REDUCTION OF $Ba_2YCu_3O_7$ AND $Y_2Cu_2O_5$ BY H_2

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ABSTRACT

The reduction of $Ba_2YCu_3O_7$ and $Y_2Cu_2O_5$ was studied in 15% H_2–85% N_2. Although considerable structure is evident in the thermogravimetric (TG) curves, X-ray diffraction studies of partially reduced samples did not reveal any obvious intermediates. At 980°C $Ba_2YCu_3O_7$ is reduced to BaO, $Ba_2Y_2O_5$ and Cu. Near 800°C there is a plateau in the TG curve corresponding to Cu^+ and 2Cu. This suggests the formation of $YCuO_2$; however, there is no X-ray evidence in the powder pattern. Similarly, $YCuO_2$ does not appear as a stoichiometric intermediate in the reduction of $Y_2Cu_2O_5$ by H_2. X-ray diffraction shows the presence of Cu at an early stage in the reduction of $Ba_2YCu_3O_7$ suggesting a surface reaction which is nearly completed before substantial reduction occurs in the interior of the particle.

INTRODUCTION

The oxygen content in the high temperature superconductors $Ba_2MCu_3O_7$, where M is Y or a trivalent rare earth, is crucial to achieving the optimum properties [1–5]. Several methods have been developed to determine the actual value of x in the system $Ba_2YCu_3O_x$ where $6 \leq x \leq 7$, e.g., thermo-gravimetry (TG) in an H_2 containing atmosphere [1], iodometric titration of the dissolved sample [6], and neutron diffraction measurements [7]. Fortunately, there is good agreement between results from these techniques [8].

The TG in H_2 might provide some insight into the stability of the starting material or the identity of intermediate products. The overall reaction is expressed by

$$2Ba_2YCu_3O_7 + 7H_2 \rightarrow 4BaO + Y_2O_3 + 6Cu + 7H_2O \tag{1}$$
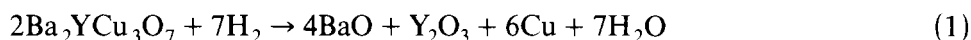
Many such TG analyses have been performed and it is worthwhile to assess some of the variations that may occur due to sample morphology and starting oxygen content x. Secondly, it is likely that some of the inter-mediate steps involve hydroxide formation and the subsequent thermal evolution of water [9]. Such reactions are generally reversible in nature and hence their kinetics will be a function of P_{H_2} and P_{H_2O} as well as tempera-ture. Under these considerations flow rates, heating rates, particle size,

porosity, degree of aggregation, type of containment, etc. will all influence the nature of the decomposition.

In following this process by weight loss it appeared that $YCuO_2$ was a logical intermediate. Hence, a study of the reduction of $Y_2Cu_2O_5$ was included. Along with the implications to be derived from the shape of the weight loss curves, powder X-ray diffraction techniques were employed. The course of the reaction was stopped at several (presumably key) points in the reduction and the X-ray diffraction pattern of the resulting powder determined. In addition, X-ray diffraction patterns were measured at selected high temperatures as a function of time.

EXPERIMENTAL PROCEDURES

Materials

A large powder batch of $Ba_2YCu_3O_7$ was prepared by ceramic techniques from $BaCO_3$, Y_2O_3 and CuO. The resulting powder was calcined at 925°C for 2 h and then pressed and sintered at 975°C for 6 h followed by an anneal at 450°C for 12 h. The sintered disk was crushed and sieved to obtain that portion having a particle size ≤ 40 μm. The microstructure of the sintered disk was single phase (i.e., no CuO) based upon optical microscopy and the crushed powder was single phase within the sensitivity of X-ray diffraction, $\sim 1\%$. The combined use of microstructure and X-ray diffraction is particularly well adapted to phase identification since the high contrast of CuO reveals its presence easily in the microstructure while BaY_2CuO_5 has a readily identifable X-ray pattern. The sintered material was highly superconducting with an onset of 92 K and a mid-point of 89 K as determined by AC susceptibility. Alternatively, a series of thin porous sintered sheets were prepared by tape casting techniques [10] from the original mix and sintered in O_2 at 975°C for 5 h followed by an anneal at 450°C for 10 h.

A powder batch of $Y_2Cu_2O_5$ was prepared by similar ceramic techniques and calcined at 850°C for 6 h in O_2. At this stage the powder had not completely reacted to form $Y_2Cu_2O_5$ as indicated by X-ray diffraction analysis. This partially reacted powder was used for the TG and DTA measurements.

