JOURNAL OF MATERIALS SCIENCE 23 (1988) 4513–4516

A structural study of the $YBa_2Cu_3O_{7-x}$ superconductor system

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X-ray photoelectron spectroscopy (XPS), X-ray diffractometry (XRD) and analytical scanning electron microscopy have been employed to investigate the structure and microstructure together with the chemical nature of the $YBa_2Cu_3O_{7-x}$ superconductor system at different stages of preparation. XRD studies showed that the original mixture assumed a structure quite similar to that of the final superconductor phase after being sintered at about 900° C in air. While XPS results showed no evidence for copper in any valency other than 2, X-ray-induced Auger features confirmed the existence of monovalent copper at low temperatures. A small shoulder on the O1s spectrum in the final compound proved to be variant with the temperature. The intensity of this shoulder increased relative to the main O1s peak by lowering the temperature. This is believed to be due to the formation of monovalent copper on the top of the sample. Microstructural studies together with point analysis and X-ray mapping showed the existence of different phases in the final compound.

1. Introduction

High-temperature superconductivity was reported by Bednorz and Müller in the system La–Ba–Cu–O [1], and later in the system Y–Ba–Cu–O by Wu *et al.* [2] and others [3]. In the latter system, high-temperature superconductivity with a transition temperature near 91 K was attributed to the compound $YBa_2Cu_3O_{7-x}$ [4] which was crystallographically identified by LePage *et al.* [5]. Despite much effort by numerous workers the true mechanism of superconductivity and the exact chemical nature of the different components involved remains uncertain. This calls for still more fundamental work, particularly on the electronic structure and chemistry of the compound. On the other hand, control and understanding of the microstructure of the material in question is also an important aspect of such studies. In view of this, we initiated a research programme to investigate different aspects of the material at different stages of preparation. We have used X-ray diffractometry (XRD), X-ray photoelectron spectroscopy (XPS), analytical electron microscopy (SEM) and crossed polarized microscopy to characterize the compounds. In an earlier communication [6] we reported a preliminary XPS study on the Y–Ba–Cu–O system at different stages of preparation. The XPS technique proved to be quite informative in spite of the existence of unanswered questions. In this paper we report the results of an extensive investigation on the Y_2O_3–BaO–CuO system in an attempt to clarify further the XPS picture presented earlier [6].

2. Experimental procedure

Detailed information concerning the materials and preparation procedure together with XPS particulars may be found elsewhere [6]. In the present work samples for microscopy studies were mounted in cold resin and polished to a fine finish with diamond paste with the last one being 1 μm. Fracture surfaces were prepared from the sintered samples broken lengthwise. No attempt was made to exclude air from the samples during the preparation processes. A JEOL 840 scanning electron microscope with an energy-dispersive analyser was used for microstructural studies and XRD patterns were recorded on a Philips PW1710 diffractometer.

3. Results and discussion

Fig. 1 shows X-ray diffraction patterns of the original mixture (Fig. 1a), the fired sample prior to any heat treatment (Fig. 1b) and the final product after being annealed in oxygen at 950° C for 12 h (Fig. 1c). The sample was then furnace-cooled in an oxygen atmosphere to ensure equilibration. While the pattern shown in Fig. 1a is a typical pattern of the mixture of oxide powders, patterns shown in Fig. 1b and c exhibit a clear resemblance, suggesting a similar structure. We have already reported, however, that a semi-quantitative XPS analysis showed a significant change in oxygen content of the compound before and after annealing [6]. The identical structures, while the oxygen content varies over a wide range, occur in other oxide systems, e.g. CdO–SnO_2, in which Cd_2SnO_4, Cd_2SnO_3 and Cd_2SnO_2 yield identical X-ray patterns [7]. It can be concluded that after the initial firing, the mixture assumes the perovskite type of structure. The subsequent heat treatment varies the oxygen content only and results in the formation of the superconductor phase. As is evident from Fig. 1c there exist other phases in minute quantities.

