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Letter

Residual phases in a bulk $YBa_2Cu_3O_{7-x}$ superconductor

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1. Introduction

High temperature superconducting products can contain a certain amount of residual phase(s) in addition to superconducting phase(s), partly owing to kinetics and/or thermodynamics of chemical reactions during the production of superconducting materials from initial mixtures of compounds [1]. For example, CuO was reported to exist in a bulk BiSrCaCuO material [2]. While the material exhibits superconductivity, the residual phase(s) can influence the superconducting and/or other (*e.g.* mechanical) properties. In the present work, the presence of residual phases in a bulk $YBa_2Cu_3O_{7-x}$ superconducting material is systematically investigated using materials science microstructural characterization methods.

2. Experimental details

Bulk ceramic $YBa_2Cu_3O_{7-x}$ high temperature superconductors are usually prepared by intimate mixing of a stoichiometric mixture of CuO, Y_2O_3 and $BaCO_3$ followed by various mechanical and heat treatments [3]. In the current work, the $YBa_2Cu_3O_{7-x}$ superconducting material was obtained from Imperial Chemical Industries Advanced Materials, Runcorn, UK, where it had been fabricated by viscous processing and extrusion, followed by sintering [4,5]. Diffraction study was carried out with a Philips X-ray diffraction instrument. A JSM T-200 scanning electron microscope fitted with a qualitative energy dispersive X-ray (EDX) analyser (incapable of light element analysis) was used for scanning electrom microscopy and transmission electron microscopy (TEM) work was carried out using a JEM 100CX electron microscope fitted with a scanning unit and quantitative EDX facility. Oxygen contents were determined by stoichiometry in all analysis results. TEM sample preparation involved ion beam thinning as the last thinning stage before perforation.

3. Results

3.1. X-ray diffraction

Plane spacings in a sample were determined by X-ray diffraction. It is almost certain that the material contains $YBa_2Cu_3O_{7-x}$ and CuO phases, since diffraction peaks at $d = 0.253$, 0.187 and 0.151 nm appeared; these corresponded to $\bar{1}11+002$, $\bar{2}02$ and $\bar{1}13$ of the CuO phase respectively [6].

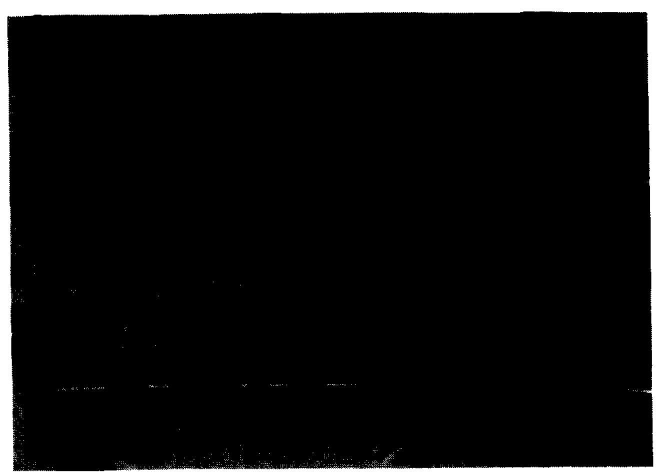

Fig. 1. Scanning electron micrograph showing the apparent two-phase structure of the superconductor material. The dark phase was found by analysis to contain almost only Cu, plus a possible light element, oxygen. The bar length is 10 μm.

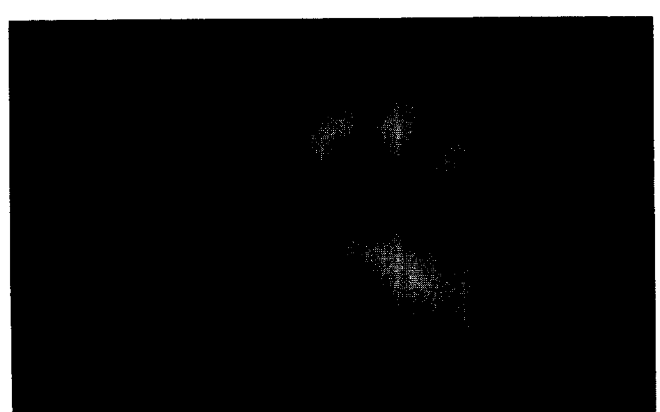

Fig. 2. Transmission electron micrograph showing a region containing CuO phase as labelled.

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3.2. Scanning electron microscopy

Fig. 1 is a backscattered scanning electron micrograph of a $YBa_2Cu_3O_{7-x}$ sample. Chemical analysis showed that the dark phase contained almost only Cu, in addition to light elements such as oxygen which the detector was not able to analyse. The volume fraction of these CuO particles is a few percent. It is not obvious whether other phases are present.

3.3. Transmission electron microscopy

TEM diffraction and analysis work showed convincingly that the sample contains the CuO phase. Fig. 2 shows a thin area containing CuO as one of the three grains. Chemical analysis indicated that it contains a very small amount of Ba, with Ba:Cu = 0.03 (at.%). Analysis showed another CuO grain which contained twice as much Ba, with Ba:Cu = 0.06.

