REACTIION BETWEEN YBa$_2$Cu$_3$O$_{7-x}$ AND WATER

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ABSTRACT

Reaction between water at 80°C and YBa$_2$Cu$_3$O$_{7-x}$ (0.8<x<0.0) is studied using x-ray absorption fine structure (EXAFS) and x-ray diffraction (XRD). Oxygen deficient YBa$_2$Cu$_3$O$_7$ reacts with water and decomposes into BaCO$_3$, CuO and at least one other Cu containing phase. YBa$_2$Cu$_3$O$_7$ reacts slowly with water and the bulk material is modified before it decomposes. The structural and chemical modifications of this material resemble those reported for YBa$_2$Cu$_3$O$_7$ reacted with hydrogen gas. We conclude that either hydrogen or water enters the bulk before decomposition.

INTRODUCTION

An important limitation hindering some applications of high T$_c$ copper oxide superconductors is their sensitivity to atmospheric moisture and water. It has been shown that YBa$_2$Cu$_3$O$_7$ samples decompose when mixed with water and x-ray diffraction patterns show that CuO, BaCO$_3$, Y(OH)$_3$ and other phases containing Y, Ba, Cu and O are the reaction products. Oxygen gas is also liberated and volumetric studies have been reported. The reactivity of the 1-2-3 phase with water is not unexpected because Cu and/or O may be in oxidation states (i.e. Cu$^{3+}$ or O$^−$) which are susceptible to reduction and both Y and Ba form oxides that are easy to hydrate. The kinetics of YBa$_2$Cu$_3$O$_7$ corrosion is likely to depend on the oxygen content. Harris and Nyang report that oxygen deficient material loses its superconductivity faster than YBa$_2$Cu$_3$O$_7$ and suggest that the presence of oxygen vacancies accelerates the reaction between 1-2-3 and water by providing channels for easy transport of water into the lattice. They also conclude that water reacts with Ba to create a bulk lattice defect.

In this paper, XRD and EXAFS and x-ray absorption near-edge structure (XANES) measurements are used to study the interaction of YBa$_2$Cu$_3$O$_{7-x}$ with water. The data show that oxygen deficient 1-2-3 material reacts completely with water during the time it is present for reaction and that a highly disordered reaction product forms. YBa$_2$Cu$_3$O$_7$ retains the perovskite structure when exposed to water for the same duration but some of the Cu ions are reduced. Comparing the data with results reported by Yang et al. for H$_x$YBa$_2$Cu$_3$O$_7$ and Harris and Nyang for the 1-2-3 material exposed to water vapor suggest that hydrogen or
water is present in the bulk material after exposure to water.

EXPERIMENTAL

YBa$_2$Cu$_3$O$_7$ and oxygen deficient samples were prepared by the well-known technique and the details are reported elsewhere. For orthorhombic YBa$_2$Cu$_3$O$_7$, the final oxygen firing was 40 hours at 970°C and 8 hours at 700°C followed by furnace cooling to room temperature. Oxygen deficient samples were prepared by re-heating YBa$_2$Cu$_3$O$_7$ at 900°C for a predetermined time. This second firing was terminated by quenching the sample in liquid nitrogen. The oxygen content was deduced from sample weight change relative to YBa$_2$Cu$_3$O$_7$ and samples produced by these techniques gave the expected single phase tetragonal or orthorhombic XRD patterns.

Water exposure was accomplished by mixing distilled water with powdered samples that had been screened through a 400 mesh sieve. Sufficient water was added to form a liquid resembling black paint and the solution was placed on a glass evaporation dish. To accelerate the rate of reaction, the solutions were heated to 80°C on a hot plate and the reaction ended by the complete evaporation of the water. The typical reaction time was approximately 10 minutes. The experimental methodology was designed, in part, to maximize the volume fraction of bulk material reacted with water and the superconductor water mixture was heated to 80°C to reduce reaction time from hours to minutes. For x-ray absorption studies, the reacted material was reground and spread out on scotch tape. Cu k-edge XANES and EXAFS studies were done on the NSLS X-11A beam line at Brookhaven National Laboratory using Si(111) monochromator crystals. A Cu foil standard was run simultaneously with each edge measurement for use as an energy calibration. All near edge spectra are energy referenced to a small peak halfway up the Cu metal edge. Full details of the background removal and EXAFS data analysis procedures employed are contained in Ref. (9). The EXAFS data have been filtered with a Gaussian window and have been weighted to place emphasis on the low z elements. XRD patterns were recorded using a GE XRD-5 x-ray diffractometer equipped with a Cu K-α x-ray source.