These three materials, i.e., crushed powder, sintered sheets and $Y_2Cu_2O_5$ powder, served as the major source of samples in this work. However, data are also included from other samples that have been subjected to oxygen analysis by the TG reduction method.

Thermogravimetry

A Perkin–Elmer System 7 high temperature TG apparatus was used. The samples were contained in a Pt pan and subjected to a controlled flow of

forming gas (15% H_2–85% N_2) at 300 ml min^{-1}. The standard temperature program was to heat at 10 °C min^{-1} to 980 °C and hold for 10 min. The sample was then furnace cooled to near room temperature under the same ambient conditions. A blank run under otherwise identical conditions, but without a sample, was subtracted from each set of data.

A number of experiments were performed in which the temperature program was set to a lower maximum temperature in order to obtain partially reduced samples for X-ray diffraction analysis. Under these circumstances the sample for X-ray study was prepared immediately after opening the cooled furnace system, and the diffraction patterns quickly measured. This was done to minimize the substantial interaction of these reduced samples with air and moisture. By the next day such samples had swollen and flecks of white material were obvious within the originally copper colored specimens.

Differential thermal analysis

A Perkin–Elmer 1700 high temperature DTA unit was used. The heating rate was 10 °C min^{-1}. Either O_2 or N_2 was passed at a rate of 50 ml min^{-1} over the sample and Al_2O_3 reference contained in Pt cups.

X-ray diffraction

A Philips automated powder diffractometer was used to obtain a diffraction pattern for each sample. The scan step size was 0.02° with a 0.5 sec count time and a 2θ range 10–100°. The peak data were converted to d-spacings and intensities which were manually matched to existing line data for possible compounds. Relative intensities of the major peaks for each compound were used to estimate the relative amount of each phase. The high temperature X-ray equipment has been previously described [1]. A sample was heated in 15% H_2–85% N_2 at 450 or 700 °C for various times, and X-ray data were obtained in situ.

RESULTS AND DISCUSSION

The great diversity in shape of the TG curves for the reduction of essentially fully oxidized $Ba_2YCu_3O_7$, i.e., $x > 6.98$ is clearly evident in Figs. 1 and 2 for the TG and DTG curves respectively. Curves (a) are for the crushed powder described in the experimental section. Curves (b) show the reduction of a fragment of the sintered disk prior to its being ground and sieved. Reduction of a single wafer of the sintered tape-cast material is presented as curves (c). The TG curves for a sintered pellet that had been fired in 300 atm of O_2 at 450 °C for 2 h are shown in curves (d) [11]. The
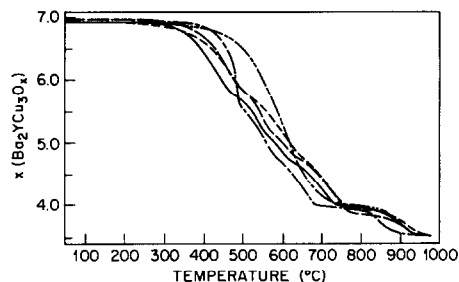
Fig. 1. TG curves for $Ba_2YCu_3O_7$ at $10\,^\circ C$ min^{-1} in 15% H_2–85% N_2. (a) Crushed powder, 117 mg, ———; (b) sintered piece, 214 mg, — — —; (c) sintered tape cast wafer, 102 mg, – – –; (d) sintered piece after high pressure O_2 anneal, 293 mg, — · —; (e) sintered piece after sealed tube anneal, 36 mg, — ·· —.

final curves (e) are for the reduction of a pellet that had been given a long time anneal, in a sealed tube at $415\,^\circ C$ [12]. In all cases, the overall weight loss indicates values of x in the range 6.98–7.03.

The one feature in common for all of these samples is the final step ($\sim 800\,^\circ C$) in the reduction curve. The weight change corresponds to the formation of one of the H_2O molecules in eqn. (1). This plateau had been recognized before but attributed to $Y_2Cu_2O_5$ [13]. The fraction of the total oxygen loss, $x = 0.5$ out of 3.5, must correspond to the reduction of one third of the Cu atoms from Cu^+ to the metal. Possible intermediates are $YCuO_2$ [14], $Ba_2CuO_{2.5}$ [15], or a reduced form of the BaY_2CuO_5 "green phase". Two other inflection points are consistently seen at $x \approx 5.7$ and 4.7 which correspond to average formal valences of $Cu^{1.5+}$ and $Cu^{0.8+}$ respectively. The valence of Cu is used herein as a "bookkeeping" tool and is not meant to indicate the specific location of the excess positive charge.