Microstructural studies of ceramic superconductors are of particular importance, especially for those with

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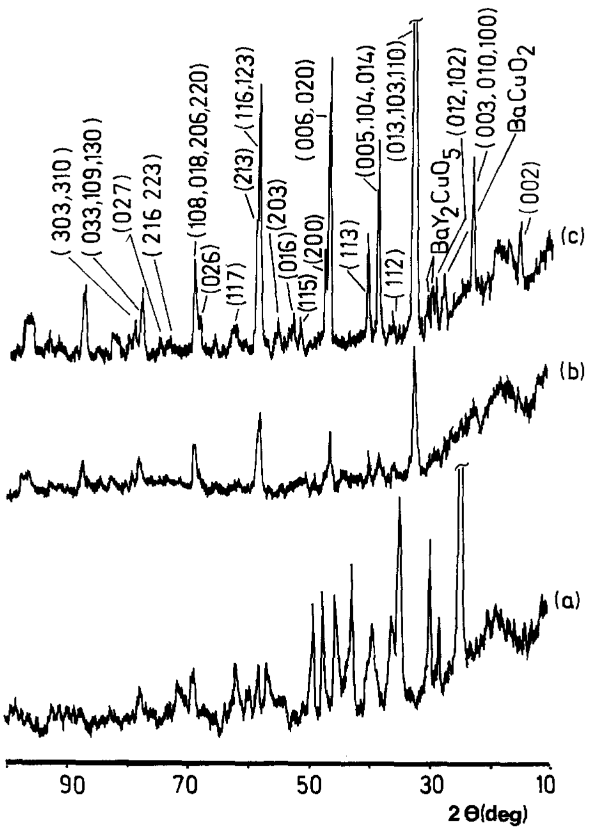


Figure 1 X-ray diffraction patterns of (a) the original mixture, (b) the fired sample prior to oxygen annealing, (c) the final annealed product.

multiphase structures. Not only are the amount and distribution of the superconducting phase, related to compositon and processing, of interest, but the phase distribution seems to determine the critical current density. Fig. 2 shows electron micrographs of a fracture surface of the final product with different magnifications. It is clear from these micrographs that the sample is quite porous and possesses large grains. The mechanical integrity of the specimens produced in this way is invariably poor, and a fracture surface for microscopic examination may frequently be produced by hand. The grains in the final product appear to be heavily grooved, indicating the presence of a wetting phase during the sintering process. The lack of obvious presence of the liquid phase at the boundaries after sintering suggests that the liquid has been mainly retracted. Analysis of this phase by the electron probe indicated that it is copper-rich and yttrium-poor in comparison with the main phase. The phase diagram for the system shows that there is a region of partial melting associated with composition toward the copper-rich, yttrium-poor side of the superconductor phase, and that melting occurs in the range 875 to 950° C. This phase may be considered as a "sintering aid" and provides an obvious mechanism to increase the toughness. However, such a phase which completely wets the grain boundaries may electrically insulate the grains and inhibit superconductivity.

It must be stated at this stage that although one would expect that the use of scanning electron microscopy in the backscattered mode (BSE) would be an ideal technique for microstructural studies in this particular case, there exist certain limitations that one must bear in mind. That is to say, BSE contrast is due to the average atomic number under the beam. Even though $YBa_2Cu_3O_{7-x}$ and Y_2BaCuO_5 (the presence of the latter compound is already confirmed by the XRD technique) have significantly different compositions, they differ in average atomic number by only 0.06, which produces 0.21% contrast between them. Because most BSE detectors fail to discriminate such low contrast, in practice there will not be any significant difference between the two phases in SEM micrographs. In order to overcome this problem, X-ray point, line, and mapping analyses were explored as the means of phase discrimination. Alternatively crossed polarized optical microscopy could well be used, as will be discussed in the next paragraph. Fig. 3 shows X-ray images for the area shown in Fig. 2b. These compositional maps indicate that the composition is uniform within the grains, but there are regions that have large deviations from overall compositions. The analyses at points A to C yielded the average compositions YBa_2Cu_3, Y_2BaCu and BaCu, respectively. Because of the insensitivity of the technique to oxygen no attempt has been made to determine the amount of oxygen in the molecules. Fig. 4 shows an X-ray line scan for the same area under the line drawn on Fig. 2b, for barium, copper and yttrium (top to bottom).