RESULTS AND DISCUSSION

XRD patterns (Fig. 1) recorded over a 2θ range 26–40° show the structure of YBa$_2$Cu$_3$O$_7$ and YBa$_2$Cu$_3$O$_{6.2}$ before, marked "a", and after, marked "b", reaction with water. During contact with water, gas bubbles which were probably oxygen are seen. Eickenbush et al. conducted volumetric measurements of the gases liberated during the water reaction with YBa$_2$Cu$_3$O$_7$ which show that this gas is oxygen and indicate that sufficient oxygen is released to suggest the reduction of one Cu$^{3+}$ or O$^-$ ion per unit cell. Both Cu$^{3+}$ and O$^-$ have electrochemical potentials sufficient to disrupt H$_2$O and release hydrogen and oxygen. Bansal and Sandkuhl and Barkatt et al. report that the pH of the water superconductor solution increases during reaction indicating that a strong
base, possibly Ba(OH)₃, forms and goes into solution. Our XRD data show that YBa₂Cu₃O₇ retains the orthorhombic structure after exposure to water while YBa₂Cu₃O₆.₂ loses the tetragonal structure. For YBa₂Cu₃O₆.₂, traces of the 1-2-3 phase, marked "S", remain and weak reflections assigned to BaCO₃, marked "B", and an unknown phase, marked "U" are seen. During reaction with water, this material changed color from black to brownish green, whereas, YBa₂Cu₃O₇ remained black. Examination of all the other oxygen deficient samples show that the same decomposition took place. The presence of BaCO₃ in the samples is due to the reaction of Ba(OH)₃ with atmospheric CO₂.

Cu k-edge XANES spectra for all the samples are shown in Fig. 2a and b. Before reaction with water (Fig. 2a), the Cu k-edge data shows a feature which undergoes a systematic variation with oxygen concentration. A peak near the onset of the Cu k-edge, (E-E₀=0), assigned to a 1s-4p transition, grows with decreasing oxygen concentration. Several earlier studies indicate that the appearance of this state is related to the formation of Cu¹⁺ in the Cu(1), (Chain) site when oxygen is removed from the O(1) site. For water exposed YBa₂Cu₃O₇(Fig. 2b), the 1s-4p state also appears on the Cu k-edge and we interpret this as indicating that a partial reduction of some Cu²⁺ ions to Cu¹⁺ has occurred. The shape of the edge above this feature remains unchanged. For oxygen deficient material (Fig. 2b), the Cu k-edge undergoes a complete change after reaction with water. The 1s-4p transition associated with Cu¹⁺ in the Cu(1) site, either does not increase or disappears into a new edge feature found at higher photon energy. This new edge feature, marked "1", is near the energy found for the 1s-4p transition in CuO reference compound. This may suggest that a compound similar in bonding to CuO has formed but this conclusion must be qualified by the observation that this system is not homogeneous. Small peaks above the main edge attributable to multiple

Fig. 1. XRD patterns for YBa₂Cu₃O₇ and YBa₂Cu₃O₆.₂₅ (a) before and (b) after reaction with water.
Fig. 2. Cu k-edge XANES for the 1-2-3 material before and after reaction with water.

Fig. 3. Cu k-edge EXAFS for the same materials.
Cu k-edge EXAFS, shown in Figs. 3 and 4, show that structural changes accompany the modification of the Cu k-edge. For YBa$_2$Cu$_3$O$_7$, the EXAFS signals (Fig. 3) appear unchanged before and after water exposure. However, Fourier transforms (Fig. 4) show that changes have occurred in the radial distribution function. The positions of the atomic shells show little or no change, but the weight of the atomic shells containing barium which are closest to the Cu(1) and Cu(2) sites is reduced. The ability of EXAFS to analyze the structure of disordered materials is of use in studying the oxygen deficient material after water exposure. All of the EXAFS signals for YBa$_2$Cu$_3$O$_{7-x}$ (0<x<0.8) show the same basic modification. Fewer EXAFS oscillations are seen and they damp out more quickly in k-space. The Fourier transforms for YBa$_2$Cu$_3$O$_6.2$ show the removal of R-space structure due to the higher order shells and this suggests that the reacted material is highly disordered. The copper-oxygen bond length remains almost unchanged because the peak in radial distribution function assigned to Cu-O nearest neighbors does not shift.