The slight variations in behavior are more readily detected in the DTG curves, Fig. 2, but these are not as easily normalized. Because the last stage
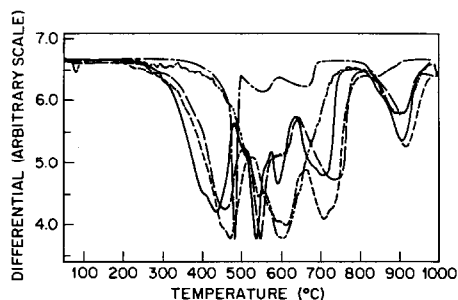

Fig. 2. DTG curves for $Ba_2YCu_2O_7$ at $10\,^\circ C$ min^{-1} in 15% H_2–85% N_2. (a) Crushed powder, 117 mg, ———; (b) sintered piece, 214 mg, — — —; (c) tape-cast wafer, 102 mg, — · —; (d) sintered piece after high pressure O_2 anneal, 293 mg, — ·· —; (e) sintered piece after sealed tube anneal, 36 mg, — —.
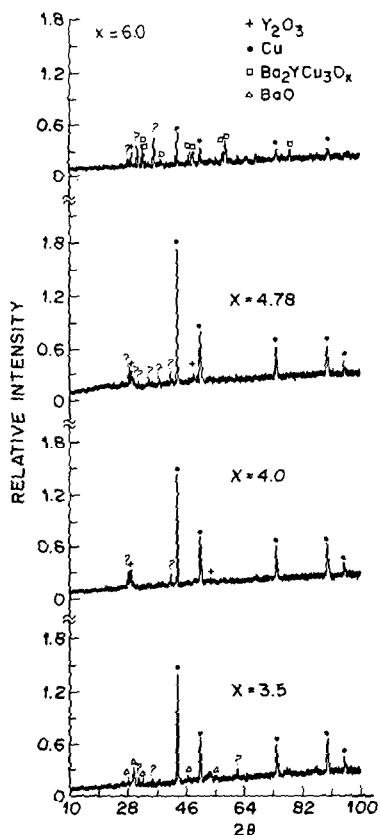
Fig. 3. X-ray diffraction patterns of partially reduced samples of crushed powder.

is virtually identical for all materials, the area of that peak is the easiest visual means of normalization.

X-ray diffraction patterns were obtained at intermediate stages by interrupting the reduction at several points and cooling the sample back to room temperature in the reducing atmosphere. A similar set of experiments was performed using the tape-cast wafers. The results for this second experimental set are completely consistent with the results for the crushed ceramic powder presented in Fig. 3. The X-ray patterns in Fig. 3 show that the initial products are tetragonal $Ba_2YCu_3O_x$, metallic copper, Y_2O_3 and unknown phase(s). The unidentified compound certainly contains Ba but no match could be found for known oxides, hydroxide, or barium yttrium oxides from the JCPDS files. At $x = 6.0$ the unknown compound(s) have major peaks at $d = 3.13$, 2.87, 2.83, 2.47. As further reduction decreases the oxygen content x, the $Ba_2YCu_3O_x$ phase disappears and the amount of Y_2O_3 decreases but unidentified peaks remain. At $x = 4.0$ only BaO and copper metal can be identified and peaks for unknown phase(s) appear at 2.98, 2.87, 2.52 and 1.49.
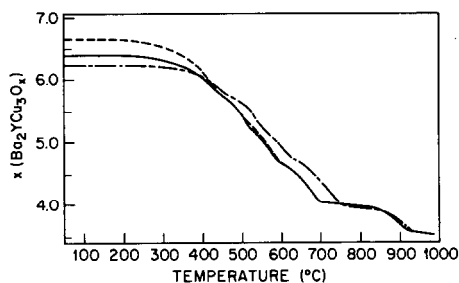
Fig. 4. TG curves for the reduction of $Ba_2YCu_3O_x$ prepared by low temperature oxidation of powder with $x = 6.28$, $10\,°C$ min^{-1} in 15% H_2–85% N_2. (a) $405°C$, 200 h, 130 ppm O_2, $x = 6.70$, 99 mg, orthorhombic phase, ———; (b) $475°C$, 80 h, 130 ppm O_2, $x = 6.44$, 95 mg, orthorhombic phase, — — —; (c) $405°C$, 400 h, 18 ppm O_2, $x = 6.28$, 221 mg, tetragonal phase, — · —.

