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Degradation Reaction of the 90K Superconductor YBa₂Cu₃O₇₋δ in H₂O

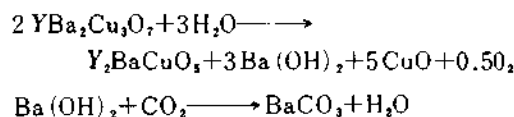**Jin-Ho Choy*, Sung-Ho Chun, Bae-Whan Kim, Duk-Young Jung, Seung-Tae Hong, and Song-Ho Byeon**

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Degradation of the 90 K superconductor $YBa_2Cu_3O_{7-\delta}$ in water and humid atmosphere were studied and its decomposition products were identified as $BaCO_3$, CuO, $Y_2(CO_3)_3 \cdot 3H_2O$ and O_2. XRD analysis, iodometric titration and IR-spectroscopy of the degraded samples suggest that the $YBa_2Cu_3O_{7-\delta}$ decomposes in three steps such as the reduction of Cu^{3+} to Cu^{2+}, followed by the hydroxylation of Ba^{2+} and Y^{3+} via hydration and finally the formation of carbonates through the uptake of ambient CO_2.

Introduction

The reactions of superconducting phase with aqueous media are of interest for several reasons, which include the need of knowledge about material handling in practical application as well as the understanding of degradation mechanism. In recent publications, some of the papers have been dealt with the reaction of the superconducting phase, $YBa_2Cu_3O_{7-\delta}$, with water and it had been gradually understood that the $YBa_2Cu_3O_{7-\delta}$ phase decomposes in water to the corresponding metal oxide, carbonates via hydroxides, and oxygen. M.F. Yan *et al.*[1] recently reported that the superconducting $YBa_2Cu_3O_{7-\delta}$ phase is decomposed by water and water vapor as follows;

$$2\,YBa_2Cu_3O_7 + 3H_2O \longrightarrow$$
$$Y_2BaCuO_5 + 3Ba(OH)_2 + 5CuO + 0.5O_2$$
$$Ba(OH)_2 + CO_2 \longrightarrow BaCO_3 + H_2O$$

B.G. Hyde *et al.*[2] also observed the bulk decomposition of the superconducting phase $YBa_2Cu_3O_{7-\delta}$ in air, whose decomposition products have been identified as $Ba_2Cu(OH)_6$, $BaCO_3$, CuO and $Y(OH)_3$. D.C. Harris and T.A. Hewston[3] found that the $YBa_2Cu_3O_{7-\delta}$ phase is readily soluble in HCl to evolve oxygen gas. F.G. Frase *et al.*[4] reported the effects of various solvents, including water, on the solubility of the superconducting phase. They observed that water reacts with $YBa_2Cu_3O_{7-\delta}$ to form $BaCO_3$ as the major phase. They

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also recorded the pH of the aqueous suspension which rose from the initial value of 6.5 to 11.5 in 4 minutes and slowly decreased to 9.0 over 24 hours. A. Barkatt *et al.*[5] investigated leaching behavior of superconducting $YBa_2Cu_3O_{7-s}$ phase in water and in 0.05 M KI. They found the selective occurrence of two processes, leaching of barium and loss of oxygen. The pH levels observed in the leachate were 10.1 after 2 hours, 9.3 after 36 hours, and 8.2 after 192 hours.

This paper deals with the water effect on the stability of the superconducting $YBa_2Cu_3O_{7-\delta}$ phase and the mechanism of degradation. $YBa_2Cu_3O_{7-\delta}$ was found to decompose in 3 steps; reduction followed by hydroxylation via hydration, and formation of carbonates by CO_2 uptake, into $BaCO_3$, CuO, $Y_2(CO_3)_3 \cdot 3H_2O$, which is inconsistent with the results of the others reported.

Experimental

Samples of $YBa_2Cu_3O_{7-s}$ were prepared by solid state reaction of Y_2O_3, $BaCO_3$, and CuO powders in a proportion corresponding to the composition of $1/2$ $Y_2O_3 \cdot 2BaO \cdot 3CuO$. The powder was thoroughly mixed in a mortar with pestle, pressed into a pellet and calcined in air at 850°C in an alumina boat for 20 hours. Then the sample was reground, pelletized and sintered at 900 °C in O_2 atmosphere for two days, followed by annealing at 400 °C in O_2 for 11 hours.

X-ray diffraction patterns were recorded with Cu-Kα radiation using a Ni filter on a Jeol diffractometer. The electrical resistivity of the sintered pellet was measured by the conventional four probe method.

The Cu^{3+}/Cu^2 ratio and the oxygen deficiency have been determined by iodometric titration, which was carried out under N_2 atmosphere to avoid air oxidation of iodide ions. Sodium thiosulfate titrant was standardized against KIO_3. Starch indicator was added immediately before the end point.

