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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.

Fig. 1 shows the infrared spectra obtained in this work for the specimen before and after the water treatment. The water-treated sample has absorptions at 1440, 857 and 690 cm^{-1}. The first two bands are also observed in the spectrum of the sample before the treatment, but they are relatively less intensive and the third band is not visible. These bands closely correspond to those reported for $BaCO_3$ in the literature (Table I).

Therefore, $BaCO_3$ is present in the superconductor even before the water treatment; however, the relative intensities increase after exposure to water which tends to suggest that water accelerates the formation

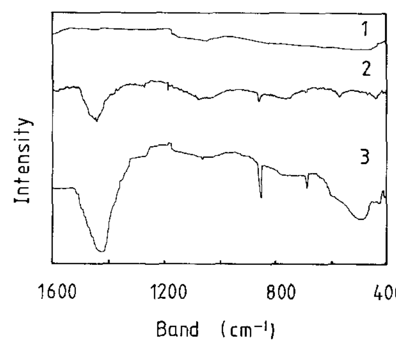

Figure 1 Infrared spectra for the specimens before and after treatment. 1, KBr disc; 2, KBr disc + powder before water treatment; 3, KBr disc + powder after water treatment.

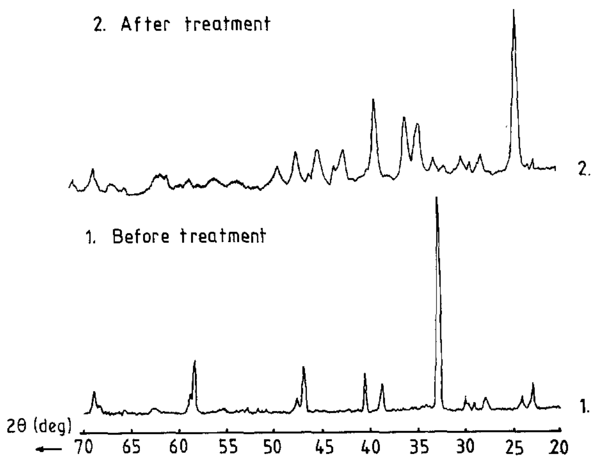

Figure 2 XRD results for the specimens before and after the water treatment.

of $BaCO_3$, possibly via the hydroxide, in which sense the overall reaction can be written as

$$Y_1Ba_2Cu_3O_{7-\delta} + CO_2(aq.)$$
$$\downarrow$$
$$Ba(OH)_2, \text{ hydroxide intermediate}$$
$$\downarrow$$
$$Y_1Ba_{2-x}Cu_3O_{7-\delta-x} + xBaCO_3$$

The presence of a small amount of $BaCO_3$ in the specimen before water treatment is considered to be due to the rapid reaction of the $Y_1Ba_2Cu_3O_{7-\delta}$ 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 $Y_1Ba_2Cu_3O_{7-\delta}$ single-phase material. In contrast, the trace for the water-treated specimen shows a strong diffraction peak $2\theta = 27.85°$, indicating the presence of $BaCO_3$.

Fig. 3 shows a bright-field transmission electron micrograph for as-sintered $Y_1Ba_2Cu_3O_{7-\delta}$ 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.

TABLE I Infrared bands (cm^{-1}) present in $BaCO_3$ and water-treated superconductor

Water-treated $BaCO_3$	[5]	[6]	Assignment
1440	1440	1420	C · O asymmetry stretching
857	858	857	CO_3 out of plane rocking
690	697	692	CO_3 in-plane deformation

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.

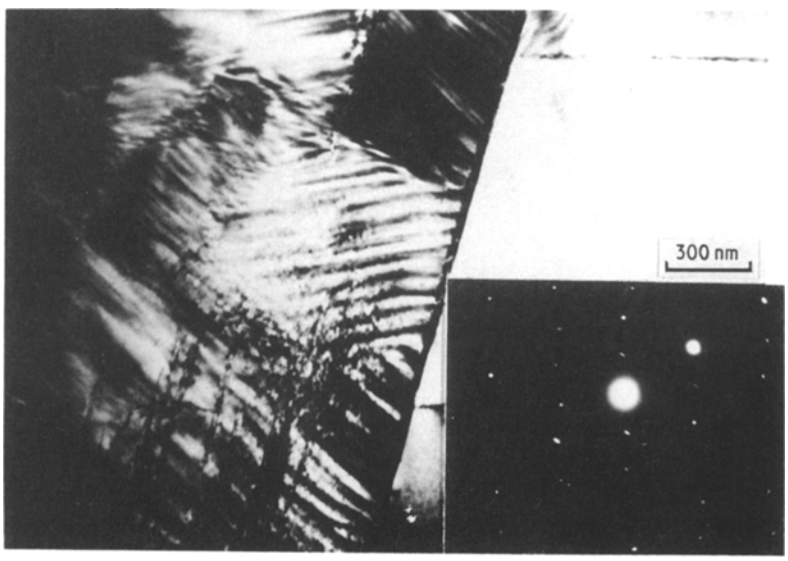

Figure 3 A bright-field transmission electron micrograph showing the perovskite structure of the as-sintered specimen.