The high temperature X-ray results at $450°C$ indicated an initial change from orthorhombic to tetraganol $Ba_2YCu_3O_x$ followed by an increase in the amount of Cu. By 24 min BaO begins to appear and persists up to 6 h. At $700°C$ BaO, $Ba_2Y_2O_5$, Y_2O_3 and Cu are present. It appears that some $Ba_4Y_2O_7$ may be starting to form but the patterns are too broad and overlapping to be definite. These reactions between BaO, and Y_2O_3, to form Ba–Y–O compounds are in general agreement with the observations of Kwestroo et al. [16].

A comparison of the effect of the starting oxygen content upon the reduction process can be made from data presented in Fig. 4. These data are for a series of samples prepared by the oxidation of material which was originally tetragonal with an x value of 6.28 [17]. Only three samples from the series $x = 6.28$, 6.36, 6.44, 6.52, 6.60, 6.70 are shown for clarity. Values of x at the inflection points do not change. A shift to higher temperature for the $x = 6.28$ composition is caused by the larger sample size which created the thermal lag. There does not appear to be any memory effect of the starting value of x or the initial phase (orthorhombic or tetragonal) upon the subsequent steps in the decomposition.

Because of the interest in $Y_2Cu_2O_5$ or $YCuO_2$ in particular, as potential intermediates in the reduction of $Ba_2YCu_3O_7$, TG analyses were performed in both O_2 and N_2 on partially reacted $Y_2Cu_2O_5$ powders and these are presented in Fig. 5. The TG reduction curve was also obtained in 15% H_2–85% N_2, see Fig. 6. The DTA curves to $1300°C$ were obtained in both O_2 and N_2 as shown in Fig. 7. Since decomposition was suspected upon melting, the DTA samples were reheated in the same atmosphere without being removed from the apparatus. There is a strong correspondence between the temperature of weight loss in O_2 (Fig. 5) and the events in the DTA curves in Fig. 7a for the sample heated in O_2. The weight change corresponding to the reduction in eqn. (2) is -4.157 wt.%, and according to
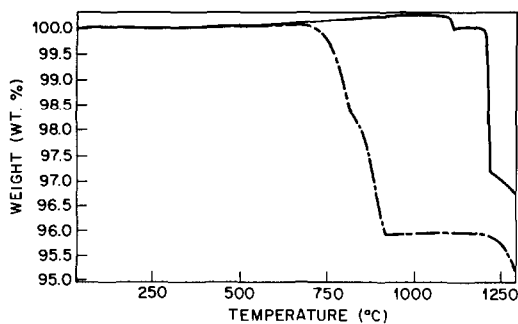
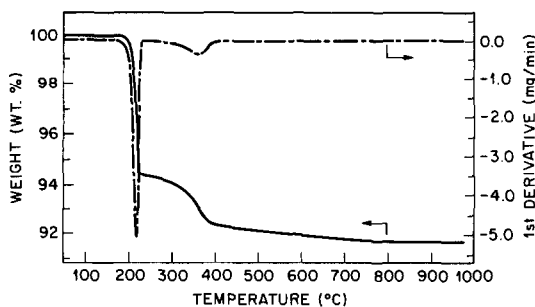Fig. 5. TG curves for $Y_2Cu_2O_5$ at $2°C$ min^{-1}. (a) In O_2, 110 mg, ———; (b) in N_2, 106 mg, — - —.

Fig. 6. TG and DTG curves of $Y_2Cu_2O_5$ at $10°C$ min.$^{-1}$ in 15% H_2–85% N_2, 134 mg.

