

Effect of carbon dioxide on the reaction of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ with water vapour

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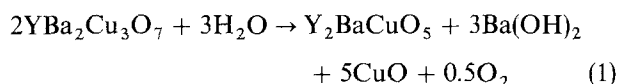
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The influence of carbon dioxide on the reaction between $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ powder and air saturated with water vapour was studied. Superconductor powder samples were exposed to air that was saturated with water vapour which (a) was free of CO_2 , (b) was saturated with CO_2 , and (c) contained ambient levels of CO_2 . In another experiment, the effect of pure, dry CO_2 (1 atmosphere partial pressure) was studied. The time variations of sample weight, oxygen content and X-ray diffraction (XRD) spectrum were determined. In water-saturated air, the rate of decrease of the oxygen content in $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ decreased with increasing partial pressure of CO_2 . XRD was used to identify the reaction products. Higher partial pressures of CO_2 favour the formation of a barrier layer (BaCO_3) which inhibits the reaction of the underlying $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ with water vapour. Very little decrease in oxygen content occurred on exposure of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ to pure, dry CO_2 .

1. Introduction

Since the discovery of high-temperature yttrium-based superconducting oxide [1] over a dozen or so papers have been published on the effect of moisture on the properties of these materials [2–12]. Some of the reported results are in disagreement. The superconductivity of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ samples is greatly degraded by interaction with water and humid air. In particular, the superconductive orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_7$ phase reacts with water and evolves oxygen. The following reactions may be expected [2]



Barkatt *et al.* [12] have reported the leaching of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ to be a highly incongruent process. Gallagher *et al.* [9] have concluded that when x in $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ changes from -0.5 to $+0.5$ the superconducting orthorhombic phase undergoes a transition to the non-superconducting tetragonal phase at $\text{O}_{6.63}$. Harris and Nyang [8] report loss of superconductivity and an associated phase change, orthorhombic–tetragonal, on exposure to moisture.

Harris and Nyang saw the phase change occurring in a sample that had been pressed into a pellet, sintered and annealed in oxygen for 1 h at 550°C , the resulting oxygen stoichiometry being determined to be $\text{O}_{6.6}$. A second sample which was annealed for 32 h at

550°C had an oxygen stoichiometry approaching O_7 , and did not exhibit the phase change on exposure to moisture. This apparently can occur when the oxygen stoichiometry approaches the lower range of that identified as orthorhombic.

The aim of the present work is to study the reaction of superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ powder with saturated water vapour in the presence of CO_2 , in the absence of CO_2 , and in dry CO_2 . The samples were exposed to: (i) a CO_2 -saturated water-vapour atmosphere, (ii) an ambient water vapour atmosphere (containing $\sim 0.033\%$ CO_2), (iii) CO_2 -free water vapour atmosphere, and (iv) pure, dry CO_2 (1 atmosphere).

2. Experimental procedure

2.1. Chemicals

All experiments were performed at ambient pressure and temperature ($18\text{--}24^\circ\text{C}$) using a $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ powder SPP-YZ, Superconductor Corporation, Milford, MA 01754, USA that was manufactured by CPS Superconductor Corporation. The average particle size of the material was $17\mu\text{m}$ (standard deviation = $0.18\mu\text{m}$) and it had a phase purity $\geq 99\%$, with a Y:Ba:Cu molar ratio of $1:2:3 \pm 3\%$. The $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ powder used in Buffalo was oxygenated by heating between $500\text{--}525^\circ\text{C}$ in an alumina boat under flowing oxygen overnight, ca. 16–20 h, and

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then cooled under flowing oxygen to room temperature over a period of ca. 3 h. Typical values of x ranged from 0.38 to 0.41 for the powders. As-manufactured powders typically had x -values of ca. 0.36 to 0.38. $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ powder was stored in glass-stoppered containers, which in turn were stored either in a dry box or a desiccator containing Drierite as a desiccant.