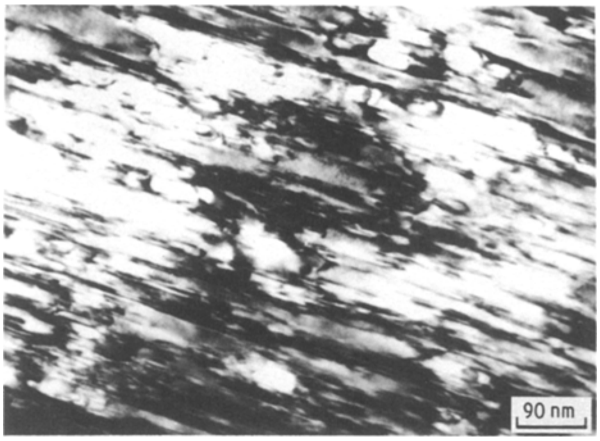

Figure 4 A bright-field transmission electron micrograph showing the partially damaged perovskite structure, combined with some microcracks along the layers.

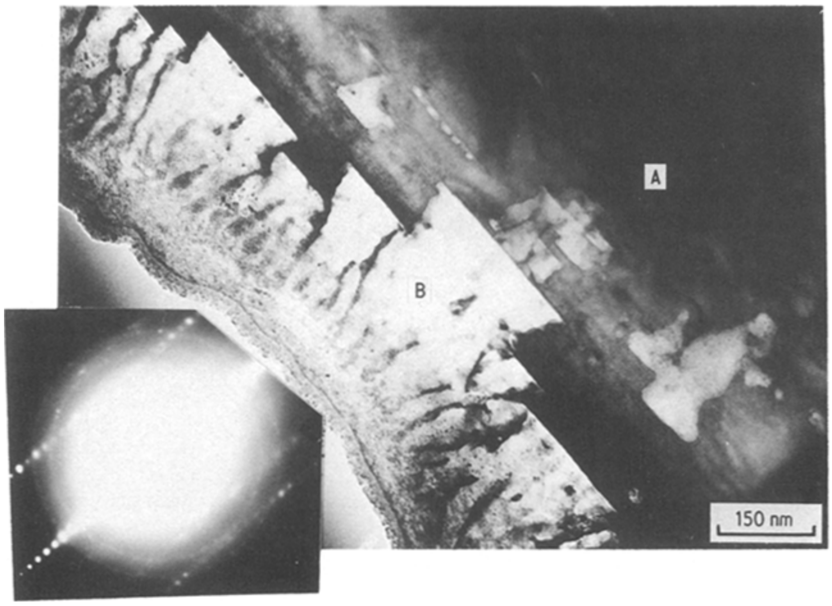

Figure 5 A bright-field transmission electron micrograph and the related SAD pattern showing partially reacted phase (A), and the fully reacted products. The SAD pattern indicates the presence of amorphous phases and microcrystals in the products.