Examination of the Fourier transforms for YBa$_2$Cu$_3$O$_7$ after reaction with water and YBa$_2$Cu$_3$O$_{6.25}$ shows that structural changes accompanying the partial reduction of Cu$^{2+}$ for both cases are not equivalent. For YBa$_2$Cu$_3$O$_7$ (unmodified) and YBa$_2$Cu$_3$O$_{6.25}$, going from the orthorhombic to the tetragonal structure causes a shift in the position of higher order shells and changes in the intensity from the shells marked Cu-Y (decreases) and Cu-O-Cu (increases). The shell marked Cu-Ba also undergoes a shift to smaller R number and a slight increase in intensity. However for the water modified YBa$_2$Cu$_3$O$_7$, the shells do not move in R-space and the Cu-Ba shell becomes weaker. In conjunction with the XRD result, we conclude that water has not caused the 1-2-3 material to undergo the
orthorhombic to tetragonal phase transition upon Cu reduction. XRD and x-ray absorption spectroscopy show that the structure of the oxygen deficient material is completely disrupted by water exposure and the material incongruently decomposes into BaCO₃, CuO, and other disordered Y-Ba-Cu-O phases containing Cu²⁺. YBa₂Cu₃O₇ undergoes a much slower reaction and most of the material retains the orthorhombic structure. Bulk changes involving the copper oxidation state, namely, the reduction of some Cu²⁺ to Cu¹⁺ and a change in the structure of the barium site are detected. Our data clearly indicate that the bulk superconductor is being modified during the interfacial reaction with water.

Similarity between the XANES and EXAFS for the water modified 1-2-3 material and 1-2-3 material reacted with hydrogen gas suggests the possible entry of hydrogen into the bulk superconductor. Yang et al.⁶ find that hydrogen readily dissolves in the 1-2-3 material up to ~0.2 atoms/unit cell. Beyond that concentration, a nonsuperconducting hydride forms. They also find that hydrogen does not form a water molecule or hydroxyl radical in the bulk because infrared absorption bands in the 3000-4000 cm⁻¹ range associated with these components are absent. However, bands at 841 and 1467 cm⁻¹ associated with a Cu–H bond were reported. XANES measurements found that hydrogen incorporation causes reduction of some of the Cu²⁺ to Cu¹⁺ and EXAFS results showed the same type of structural modification illustrated in Fig. 4 for YBa₂Cu₃O₇ after exposure to water. Yang et al. report that the Y K and Ba L₂,₃ edges are unmodified by hydrogen uptake.

Loss of oxygen could also cause a reduction of some of the 2+ copper. However, specific changes in the transformed EXAFS spectra which are related to structure for the 1-2-3 phase exposed to water and the tetragonal oxygen deficient phase when compared to YBa₂Cu₃O₇ suggest that this is an unlikely explanation for our experimental results. Ba removal from the unit cell does occur during some stage of the reaction of YBa₂Cu₃O₇ with water. Ba leaching leading to vacancies in the atomic shell containing barium could account for the reduction in those shells, but removal of Ba ions should destabilize the whole YBa₂Cu₃O₇ unit cell. Since little change is seen in the position or intensity of nearby atomic shells, we believe the removal of Ba from the bulk is unlikely at this early stage of reaction between water and the 1-2-3 material.

Reaction of YBa₂Cu₃O₇ with water causes a loss of superconductivity. Harris and Nyang⁵ studied the change in the Meissner effect upon exposure to water and found that oxygen deficient material lost the superconducting phase faster than YBa₂Cu₃O₇. They concluded that oxygen vacancies provide pathways which allow the easy transport of water molecules into the bulk and report that water goes into vacancies in the Cu-O chains near the Ba ion. Reaction with the Ba ion leads to the formation of a lattice defect which at high concentration causes the disruption of the YBa₂Cu₃O₇ lattice. Such lattice defects have been observed in transmission electron micrographs of YBa₂Cu₃O₇ samples exposed to water vapor.¹² Our results are in good agreement with these earlier findings. Entry of water and its interaction with barium would change Cu Is photoelectron scattering from the shells containing
barium and the insertion of hydrogen in an O(1) site for \( O^2^- \) should reduce the copper valence. We do not see the orthorhombic to tetragonal phase transition reported by Harris and Nyang upon the loss of superconductivity in the 1-2-3 samples exposed to water. Vacancies play a key role in the diffusion of oxygen and apparently water in the high \( T_c \) material. Lack of these vacancies in the Cu-O chains reduces the mobility and probably explains the greater stability of \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) relative to the oxygen deficient material.

CONCLUSIONS

We find that the rate of reaction between water and \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) at 80°C is strongly dependent on the presence of oxygen vacancies. Oxygen deficient material with as little as 0.2 oxygen vacancies per unit cell is completely decomposed during the ten minute exposure to water and the reaction produces a highly disordered material containing \( \text{BaCO}_3 \), CuO and at least one other phase containing \( \text{Y, Ba, Cu and/or O} \). \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) is more stable and is not decomposed. XRD and x-ray absorption data show that the orthorhombic structure remains but some of the Cu ions are reduced from \( 2^+ \) to \( 1^+ \) and Cu is photoelectron scattering from the first atomic shell containing Ba is modified. Our data suggest that hydrogen or water is intercalating into \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) prior to the decomposing reaction. If hydrogen or water is being intercalated, comparison with data for \( H_x\text{YBa}_2\text{Cu}_3\text{O}_7 \) and 1-2-3 exposed to water indicates that \( T_c \) and the Meissner effect would be reduced.

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