Deionized water was prepared using a Millipore Water System (four cartridge). All solutions were prepared from analytical-reagent-grade chemicals and dried as needed according to standard volumetric-analysis procedures. Sodium thiosulphate (ca. 0.1 M) was standardized against potassium dichromate as the primary standard using 4 ml of 0.2% starch as the indicator. Details of the preparation of solutions, standardization, drying etc. are given elsewhere [13]. Nitrogen was used as the purge gas to remove oxygen from solution.

2.2. Weighing

0.2 g samples of oxygenated $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ powder were weighed (rapidly) to the nearest 0.1 mg onto small watchglasses, or into XRD sample holders, in the ambient laboratory atmosphere.

2.3. Apparatus

The XRD patterns were recorded using a Rigaku Giegerflex X-ray diffractometer employing $\text{CuK}\alpha$ radiation in the 2θ range of 21 to 36° and the range of 6 to 50°.

2.4. Experimental method

Powder samples on watchglasses or in XRD sample holders were placed in desiccators containing either carbonated water, deionized water, or 1 M sodium hydroxide. The samples were exposed to these atmospheres for times in the range 1 h to 5 days. All samples were weighed before and after exposure to these atmospheres. Samples were also placed in dry carbon dioxide (1 atmosphere) with weight changes determined over a 25 h period. The iodometric titration method was used to determine the oxygen content ($6.5 + x$) of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ powder before and after exposure to 1 M sodium hydroxide (CO_2 -free water vapour).

2.5. Titration by iodide method

The sample was placed in a flask containing 100 ml of oxygen-free 0.33 M hydrochloric acid and 7.76 g of potassium iodide. The stoppered erlenmeyer flask was placed in an ultrasonic bath for several minutes to dissolve the sample which was then immediately titrated with standardized 0.1 M sodium thiosulphate using 4 ml of 0.2% starch solution as an indicator. The value of x was calculated from the relation:

$$x = \frac{2g - 16MV}{658.22MV - 3g} \quad (3)$$

The value of x was calculated from the weight of sample taken (g in grams), the volume of thiosulphate required to reach the endpoint (V in litres) and the molarity of the thiosulphate (M).

3. Results and Discussion

The results of reacting $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ powder with saturated water vapour, both CO_2 -free and in the presence of two levels of CO_2 , are presented in Figs 1 and 2. The samples exposed to the saturated water vapour free of CO_2 gained about 43 wt % after exposure for 24 h (Fig. 1). The samples exposed to the ambient water-vapour atmosphere (0.033% CO_2) steadily gained weight over a 25 h period, attaining a final weight gain of 33.3%. Significantly, the samples exposed to a water vapour atmosphere saturated with CO_2 gained only a total of about 3 wt % even after exposure of 24 h. Remarkably, in the absence of water vapour, CO_2 produces a negligible weight change. Accordingly, the reaction of CO_2 with $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ requires the presence of water.

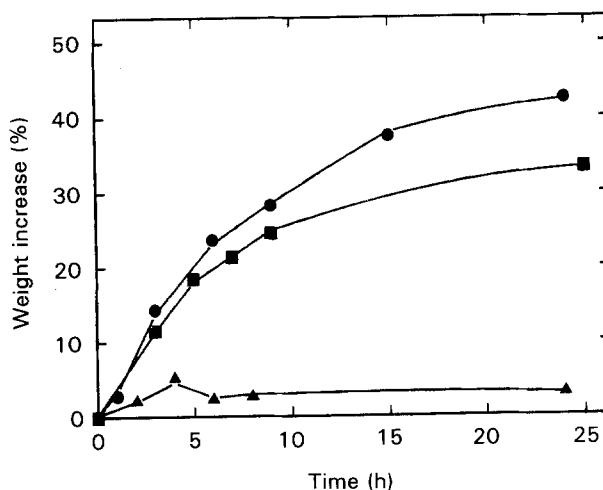


Figure 1 Weight gain versus time. The samples were exposed to: (●) a CO_2 -free water-vapour atmosphere, (■) an ambient water-vapour atmosphere, and (▲) a CO_2 -saturated water-vapour atmosphere.