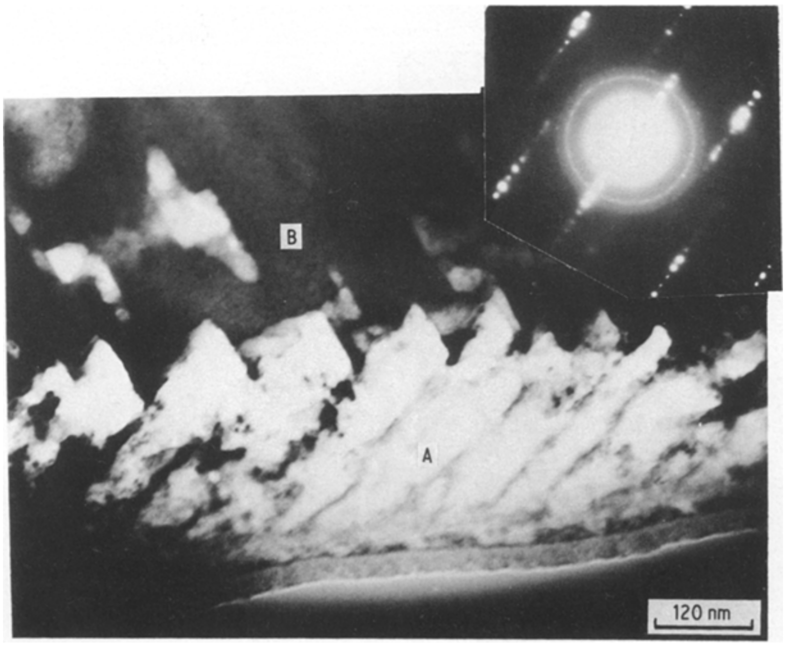

Figure 6 Another example showing the microcracked perovskite structure and the reacted products.

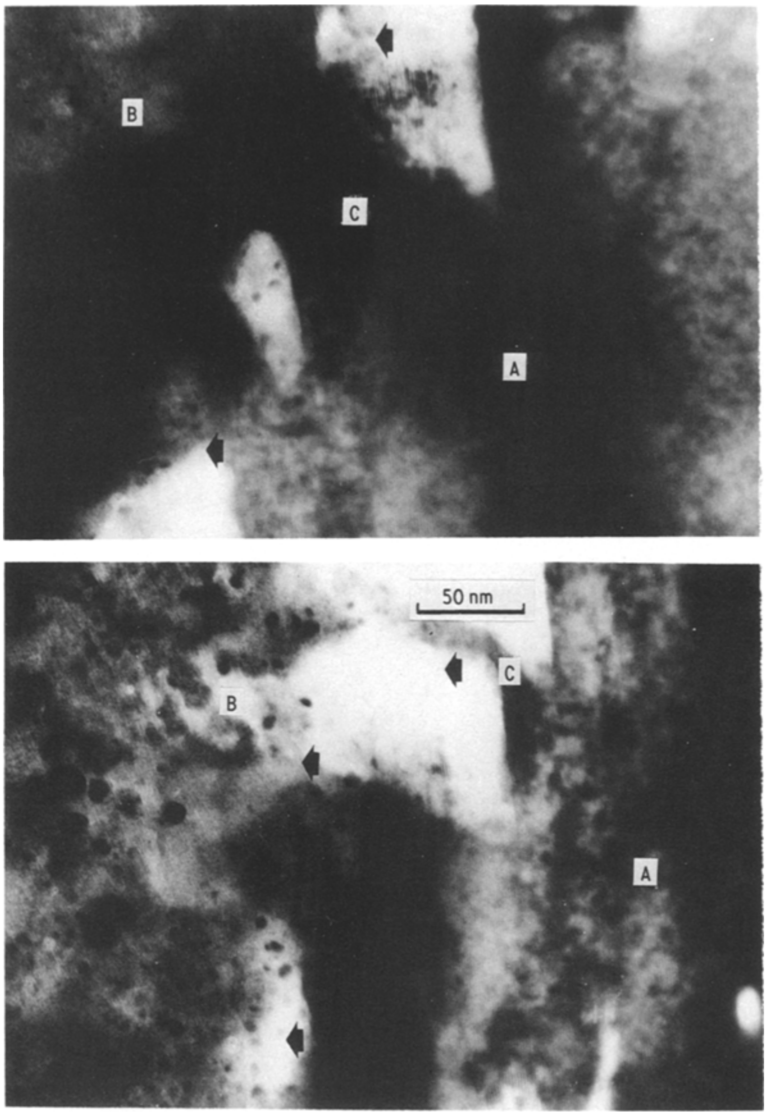

Figure 7 A closer observation of the reaction, indicating the "order–disorder" conversion. Region A is the partially reacted phase; region B is the products and region C is the transition area. It is interesting to note water first penetrates to the spaces between the layers, causing formation of microcracks and eventually the layers collapse toward region B.

Closer observation, Fig. 7, indicates that this region can be described as an "order–disorder" conversion. In region A of Fig. 7, the unreacted perovskite structure shows a clear lattice image. In comparison, the reacted products in region B exhibit a non-crystalline image, although there are some microcrystals present. In the transition region (region C), the processes of the reaction are clearly shown. Water first penetrates into the open sides between layers, causing the lattice spacing to increase, and eventually collapse towards region B.