A confirmation for the oxygen evolution was made by the Winkler method,[6] which is used for the determination of dissolved oxygen in natural water. In this method, the sample is first treated with an excess of manganese(II), potassium iodide, and sodium hydroxide. The white manganese(II) hydroxide that formed reacts rapidly with oxygen to form brown manganese(III) hydroxide.

Infrared spectra was obtained using a Amalect FX 6160 spectrometer by the usual KBr pellet technique.

Scanning electron micrographs were obtained using a Jeol JSM-35 scanning electron microscope.

Results and Discussion

According to the X-ray powder diffraction analysis, a single phase of $YBa_2Cu_3O_{7-\delta}$ has been identified as an orthorhombic crystal system. Its space group is Pmmm with cell dimensions of a = 3.8218 Å, b = 3.8913 Å and c = 11.677 Å, which are in good agreement with the previous work.[7] Measuring the temperature dependence of resistivity for the sintered pellet, a superconducting transition was observed at around 90 K. After keeping in air ($P_{H_2O} \cong 0.032$ atm) for 3 days, this high Tc-phase was analysed by IR-spectroscopy. As shown in Fig. 1, a typical absorption band at 1440 cm⁻¹ was observed and could be assigned to the stretching vibration of the C-O bond due to the formation of $BaCO_3$ on the
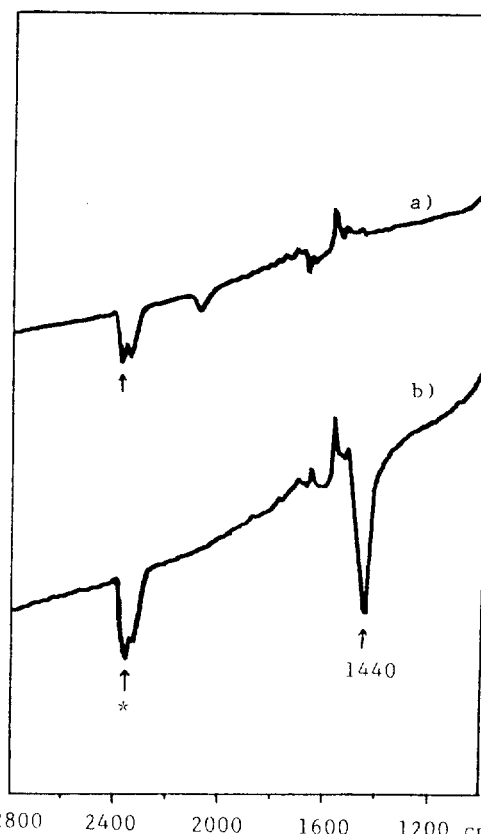

Figure 1. IR Spectra of a) 90 K superconductor $YBa_2Cu_3O_{7-s}$ b) $YBa_2Cu_3O_{7-s}$ kept in humid atmosphere at room temp.
*The absorption band at 2349 cm⁻¹ is due to the C-O stretching vibration of an ambient CO_2.[11]

pellet surface which could not be detected in the 90 K superconductor.[8] The Cu^{3+}/Cu^{2+} ratios of 90 K-superconductor and the air-contacted sample were measured by iodometric titration from which the compositions could be calculated to be $YBa_2Cu_{0.69}^{3+}Cu_{2.31}^{2+}O_{6.85}$ and $YBa_2Cu_3^{2+}O_{6.5}$, respectively. This reulst may indicate that all Cu^{3+} ions present in the 90 K superconductor were reduced to Cu^{2+} ions. Therefore the reactions can be considered as follows;

$$4Cu^{3+} + 4e^- \longrightarrow 4Cu^{2+} \quad (Red.)$$
$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- (Ox.)$$
$$\overline{4Cu^{3+} + 2H_2O \longrightarrow 4Cu^{2+} + O_2 + 4H^+}$$
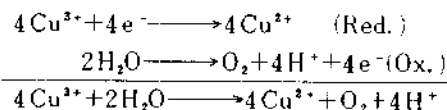
The driving force for the degradation is the high hydration enthalpy of Cu^{3+} compared with Cu^{2+}. According to the Latimer's approximation,[9]

$$\Delta H_h = -69500(\frac{Z^2}{r_{eff}}) \text{ kJmol}^{-1}$$

where Z: charge of the metal ion
r_{eff}: its ionic radius in pm plus a constant, 85 pm, the radius of the oxygen atom in H_2O.

the enthalpies of hydration ΔH_h, for Cu^{3+} ($r_{eff} = 139.7$ pm) and Cu^{2+} ($r_{eff} = 151.7$ pm) ions are -4477 and -1832 kJmol⁻¹, respectively. The radii of Cu^{3+} and Cu^{2+} ions are estimated by averaging the axial and equatorial Cu-O bond distances calculated from the neutron diffraction analysis.[10]