Fig. 5 shows an optical micrograph of a polished superconductor specimen taken under the crossed polarized condition in reflected light. Large grains and the presence of a small amount of the second phase along the grain boundaries are consistent with the

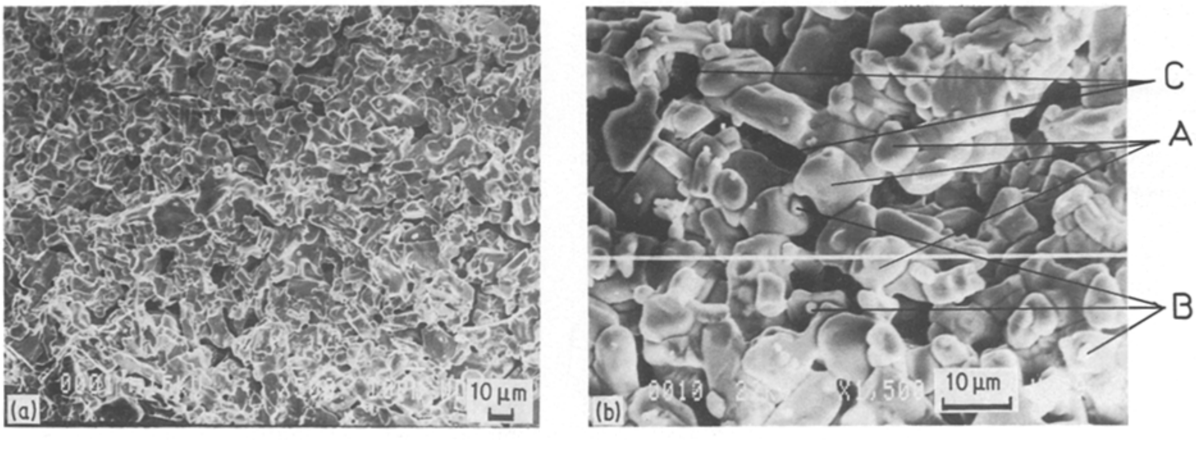
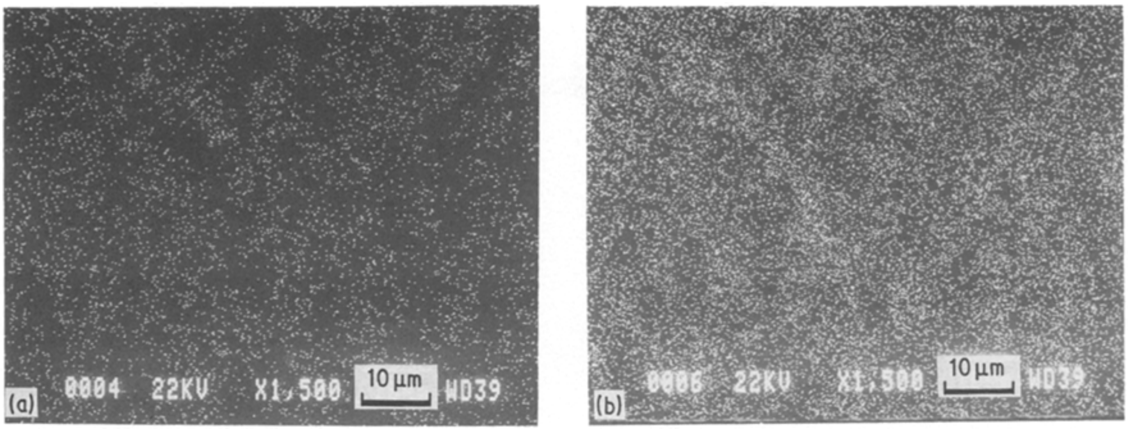


Figure 2 Electron micrograph of a fracture surface with two different magnifications.



