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Stability of superconducting $Y_1Ba_2Cu_3O_{7-x}$ phase at 925° C in air

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We have investigated and analysed the stability of superconducting $Y_1Ba_2Cu_3O_{7-x}$ material at 925° C in the normal atmosphere. The material decomposes to $BaCO_3$, CuO, and Y_2O_3 due to the action of moisture and atmospheric gases. The decomposed materials surround grains of the superconducting phase. The decomposed boundary layer appears to be a limiting factor for grain growth and densification. The superconducting materials also develop defects such as stacking faults and/or twins due to prolonged heat treatment.

1. Introduction

Since the first report of high T_c superconductivity in the Y_2O_3–BaO–CuO system in March, 1987 [1], many research groups throughout the world have produced superconducting materials having critical temperatures around 100 K. The superconducting phase has been identified as one having a chemical composition corresponding to $Y_1Ba_2Cu_3O_{7-x}$, hence the shorthand notation of "123" used in referring to these materials. Several investigators have reported synthesizing single-phase materials having the 123 composition.

Before these materials can find wide application as an engineering material, however, a processing technology must be developed that will permit production of these materials in forms that will exhibit high critical current density and mechanical integrity without reduction of their high T_c. As a ceramic material, the 123 superconducting compound has been processed by conventional oxide processing procedures. Contrary to most stable ceramic materials, the properties of the 123 compound have been found to be very sensitive to the oxygen stoichiometry. As such, it has been found that processing parameters such as heating and cooling rates, calcining and sintering times and temperatures, and sintering atmosphere have a profound effect on the end-product properties.

Solid state sintering is commonly used in the production of many high-purity ceramic products and offers a potentially attractive manufacturing process for the 123 material. In general, this process permits control of densification and grain growth through manipulation of time and temperature and also permits control of the oxygen stoichiometry by control of the sintering atmosphere. For solid state sintering to be effective, however, the powders being processed must be stable and chemically inactive. The objective of this investigation was to study the effect of prolonged heat treatment on the stability and sintering characteristics of the 123 compound at 925° C under an ambient atmosphere.

2. Materials and methods

Appropriate molar quantities of Y_2O_3, $BaCO_3$, and CuO were weighed and mixed in a porcelain mortar and pestle. The mixture was doubly calcined at 925° C in a platinum crucible with intermediate grinding and mixing steps. Total calcination time was 30 h. Following calcination, X-ray diffraction showed the product to be predominantly $Y_1Ba_2Cu_3O_{7-x}$. The calcined cake was ground once again and pressed in the shape of a disc approximately 3.2 cm diameter and 0.5 cm thick at a pressure of 2.2 MPa. This disc was then sintered for 12 h at 925° C and then cooled at approximately $2° C\,min^{-1}$. Both the calcining and sintering steps were carried out in a normal atmosphere as opposed to the oxygen-rich atmosphere most often cited by other investigators. Other processing details and properties of the resulting product have been reported elsewhere [2].

Following sintering, the disc was cut into six pieces

TABLE I Density variations in heat-treated high T_c superconductor materials

Sample	Heat time (h)	Density ($g\,cm^{-3}$)		
		As-prepared	Quenched	Slowly cooled
SC-D1	24	5.93	5.78	5.81
SC-D2	48	5.97	5.59	5.78
SC-D3	72	5.55	5.62	5.59
SC-D4	96	5.66	5.66	5.84
SC-D5	120	6.13	5.43	5.81
SC-D6	144	5.94	5.56	5.91

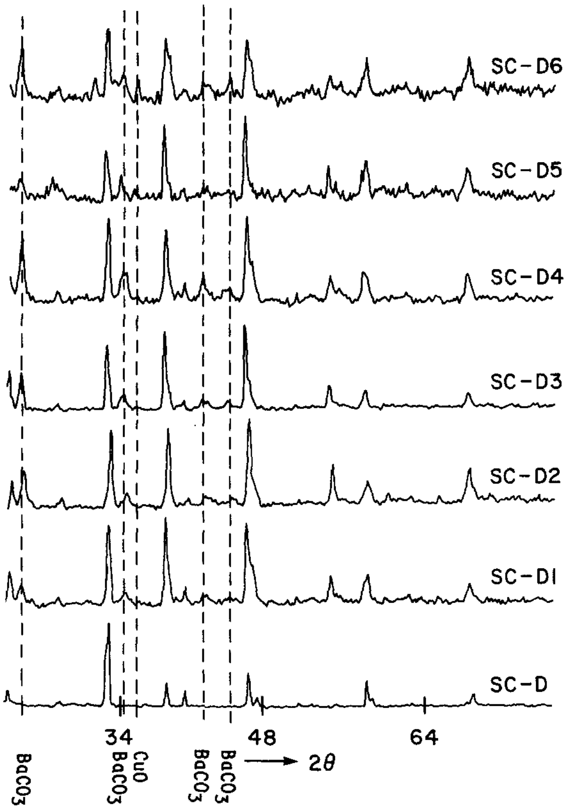

Figure 1 X-ray diffraction patterns from heat-treated specimens rapidly cooled.