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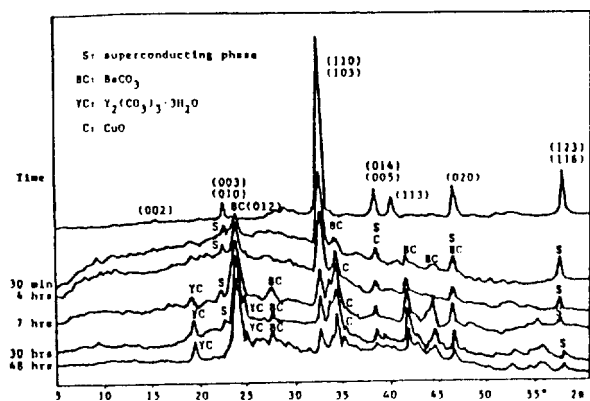**Figure 2.** X-ray powder diffraction patterns for superconducting phase ($YBa_2Cu_3O_{7-\delta}$) and its hydrated products treated with water and kept in an ambient atmosphere.
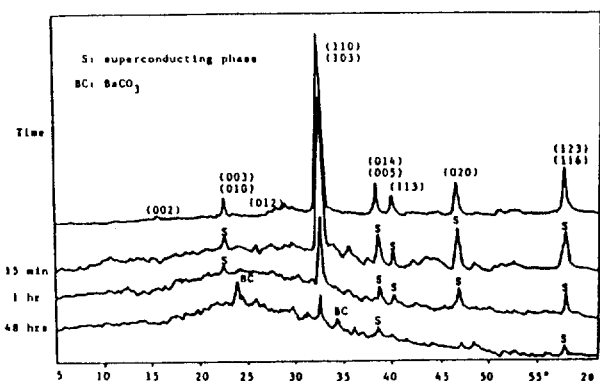

Figure 3. X-ray powder diffraction patterns for superconducting phase ($YBa_2Cu_3O_{7-\delta}$) and its hydrated products kept in de-ionized and de-gased water.

In order to investigate water effect on the stability of the superconductor $YBa_2Cu_3O_{6.85}$, the powder sample was treated with water. Figure 2 and 3 show the X-ray diffraction patterns as a function of time for the samples treated with water and kept in an ambient atmosphere, and in the de-ionized de-gased water at room temperature, respectively. In the former case, the diffraction lines for $BaCO_3$ appeared in 30 minutes and those of $Y_2(CO_3)_3 \cdot 3H_2O$ and CuO about 7 hours later as shown in Figure 2. But in the latter case (Fig. 3), the identifiable diffraction lines due to the formation of $BaCO_3$ could be observed after ~48 h of reaction, which means that the superconducting $YBa_2Cu_3O_{7-\delta}$ phase was degraded more rapidly under the presence of CO_2 in the humid atmosphere than in the de-ionized de-gased water. In addition, when X-ray analysis was performed for the sample mounted on a X-ray sample holder, which was treated with the de-ionized de-gased water, and then covered with a mylar foil (6 um thickness) being not able to protect CO_2 attack completely, $YBa_2Cu_3O_{7-\delta}$ was degraded more rapidly than in water. This may indicate that CO_2 as well as H_2O plays a considerable role in the degradation process. Above observations are consistent with the report from A. Barkatt, *et al.*[5] that the leach behavior of the ternary oxide is highly incongruent, and they observed that a significant fraction of barium is leached away even within the first period of exposure, while copper and yttrium stay undissolved.
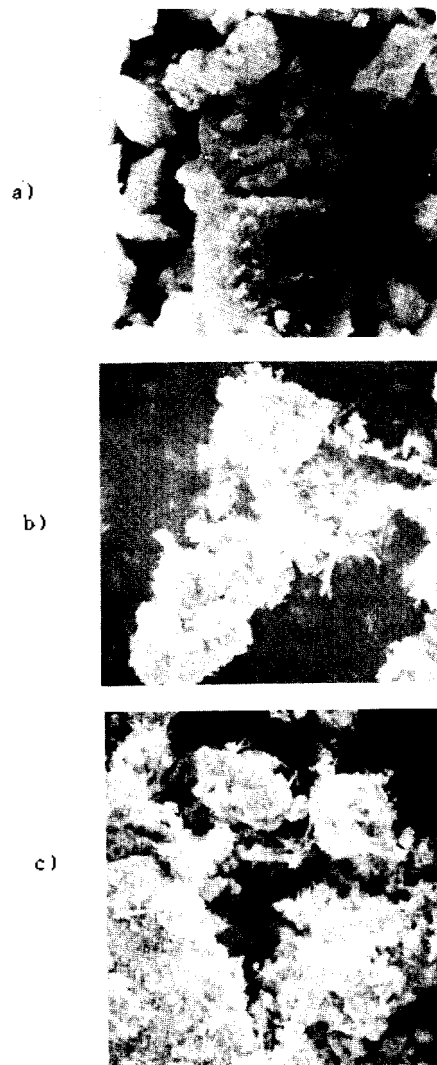
Figure 4. Scanning electron micrographs of superconducting phase ($YBa_2Cu_3O_{7-\delta}$) kept in water for a) 0 min.($\times$ 1200), b) 20 min.($\times$ 5000) and c) 2 days($\times$ 5000).