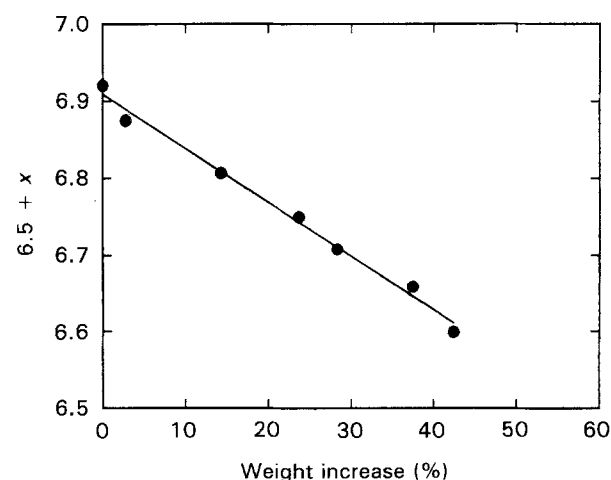


Figure 2 Relationship between sample weight and oxygen decrease. The samples were exposed to a CO_2 -free water-vapour atmosphere.

Plotting the oxygen content ($6.5 + x$) against the increase in wt %, as in Fig. 2, shows that the two are linearly correlated.

XRD experiments were undertaken to identify, as a function of time, the phases present in $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ during its reaction with water vapour and CO_2 . XRD spectra were obtained over regular time intervals for as long as 26 days. Initially the behaviour over the first 24–25 h is discussed. For

brevity, XRD spectra are given only for the 24–25 h experiments. Fig. 3 summarizes these results obtained after exposure of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ to various water/ CO_2 atmospheres after 24–25 h. These X-ray data confirm that CO_2 drastically influences the degradation of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ powder upon exposure to water vapour.

In the presence of $\text{CO}_2 +$ saturated water vapour at one atmosphere very little degradation of the