Fig. 5 is not complete in O_2 below $1300°C$ at $2°C$ min^{-1}

$$2Y_2Cu_2O_5 \rightarrow 4YCuO_2 + O_2 \tag{2}$$

In N_2, however, it is complete around $900°C$ and is represented by a single broad endothermic peak in Fig. 7b. The endotherm around $1100°C$ does not have any corresponding event in the TG curve; however the endotherm
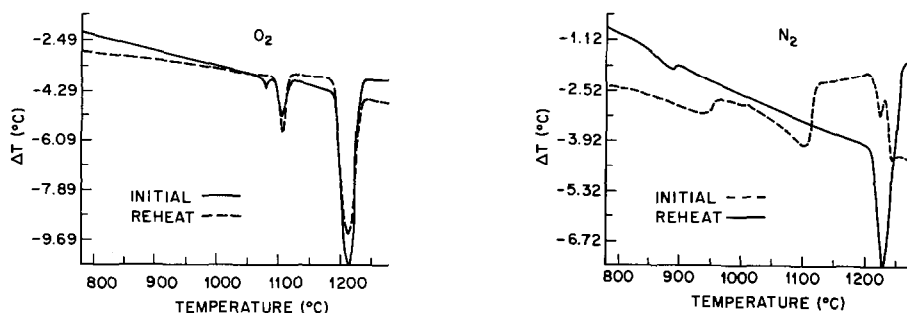

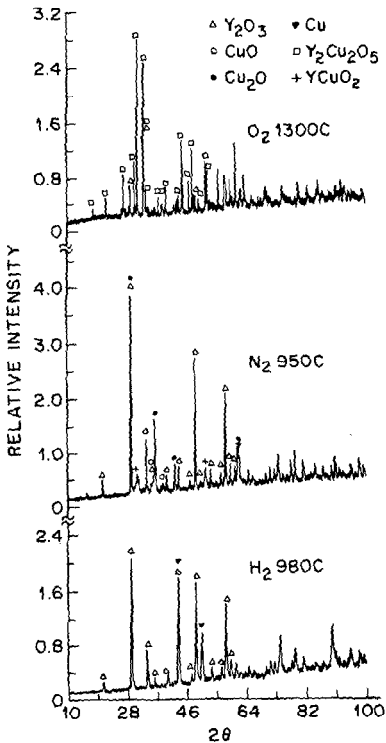Fig. 7. DTA curves for $Y_2Cu_2O_5$ at $20°C$ min^{-1}. (a) In O_2, 61.44 mg; (b) in N_2, 64.71 mg.

Fig. 8. X-ray diffraction patterns of Y_2CuO_5 after TG treatments of Figs. 6 and 7. (a) In O_2, 1300 ° C; (b) in N_2, 950 ° C; (c) in H_2, 980 ° C.

around 1210°C corresponds to melting of $YCuO_2$ and this gives rise to further loss of O_2.

The reheat in O_2 (Fig. 7a) indicates the presence of a small endothermic peak at 1080°C which was not present in the original heating. Outside of this very small change the curves are very similar, consistent with the pick-up of O_2 during cooling. The cooling TG curve, which is not shown, indicated about 65% of the weight loss on heating was regained during cooling. In N_2, however, the sample is unable to regain the oxygen and the initial endotherm around 850 ° C is much smaller. The endotherm at 1100 ° C is entirely absent and the melting at 1210°C is much sharper and more pronounced. The presence of the endotherm around 1100°C and the split melting peak during the initial heating in N_2 indicate that the reaction of eqn. (2) is not as complete at 10°C min^{-1} in the DTA apparatus as is suggested by the TG curve at 2°C min^{-1} in a more rapid flow of N_2.

The complete reduction of Cu by forming gas is indicated by eqn. (3) and represents a calculated loss of 8.314 wt.%. This agrees well with the overall loss seen in Fig. 6

$$Y_2Cu_2O_5 + 2H_2 \rightarrow Y_2O_3 + 2Cu + H_2O \tag{3}$$

The intermediate suggested by the brief plateau at around $220°C$, however, does not correspond to $YCuO_2$ as would be expected. Instead, this inflection point represents an average Cu valence of about 0.63. It might be that the considerable heat generated by the reduction process has possibly overheated the sample beyond that needed for reduction to stoichiometric $YCuO_2$. A more likely alternative is that the change in rate of reduction around $220°C$ is simply due to the partially protective nature of the Cu product layer formed and that the reduction process would otherwise take place in a single step. This latter explanation is consistent with tendency of all partially reduced samples of $Ba_2YCu_3O_7$ to show a strong pattern for Cu in their X-ray diffraction.

The X-ray diffraction patterns shown in Fig. 8 indicate that at $950°C$ in nitrogen $Y_2Cu_2O_5$ has decomposed to Y_2O_3, Cu_2O and a small amount of $YCuO_2$ while at $1000°C$ in H_2 the reaction products are copper metal and Y_2O_3.

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