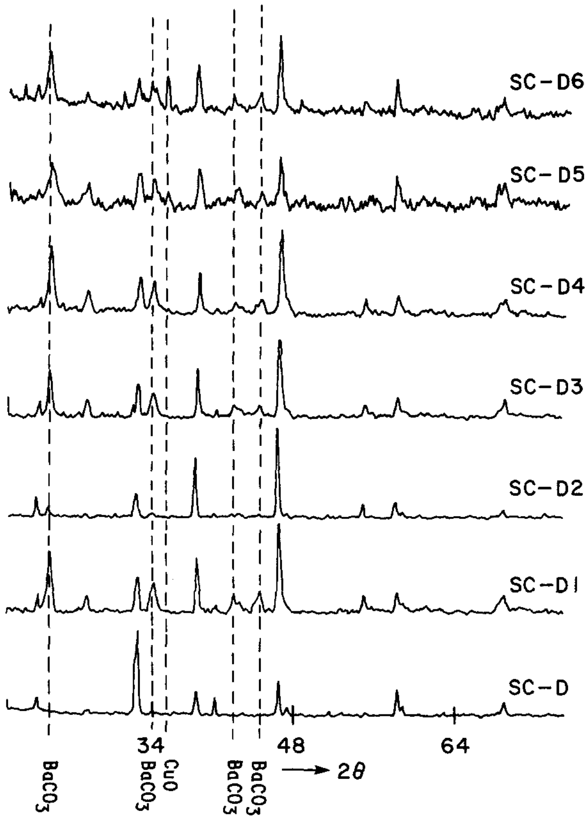

Figure 2 X-ray diffraction patterns from heat-treated specimens slowly cooled.

to be used in the heat treatment study. The apparent density was determined for each piece by the Archimedes method using water as a saturating and suspending medium. After determination of initial densities, the samples were simultaneously placed in a furnace and the temperature was raised to 925° C. At 24 h intervals, an individual sample was removed from the furnace, air-quenched to room temperature, and examined for changes in density, microstructure, and superconducting properties. Characterization of the samples included optical microscopy, SEM, TEM, X-ray photoelectron spectroscopy (XPS), X-ray diffraction, and Meissner effect.

3. Results

Initial density measurement showed an unexpectedly wide variation. The apparent densities, ranging from 5.55 to 6.13 g cm^{-3}, is attributed to non-uniform pressure during the pressing operation. Although the disc was of low aspect ratio, special care was not taken to ensure uniform filling of the die cavity.

Table I shows the changes in density associated with the various heat treatments. In general, the density was observed to decrease with increased thermal exposure. Exceptions to this trend were samples SC-D3 and SC-D4 which correspond to the 72 and 96 h heat treatments.

Following the density determination and X-ray characterization of these samples, all were re-heated to 925° C for approximately 12 h and then furnace cooled at about $2°\text{C min}^{-1}$ as opposed to the earlier quenching. With the exception of sample SC-D3, all samples showed a slight increase in density over the densities of the corresponding quenched samples. These data are also presented in Table I.

Contrary to normal expectation, increasing heat

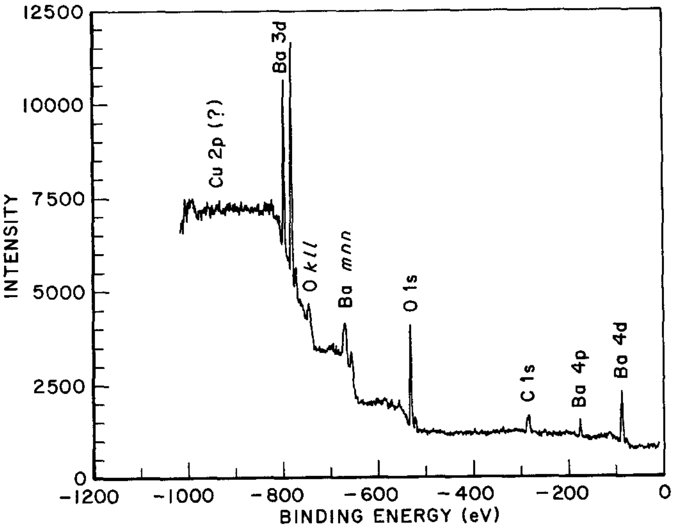

Figure 3 XPS survey scan of the surface of specimen SC-D1.