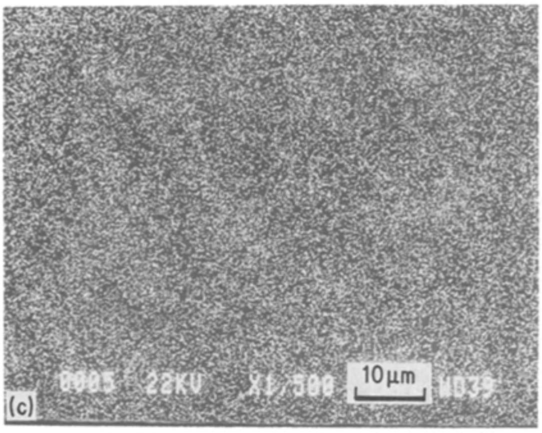


Figure 3 X-ray mappings for the same area as shown in Fig. 2b for the elements (a) yttrium, (b) copper, (c) barium.

samples heated at 950° C. Samples sintered at 900° C had very fine microstructure with a grain size of the order of that in the original powder.

X-ray photoelectron spectroscopy has been shown to be a powerful technique for studies of the electronic structure and the chemical nature of the complex oxide sytems [6, 7]. In a previous report [6] we concluded that the small chemical shift of the O1s peak to higher binding energy compared to the intermediate stage (i.e. prior to oxygen annealing) is due to the difference in oxygen hole concentration. Also we noticed a small shoulder on the lower binding energy side of the main peak with an unknown origin. This shoulder has also been noticed by Kohiki and Hamada [8] and has been attributed by them to Ba–O and Y–O while the main peak is due to Cu–O. While the intensity of this peak is much too small to be explained by both Ba–O and Y–O, its relative intensity increased compared to the main peak with decrease in temperature, while the peaks due to both barium and yttrium remained unchanged. Fig. 6 shows the XPS spectrum of a superconductor sample in the region of O1s for three different temperatures. Clearly the intensity of the shoulder has been increased by lowering the temperature. No other XPS peaks showed any detectable change, in the case of Cu2p perhaps because of poor statistics due to the sharply rising background. Close examination of Auger features, however, revealed that a second peak appears on the lower kinetic energy side of the Auger *LLM* peak characteristic of monovalent copper. Fig. 7 shows X-ray-induced Auger spectra of copper in the copper *LLM* region at three different temperatures. The growing intensity of Cu(I) species is consistent with the increase in the O1s shoulder. Considering these facts it is logical to assume that the two growing peaks are related to each other, and indeed a Cu_2O species is formed at the low temperatures.

Finally, we have also reported a shoulder on the lower binding energy side of the Ba3d spectrum in a superconductor compound [6]. Since the last report, we have noticed the same behaviour in other systems with BaO as a constituent, for example in thermionic dispenser cathodes with BaO as an impregnant. The shoulder on the lower binding energy side of the peak

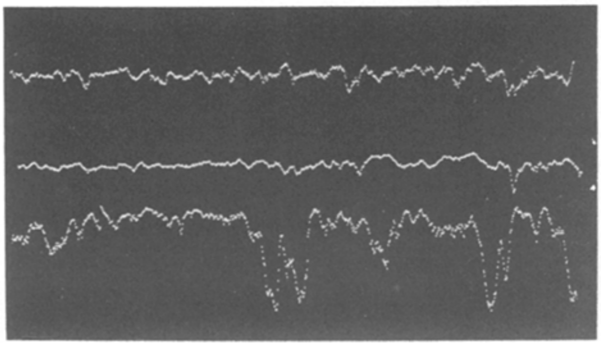


Figure 4 X-ray line scans for the same area under the line drawn on Fig. 2b; barium, copper and yttrium from top to bottom.

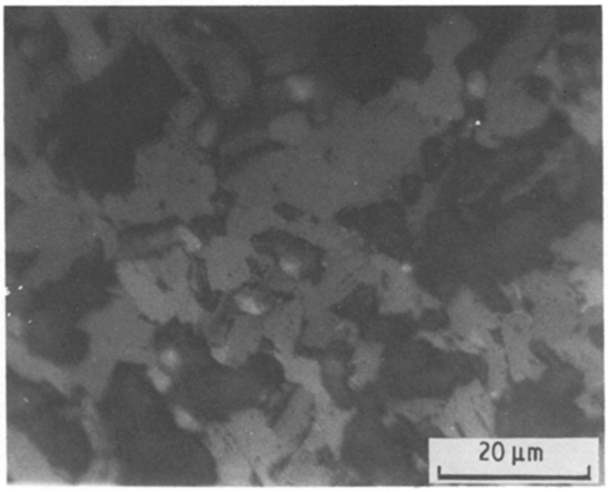


Figure 5 Optical micrograph of a polished superconductor specimen taken under crossed polarized conditions.