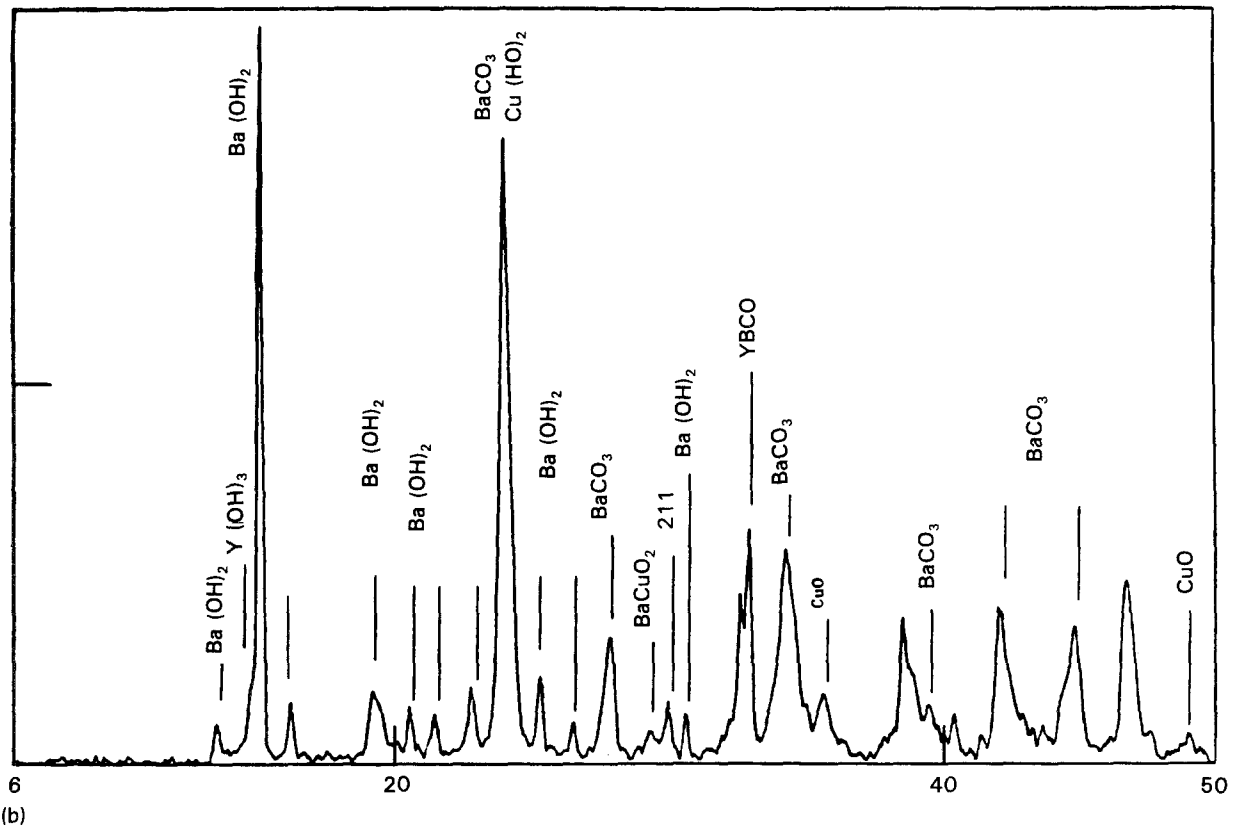
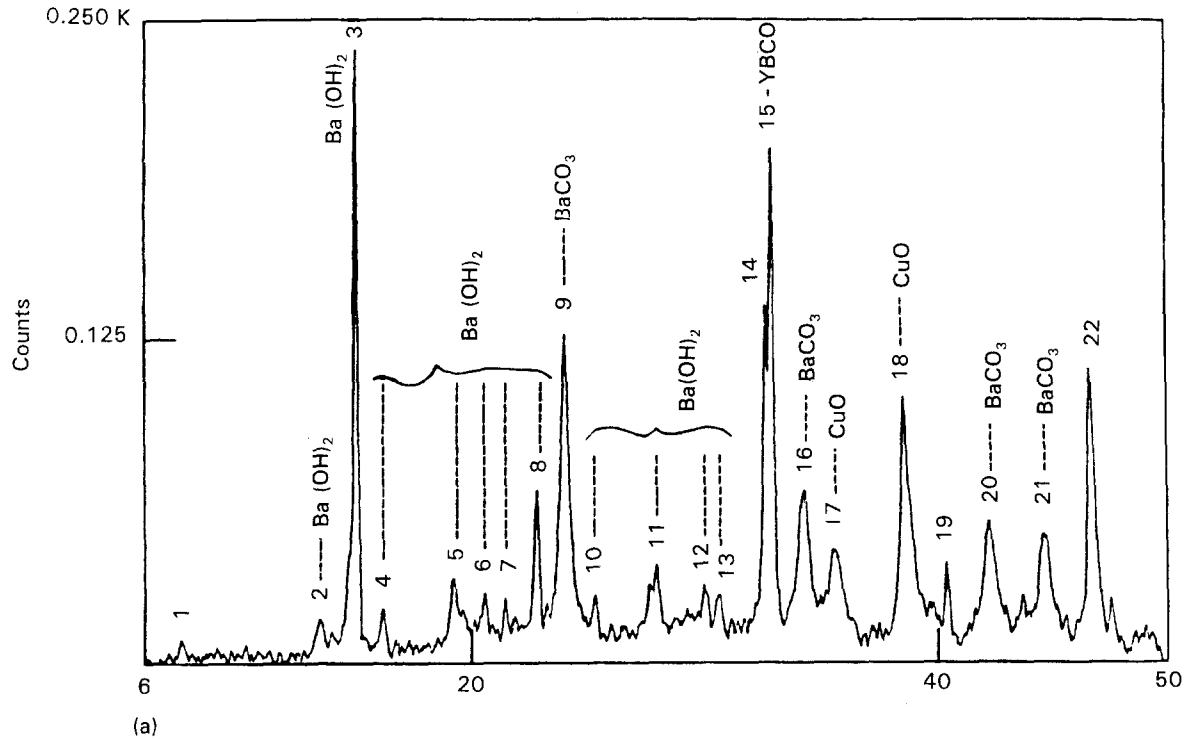


Figure 3 XRD patterns after 24–25 exposure of the $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ sample to the following atmospheres: (a) CO_2 -free, 24 h; (b) ambient, 25 h; and (c) pure CO_2 in a saturated water-vapour atmosphere, 24 h. Patterns were run for 2θ in the range $6\text{--}50^\circ$.

