A study of the reaction of $Y_1Ba_2Cu_3O_{7-\delta}$ superconducting ceramics with water

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The detrimental effect of water on the $Y_1Ba_2Cu_3O_{7-\delta}$ superconducting ceramics has been studied using X-ray diffraction, infrared spectroscopy and transmission electron microscopy. It has been shown that barium carbonate is the major reaction product after reaction. From the viewpoint of the process, the reaction is shown to occur in three stages, e.g. (I) microcrack formation along the layers perpendicular to the c-axis; (II) lattice dissolution which is a consequence of the increasing microcrack density and their subsequent propagation; (III) the formation of the corrosion product.

1. Introduction
An enormous research effort has been made on the $Y_1Ba_2Cu_3O_{7-\delta}$ superconducting ceramics since they were first announced at the end of 1986. Both the physical properties and crystallography have been widely characterized [1, 2]. However, it is essential to understand the environmental effects on this material before any recognized applications are made. It has been reported that both water and certain organic solvents react with this superconducting material. The superconducting ceramic has also been shown to be extremely unstable in the presence of strong acids and bases [3, 4].

The reaction of $Y_1Ba_2Cu_3O_{7-\delta}$ compound with either water or chemical solvents has been studied using such techniques as leaching the powders in the solvents, followed by phase characterization. In the present work, we report a study on the reaction of $Y_1Ba_2Cu_3O_{7-\delta}$ superconducting ceramics using X-ray diffraction (XRD), transmission infrared spectroscopy and transmission electron microscopy (TEM). This work gives more information about the processes of this reaction.

2. Experimental procedures
The bulk specimens were prepared using the well established mixed-powder route, i.e. calcining mixed $Y_2O_3$, BaCO$_3$ and CuO powders, followed by sintering in oxygen at 950°C for 12 h to develop superconducting $Y_1Ba_2Cu_3O_{7-\delta}$ phase. For XRD and infrared spectroscopic analysis, a small amount of the as-sintered specimen was ground into fine powder. The powder was then treated in distilled water for 1 h. XRD phase analysis was made before and after the water treatment. A 300 mg potassium bromide disc was pressed together with two smaller discs containing 1.2 mg of the superconductor before and after the water treatment, respectively. The infrared spectra were measured using a Pye-Unicam SP1100 spectrometer.

Thin foils for TEM examination were prepared using the standard technique, i.e. microslices were obtained from the sintered body, followed by hand polishing and ion-beam thinning. Some ion-beam thinned specimens were immersed in distilled water at room temperature for 12 h. TEM characterizations were performed on the thin foils before and after immersion treatment using a Jeol-200CX transmission electron microscope.

3. Results and discussion
Firstly, the water-treated powder contained small particles of white material on the surface. The white material was not seen in the untreated powder.

![Figure 1](image-url) Infrared spectra for the specimens before and after treatment. 1, KBr disc; 2, KBr disc + powder before water treatment; 3, KBr disc + powder after water treatment.
of BaCO₃, possibly via the hydroxide, in which sense the overall reaction can be written as

\[ Y_{1}Ba_{2}Cu_{3}O_{7-δ} + CO_{2}(aq) \rightarrow \]

\[ Ba(OH)_{2}, \text{ hydroxide intermediate} \]

\[ Y_{1}Ba_{2-x}Cu_{3}O_{7-δ-x} + \delta BaCO_{3} \]

The presence of a small amount of BaCO₃ in the specimen before water treatment is considered to be due to the rapid reaction of the \( Y_{1}Ba_{2}Cu_{3}O_{7-δ} \) superconducting phase with moisture in air during specimen preparation process.

Fig. 2 shows the XRD results for the specimens before and after the water treatment. It can be noted from the results that the as-sintered specimen is a \( Y_{1}Ba_{2}Cu_{3}O_{7-δ} \) single-phase material. In contrast, the trace for the water-treated specimen shows a strong diffraction peak \( 2θ = 27.85° \), indicating the presence of BaCO₃.

Fig. 3 shows a bright-field transmission electron micrograph for as-sintered \( Y_{1}Ba_{2}Cu_{3}O_{7-δ} \) superconducting ceramics. The characteristic feature of the as-sintered specimen is the perovskite structure. The perovskite structure is well indicated in Fig. 3 as the layered structure.

In contrast, Fig. 4 is a bright-field transmission electron micrograph showing the microstructure for the immersion-treated specimen. The most obvious observation is that the perovskite structure has been partially destroyed, combined with formation of microcracks along the layers perpendicular to the c-axis. The microcrack is considered to be a consequence of water diffusion into more open sides of the structure, i.e. between the layers. This may result in a dimensional expansion of the c-axis.

The reaction is well shown at the edges of the thin foil, Fig. 5, which is a bright-field image and the related selected-area diffraction (SAD) pattern. Two distinguished regions can be noted in Fig. 5. Region A, which is thicker compared to region B, shows the partially reacted perovskite structure, combined with some microcracks formed. In region B, however, the reaction is completed, a consequence of thinner cross-section. Another interesting observation for this micrograph is the straight boundaries between the partially reacted regions (A) and the fully reacted regions (B). This is because the reaction proceeds along the direction of the c-axis i.e. the reaction takes place sequentially, moving from one layer to another. The formed products, which have been shown to comprise barium carbonate as the major phase, diffuse away from the boundaries [3].

Fig. 6 is another example showing the microcrack formation along the layers perpendicular to the c-axis. Region A shows the microcracked perovskite structure and region B the reacted products, including some large “debris” from the microcracked structure.