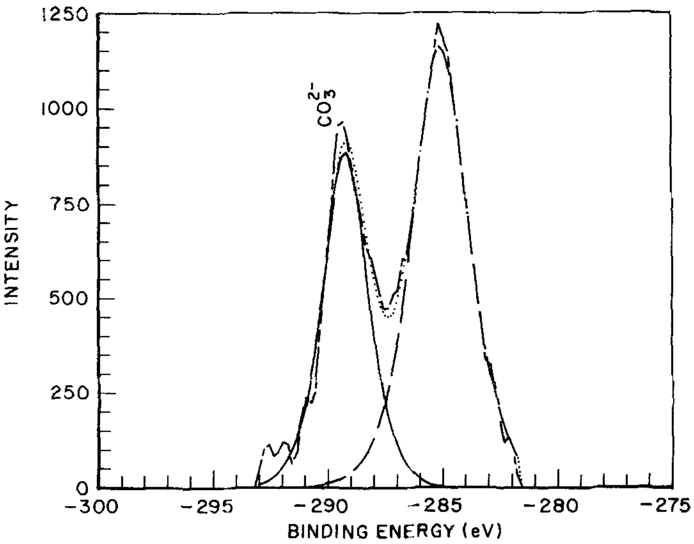

Figure 4 C 1s scan from the surface of SC-D1.

treatment did not result in increasing densification. In fact, all but one sample had lower densities following the heat treatments than they had following the initial sintering. This suggests that the surface activity of the powders was too low to drive the sintering process, that particle sizes of the powders was too large, that the initial sintering was carried out at too high a temperature for too long a time, or that the samples are not stable and are decomposing or reacting at some stage of the investigation.

X-ray diffraction data from the rapidly cooled samples are shown in Fig. 1. Sample SC-D (as sintered) was shown to be single-phase orthorhombic $Y_1Ba_2Cu_3O_{7-x}$. The samples subjected to additional heat treatment showed significant changes in their diffraction patterns. Secondary phases, subsequently identified as barium carbonate and copper oxide, were present in all heat-treated samples. X-ray diffraction studies of the slowly cooled samples, Fig. 2, also show the presence of barium carbonate and copper oxide. In addition, the slowly cooled samples show a significant reduction in the diffracted intensities of the (1 0 3) and (1 1 0) maxima located at about 33° 2θ and the (0 0 5) maximum located near 38.5° 2θ.

Macroscopically, all heat-treated samples developed an uneven, white hazy substance on their exposed surfaces. X-ray photoelectron spectroscopy, Fig. 3, showed the presence of barium, carbon, oxygen. The carbon 1s peak, Fig. 4, showed much of the carbon to be associated with the carbonate group. A semiquantitative analysis showed the Ba : C : O ratio to be approximately 1 : 1 : 3 suggesting the white haze to be barium carbonate. Polishing the white haze from the sample and reexamining with XPS, Fig. 5, shows a reduction in the barium level and an increase in the yttrium and copper levels.

Optical micrographs obtained from polished sections of samples SC-D, SC-D5, and SC-D6 are shown in Fig. 6. The as-sintered samples, SC-D, show the superconducting phase as elongated grains several times longer than wide. A thin boundary layer surrounds each grain and even appears between grains joined together. A highly reflective second phase, indicated by an arrow, was identified by energy dispersive X-ray spectroscopy to be copper oxide. The low apparent density of the sample is obvious from the conspicuous porosity. In general, the microstructure has the appearance of a liquid-phase sintered material rather that of a solid-state sintered material.

Sample SC-D5, which was heat treated for 120 h, exhibits a similar microstructure except for the presence of numerous microcracks or twin boundaries parallel to the long axis of the 123 grains. These were not present in "as sintered" sample.