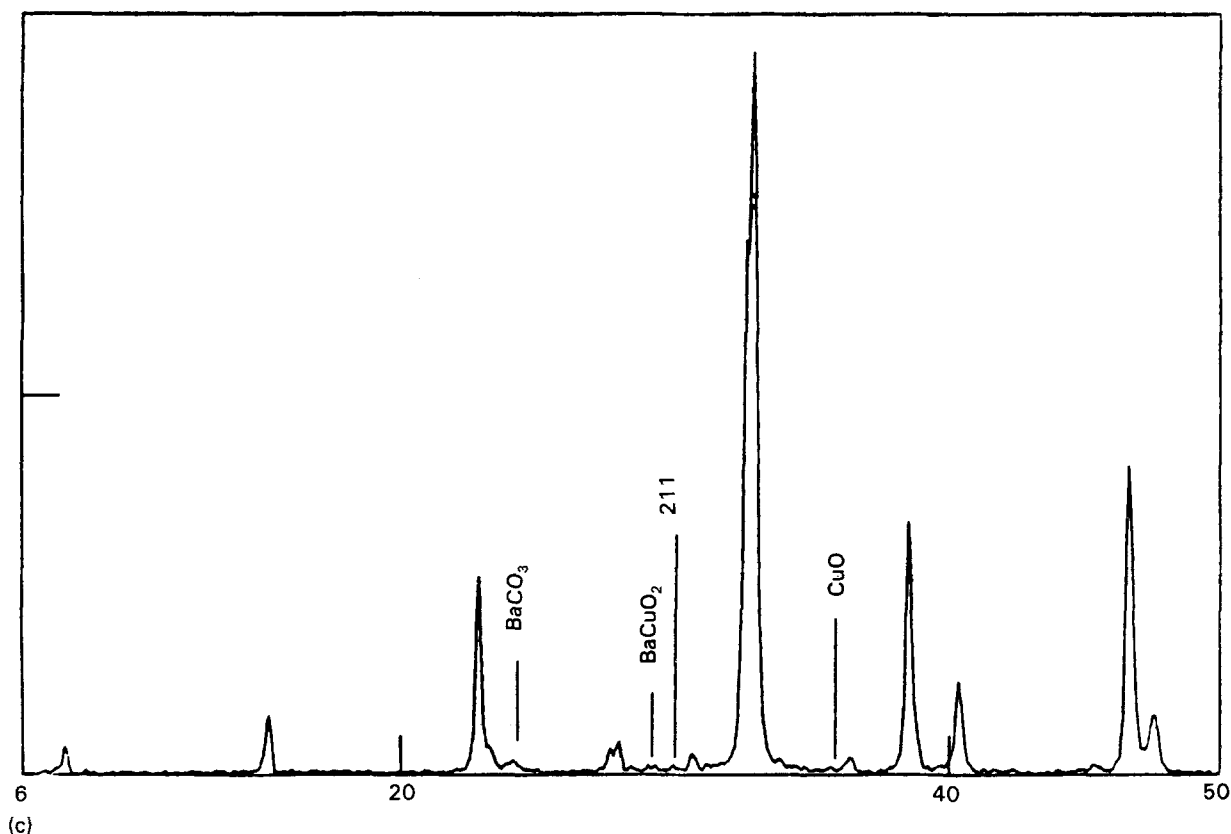


Figure 3 (Continued)