Fig. 8 is a micrograph showing the fully reacted

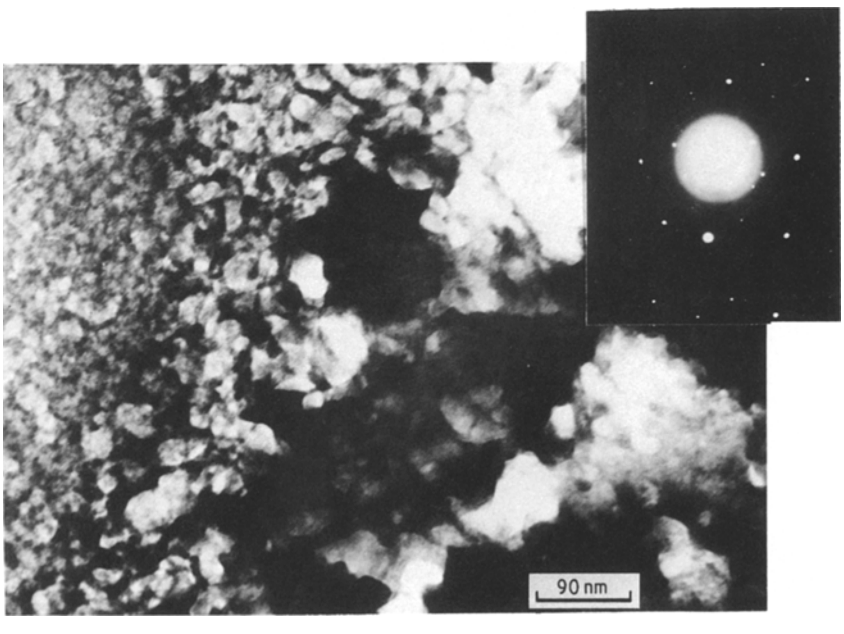

Figure 8 A bright-field TEM image showing the fully reacted products. The related SAD pattern indicates the non-perovskite amorphous phases and some microcrystals.

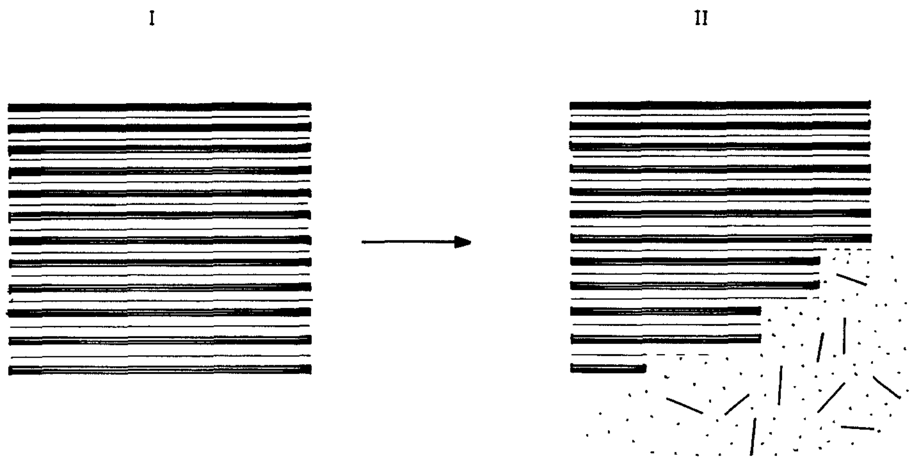

Figure 9 A diagrammatic representation for the reaction of the $Y_1Ba_2Cu_3O_{7-\delta}$ superconducting ceramics with water. I, Water penetrates into the spaces between the layers perpendicular to the c-axis; II, collapse of the lattice caused by the water penetration.

products. The reaction is first considered to result in formation of amorphous phases, which recrystallize and grow to large crystallized phases.

In summary, the reaction of the $Y_1Ba_2Cu_3O_{7-\delta}$ superconducting ceramics with water can be expressed diagramatically by Fig. 9. Water first penetrates into the open spaces between the layers perpendicular to the c-axis. This results in formation of microcracks along the layers. The penetration, and therefore the density of the resultant microcracks, will be increased with reaction time. Eventually, the increasing density of the microcracks and their subsequent propagation destroys the lattice of the material.

4. Conclusions

Both XRD and infrared analysis have shown that the reaction of $Y_1Ba_2Cu_3O_{7-\delta}$ superconducting ceramics with water will result in the formation of $BaCO_3$. TEM study on the reaction indicates that the reaction proceeds in three stages. The first stage is that water penetrates into the open sides of the perovskite structure, resulting in formation of microcracks along the layers perpendicular to the c-axis. The second stage is that the propagation of the microcracks induces an "order–disorder" conversion, which destroys the lattice of the perovskite structure. In the third stage the reaction first produces amorphous phases, which undergo recrystallization and growth to form large crystals.

Acknowledgements

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