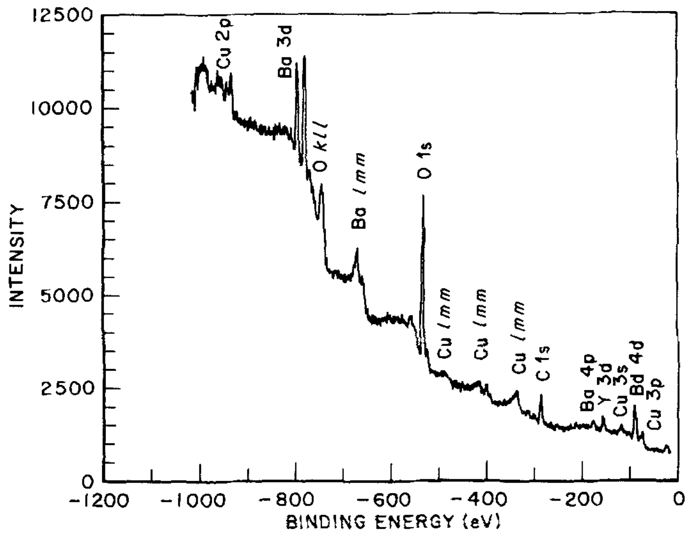

Figure 5 XPS survey scan of polished SC-D1 specimen.

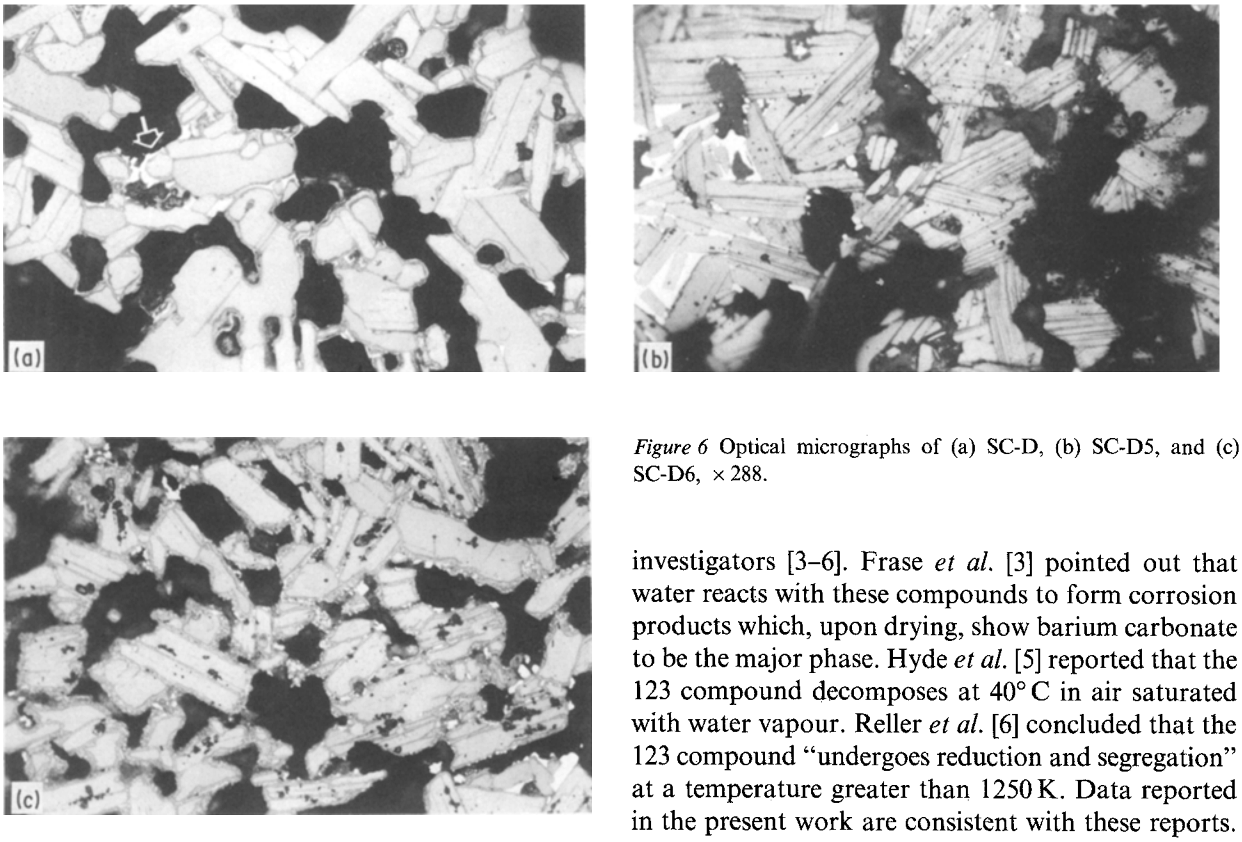

Figure 6 Optical micrographs of (a) SC-D, (b) SC-D5, and (c) SC-D6, × 288.