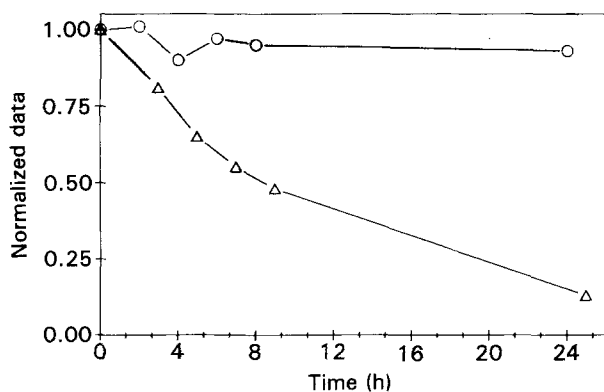


Figure 4 Normalized X-ray intensity as a function of time for the 103/110 $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ peak. $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ exposed to water-vapour containing (Δ) ambient level CO_2 or (\circ) one atmosphere of CO_2 . The values are normalized to their values at zero time.

$\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ powder is seen (see Figs 3 and 4). The only reaction products detected are BaCO_3 (the primary product) and a small amount of CuO .

In the presence of atmospheric levels of CO_2 the initial reaction product observed at short times is $\text{Ba}(\text{OH})_2$. At longer time, $\text{Ba}(\text{OH})_2$ is converted to BaCO_3 by a reaction with the 0.033% CO_2 in the atmosphere. The two major phases are $\text{Ba}(\text{OH})_2$ and BaCO_3 after one day. There is some evidence of the formation of $\text{Y}(\text{OH})_3$ and $\text{Cu}(\text{OH})_2$, along with BaCuO_2 , Y_2BaCuO_5 and CuO as other decomposition products.

The effect of CO_2 -free water vapour is much more dramatic than that found in the presence of atmo-

spheric levels of CO_2 . $\text{Ba}(\text{OH})_2$ starts to appear after only 2 h exposure along with BaCO_3 and CuO . After 24–25 h exposure, $\text{Ba}(\text{OH})_2$ is the major phase seen, with $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$, BaCO_3 , and CuO occurring as secondary phases. Neither $\text{Y}(\text{OH})_3$ nor $\text{Cu}(\text{OH})_2$ were observed although it is possible that they are present as amorphous phases. Yan *et al.* [2] found evidence of an amorphous surface layer with some indication of the presence of $\text{Cu}(\text{OH})_2$. Trolier *et al.* [11] report data supporting the presence of $\text{Y}(\text{OH})_3$ while Bansal and Sandkuhl [7] found no reaction products containing yttrium. After four days in the desiccator all of the $\text{Ba}(\text{OH})_2$ had converted into BaCO_3 , which is the primary phase present along with $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$, Y_2BaCuO_5 , and CuO . The formation of BaCO_3 is the result of unavoidable exposure of the sample to CO_2 in the atmosphere during the XRD measurements. These same reaction products were reported by Yan *et al.* [2]. After 11 days in the desiccator, the X-ray pattern was essentially the same as the four day result.

Overall, the sample gained approximately 53 wt % while stored in the wet atmosphere, and subsequently lost approximately 25 wt % while stored in a desiccator. None of our data (Fig. 5) show evidence of an orthorhombic–tetragonal phase change. The intensity ratios of the 200 to the 020 $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ peaks are essentially unchanged with time on exposure to water vapour, thus indicating that orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ degrades directly to the decomposition products without going through an intermediate tetragonal phase change which then decomposes.

Fig. 6 is a plot of the normalized X-ray intensity and X-values as a function of time. The maximum number

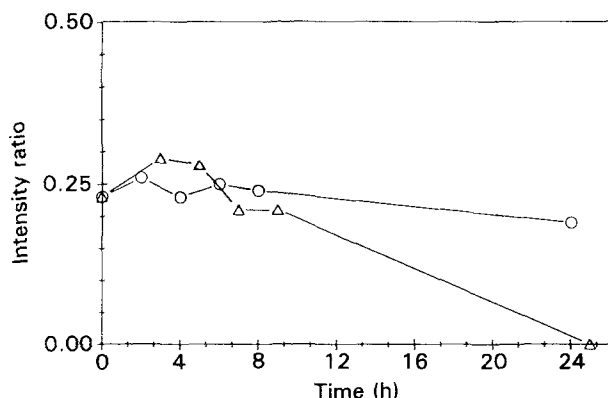


Figure 5 Intensity ratio of the 200 and 020 $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ peaks for $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ exposed to water vapour containing (Δ) ambient level CO_2 or (\circ) one atmosphere of CO_2 . The ambient-level datum at 25 h is unreliable as the split between the two peaks could not be resolved.