From these results, we propose the following 3-step mechanism for the degradation of $YBa_2Cu_3O_{7-\delta}$.

Step 1; Reduction of Cu^{3+} to Cu^{2+}.

$$4\,YBa_2Cu^{3+}Cu_2^{2+}O_7 + 4e^- + 4H^+ \rightarrow 4\,YBa_2Cu_3^{2+}O_{6.5} + 2H_2O$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

$$4\,YBa_2Cu^{3+}Cu_2^{2+}O_7 \longrightarrow 4\,YBa_2Cu_3^{2+}O_{6.5} + O_2 \text{--a)}$$

Step 2; Hydroxylation via hydration.

$$4\,YBa_2Cu_3^{2+}O_{6.5} + 14H_2O \longrightarrow$$
$$4\,Y(OH)_3 + 8\,Ba(OH)_2 + 12CuO \text{--b)}$$
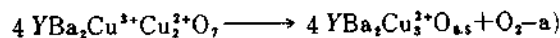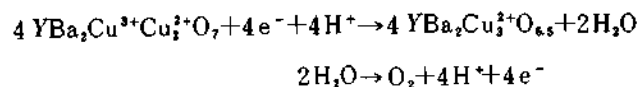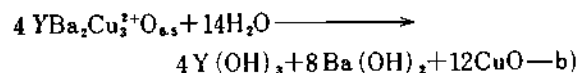
The leached Ba^{2+} ion exists as a hydrated $Ba(OH)_2$ form and the Y^{3+} ion is also hydrolyzed.

a) + b) gives

$$4\,YBa_2Cu^{3+}Cu_2^{2+}O_7 + 14H_2O \longrightarrow$$
$$4\,Y(OH)_3 + 8\,Ba(OH)_2 + 12CuO + O_2 \text{ --c)}$$

Step 3; Formation of carbonates by CO$_2$ uptake.

As the atmospheric CO$_2$ is absorbed, the corresponding carbonates can be formed

$$4\,Y(OH)_3+12H^++6CO_3^{2-} \longrightarrow$$
$$2\,Y_2(CO_3)_3\cdot 3H_2O+6H_2O-d)$$
$$8\,Ba(OH)_2+16H^++8CO_3^{2-} \longrightarrow$$
$$8\,BaCO_3+16H_2O-e)$$

c) + d) + e) gives the overall reaction,

$$4\,YBa_2Cu^{3+}Cu_2^{2+}O_7+6H_2O+14CO_2$$
$$\longrightarrow 8\,BaCO_3+2\,[Y_2(CO_3)_3\cdot 3H_2O]+12CuO+O_2$$

and the reaction products were all found in X-ray diffraction patterns (Fig. 2). And the evolved oxygen was also detected by the Winkler method, that is

$$4\,Mn(OH)_2(s)+O_2+2H_2O \longrightarrow 4\,Mn(OH)_3(s)$$
$$\text{(white)} \qquad\qquad \text{(brown)}$$

The color change of the precipitate from white to brown has been actually observed, which indicates the evolution of oxygen due to the reduction of YBa$_2$Cu$_3$O$_{7-\delta}$ phase and the oxidation of water as described in eq.(a). From the quantitative determination of oxygen evolution, δ value was estimated as 0.16, which is consistent with that from the iodometric titration($\delta=0.15$).

As shown in Fig. 4-b) and c), another strong evidence for the decomposition of YBa$_2$Cu$_3$O$_{7-\delta}$ phase is the morphology of the decomposition products, whose particle size is heavily reduced due to the formation of the corresponding carbonates. No clean surface was maintained, as compared with the original sample (Fig. 4-a)), even after 20 min. of reaction with water.

Conclusion

The superconducting YBa$_2$Cu$_3$O$_{7-\delta}$ phase is very unstable in water and water vapor. Products of its degradation reaction are BaCO$_3$, Y$_2$(CO$_3$)$_3$·3H$_2$O, CuO and O$_2$. The degradation reaction of the superconducing YBa$_2$Cu$_3$O$_{7-\delta}$ phase in water and water vapor proceeds through a series of three steps. The first step is reduction, the second step is hydroxylation via hydration, and the final step is the formation of carbonates by CO$_2$ uptake.

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