Sample SC-D6, heat treated 144 h, exhibits a much thicker boundary layer on each grain. This boundary layer which shows a uniform thickness, appears to be multiphase and is suspected to be a mixture of $BaCO_3$, Y_2O_3, and CuO. Both the barium carbonate and the copper oxide were detected in this sample by X-ray diffraction.

An electron micrograph of specimen SC-D6 is shown in Fig. 7. Stacking faults are clearly shown. Electron diffraction patterns from sample SC-D established lattice parameters for the as-sintered material to be $a = 0.385$ nm, $b = 0.397$ nm and $c = 1.19$ nm. This corresponds to a unit cell volume of 0.181 88 nm^3. Similar data gathered for sample SC-D6 yielded values of $a = 0.388$ nm, $b = 0.392$ nm, and $c = 1.169$ nm and a unit cell volume of 0.177 80 nm^3.

4. Discussion

The data presented show a clear degradation of the 123 material with increasing heat-treatment time at 925° C in an air atmosphere. It appears that the compound progressively reacts with atmospheric moisture and gases and is decomposed to $BaCO_3$, CuO, and Y_2O_3. These constituent materials are observed to surround the individual grains of the superconducting phase and the thickness of this boundary layer appears to increase with exposure time. The barium carbonate has also been shown to have a tendency to be leached from the interior of the sintered material and accumulated on the surface of the sample. In addition, crystalline defects in the form of microcracks, stacking faults, or twins appear to develop within the grains during heat treatment.

The unstable character of the 123 compounds at lower temperatures has been reported by several investigators [3–6]. Frase *et al.* [3] pointed out that water reacts with these compounds to form corrosion products which, upon drying, show barium carbonate to be the major phase. Hyde *et al.* [5] reported that the 123 compound decomposes at 40° C in air saturated with water vapour. Reller *et al.* [6] concluded that the 123 compound "undergoes reduction and segregation" at a temperature greater than 1250 K. Data reported in the present work are consistent with these reports.

In addition to the degrading effects of prolonged heat treatment, we also believe that our density measurements, which used water as a saturating and suspending agent, may have contributed to the leaching of the barium carbonate. Preparation for microstructural examination, which used a water–alumina suspension as a polishing medium, may also contribute to the formation of the decomposition products. The possibilities are currently under investigation.

Changes in the 123 compound were also shown by the unit cell parameters determined by electron diffraction. The greatest change was a shrinking of the *c*-axis parameter from 1.190 nm in the sintered material to 1.169 nm in the heat-treated material. Compared to other investigations, the initial 1.190 nm value seems rather high for stoichiometric 123 whereas the 1.167 nm is rather typical. More significantly, prolonged heat treatment resulted in expansion of the *a*-axis and shrinking of the *b*-axis. The result of this change is that

Figure 7 Transmission electron micrograph from specimen SC-D6, × 4519.

the structure appears moving from the original orthorhombic structure toward a tetragonal structure. The shrinking of the *c*-axis and the approach of tetragonal symmetry suggests that prolonged heat treatment in the air environment decreases the oxygen content of the cell. At the point that the oxygen content drops below stoichiometric levels, the 123 compounds are reported to be tetragonal and loose their superconducting properties [7]. The relatively low partial pressure of oxygen in air most likely caused an oxygen-deficient structure.

It is interesting to point out that all the heat-treated samples continued to exhibit the Meissner effect. The samples were cooled to liquid nitrogen temperature and levitated above a magnet. The distance separating the sample from the magnet was taken to be a measure of the superconducting fraction within the sample. As such, it was noted that although the heat-treated samples remained superconducting at liquid nitrogen temperatures, the volume of the 123 superconducting phase decreased with increasing heat treatment.

Although no densification was observed, this is to be expected when one considers the very high porosity of the samples coupled with the apparent instability of the 123 materials discussed earlier. Further work will be necessary to evaluate the effectiveness of solid-state sintering as a fabricating process for these materials.

5. Conclusions

Although we have calcined and sintered 123 material in the normal atmosphere and reasonably good quality specimens have been obtained, the results of this study suggest that the material is unstable at 925° C in air and decomposes yielding $BaCO_3$ and CuO. The decomposition products appear to surround individual grains in the materials as a boundary layer. The thickness of this layer increases with time. The layer is believed to be a limiting factor for sintering and densification. In addition to the decomposition, individual crystals of the material show the presence of defects such as stacking faults and/or twins. As expected, such an unstable nature of the crystals leads to little grain growth and densification as evidenced by density data and optical microscopy. In spite of the degradation, all the specimens exhibited the Meissner effect although with a slight reduction as the heat-treatment time increased.

Acknowledgements

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