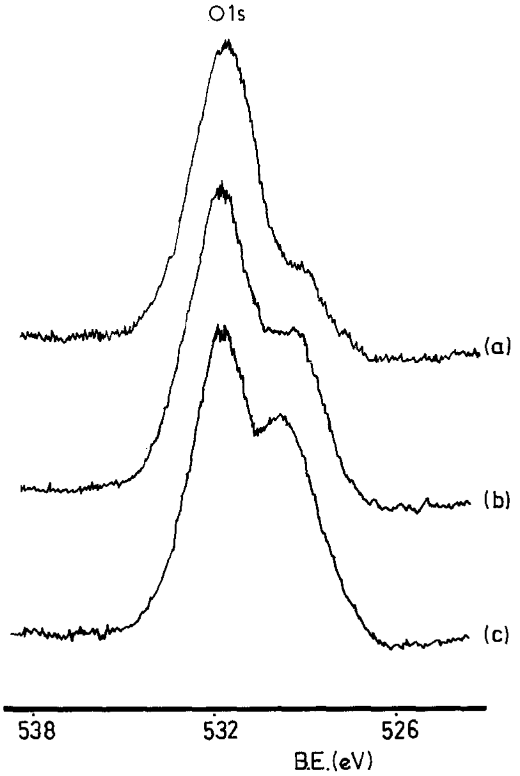


Figure 6 XPS spectra of a superconductor sample in the region of O1s at three different temperatures: (a) 350, (b) 230, (c) 180 K.

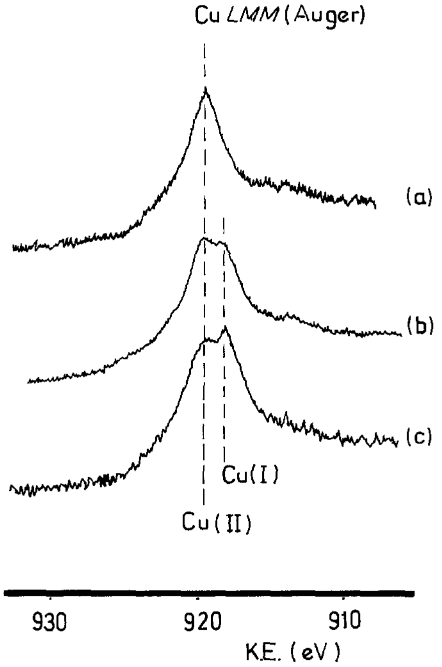


Figure 7 X-ray-induced Auger spectra in the copper *LLM* region at three different temperatures: (a) 350, (b) 230, (c) 180 K.

is believed to be due to metallic barium, judging by the close resemblance to the known binding energy for metallic barium.

4. Conclusions

Investigation of the structure and microstructure together with the chemical nature of the $YBa_2Cu_3O_{7-x}$ superconductor system at different stages of preparation was carried out using XPS, XRD, SEM, and crossed polarized optical microscopy. XRD studies showed that the original mixture assumed a structure quite similar to that of the final compound after an initial firing process at 900° C in air. Microstructural studies showed the existence of different phases in the final compound. Phase discrimination was achieved by means of X-ray mapping, line scans and point analysis. XPS results showed that the small shoulder on the lower binding energy side of the O1s peak in the final phase is due to the formation of monovalent copper at very low temperature, also manifested by the appearance of a peak characteristic of a Cu(I) compound on the X-ray-induced Auger features. The similar shoulder on the Ba3d peak is believed to be due to metallic barium.

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Received 8 February
and accepted 23 February 1988