIG. 16 IN OXYGEN
(1st CYCLE)

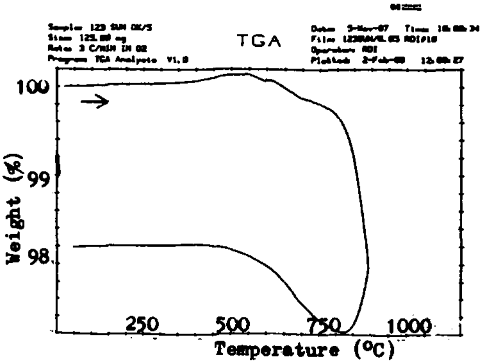

FIGURE 18:

SAMPLE FROM FIG. 17 IN OXYGEN
(2nd CYCLE)

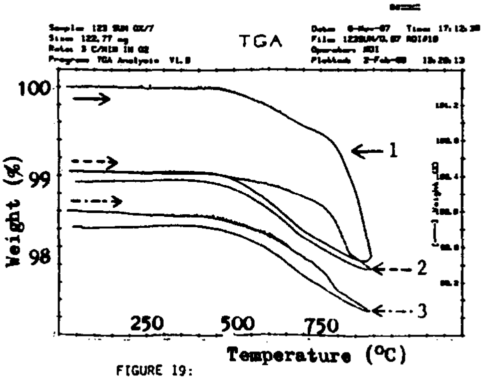

FIGURE 19:

COMPOSITE OF OXYGEN CYCLES 2-4
FROM FIG. 16

impurities. This "phase-out" which occurs near the O_6 stoichiometry is also completely reversible by annealing in oxygen. Figures 10 - 15 demonstrate the reproducibility of the redox cycle in helium, starting with oxidation of the reduced sample at 500°C (the maximum oxygen uptake occurs at 450°C), partial reduction in slightly impure helium, recovery in oxygen and finally (figures 14 and 15) demonstrating the dependence of the final composition on the oxygen partial pressure.

The next set of figures shows the effect of forced reduction of the 1,2,3 compound with heptane. This reduction has also been observed with acetone (5). In a flow of heptane-saturated helium, reduction starts near 250°C and increases rapidly (figure 16). Regeneration in oxygen undergoes the following reactions (figure 17): At about 300°C adsorbed organics are burnt, followed by oxidation of the 1,2,3 compound around 500°C. Beginning at 700°C carbon is oxidized to carbonate, which is decomposed between 800 and 900°C. On cooling, the weight gain is characteristic for the equilibrium of the 1,2,3 compound in oxygen. Complete reoxidation in this case is considerably more difficult than after reduction in inert gases. Only after repeated cycling in oxygen could the sample be regenerated (figures 18 and 19). Reduction of the 1,2,3 compound with organic materials at temperature above about 400°C irreversibly destroys it.

CONCLUSION

It has been shown that Thermogravimetry of the 1,2,3 compound under reducing and oxidizing conditions can be used successfully to evaluate the purity of this superconducting material, including the presence of non-crystalline species and especially with respect to oxygen stoichiometry of the samples under test.

REFERENCES

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