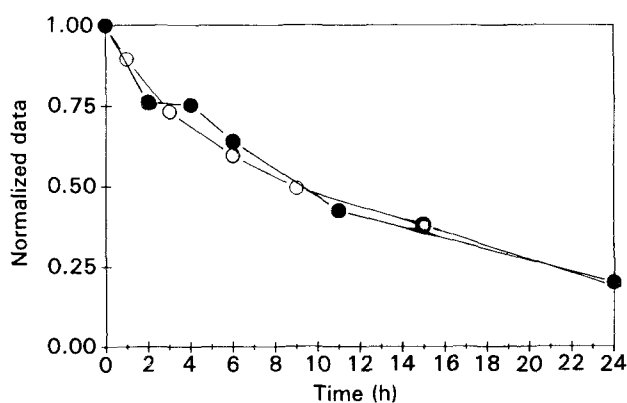


Figure 6 Normalized (\bullet) X-ray intensity and (\circ) measured X value as a function of time in CO_2 -free water-vapour. Both values are normalized to their values at zero time 103/110 $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ peak.

of counts at the 103/110 $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ peak was normalized. The two curves represented in Fig. 6 practically superimpose. Consequently the value of X as determined by titration and XRD is essentially the same.

Fig. 7 is a plot of the normalized X-ray intensity and X -values as a function of the *square root* of time. The two lines in Fig. 7 are practically linear which suggests that the reaction of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ powder with water vapour is diffusion controlled. This has been shown previously in the literature [6]. The differences in degree of reaction between the CO_2 saturated, ambient and CO_2 -free water-vapour environments are striking. The presence of a high concentration of CO_2 causes the formation of an impervious surface-reaction product (BaCO_3) which then protects the underlying $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ from continued decomposition. This idea is supported by the weight-change data as seen in Fig. 1. The data for samples exposed to the CO_2 -saturated atmosphere show hardly any change in the intensity of the 103/110 $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ peak after 24 h exposure while the samples exposed to the ambient atmosphere show a

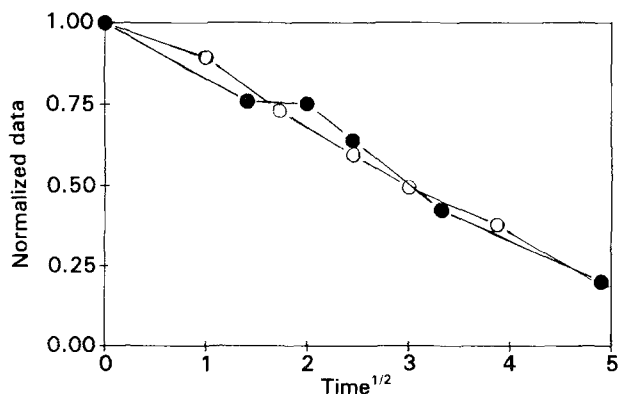


Figure 7 (\bullet) X-ray intensity and measured (\circ) X -value as a function of the square root of time in CO_2 -free water vapour. Both values are normalized to their values at zero time 103/110 $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ peak.

continuous decrease in the intensity of this peak (see Fig. 4 also).

4. Conclusion

The rate of reaction of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ with water vapour decreases in the presence of CO_2 . The initial reaction product between the superconductor and water is $\text{Ba}(\text{OH})_2$. A decreased rate of reaction is caused by the formation of a thin, protective overlayer of BaCO_3 produced by reaction of $\text{Ba}(\text{OH})_2$ with CO_2 . There is no evidence for a significant, direct reaction of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ with dry CO_2 .

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