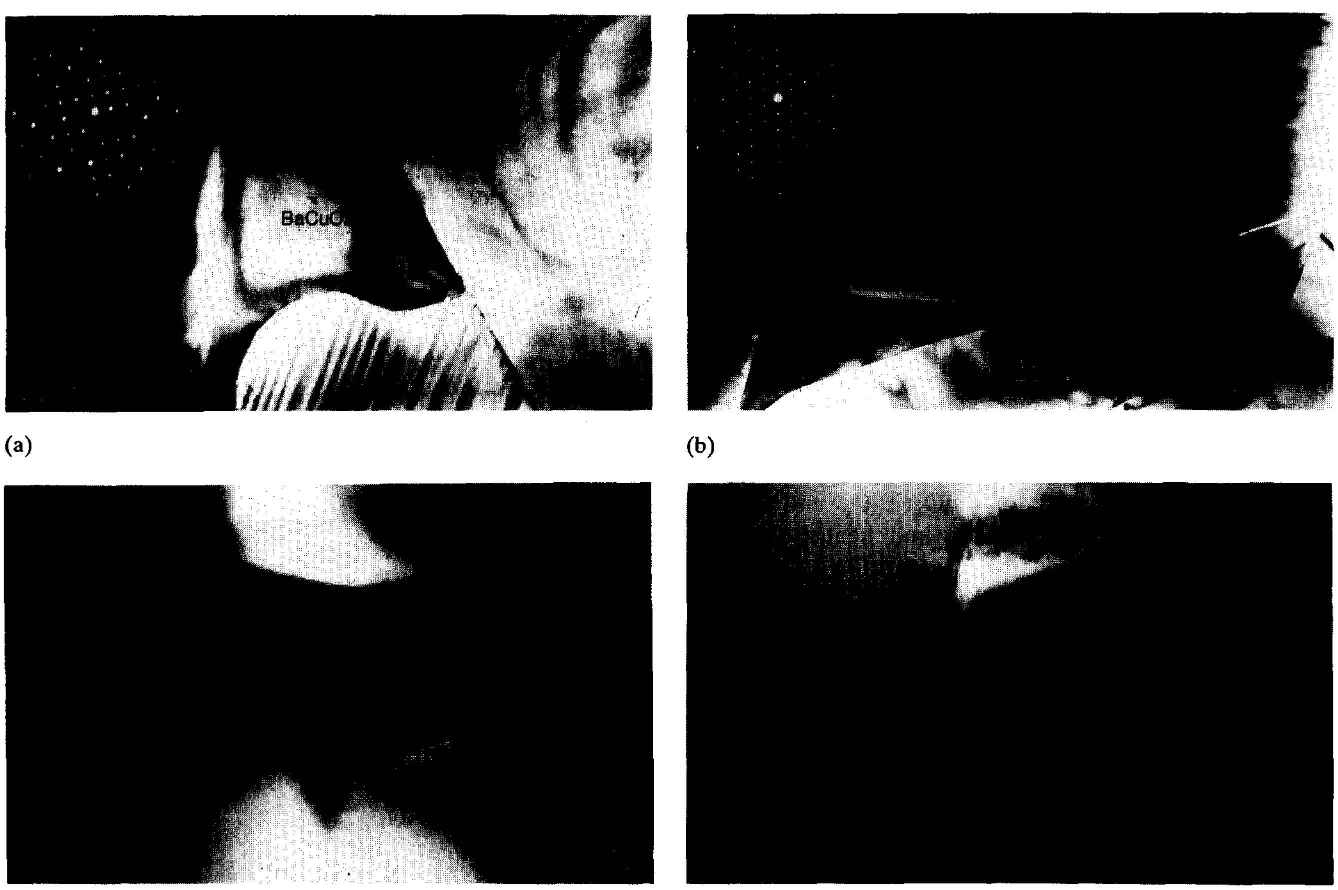
In addition to the residual CuO phase, TEM also showed the existence of a third phase, identified by electron diffraction as $BaCuO_2$. Figure 3 shows several electron micrographs of regions containing this phase illustrating its different morphologies; inevitably it appears dark in all images with any sample orientation, due to a high average atomic mass compared with $YBa_2Cu_3O_{7-x}$ and CuO. Chemical analysis showed that the particle in Fig. 3(c) has a Cu:Ba ratio of 1.2 (at.%), while the particle in Fig. 3(d) has a Cu:Ba ratio of 1.5 (at.%). The excess Cu in these samples could be due to contributions from the surrounding $YBa_2Cu_3O_{7-x}$ phase or instrumental accessories containing Cu inside the microscope.

Figure 4 shows a case where a $BaCuO_2$ particle is embedded in a CuO grain, the latter having dislocation as well as twin structures. Both the twin and the matrix of CuO were analysed and found to be free from Ba, while the $BaCuO_2$ particle was found to have a composition of $BaCu_{1.1}O_{2.1}$.

No apparent orientation relationship between the three phases was identified.

4. Discussion

Traditionally, a $BaCuO_2$ sample was made by heating a pellet of a 1:1 molar mixture of $BaCO_3$ and CuO at temperatures similar for the reaction to form



(a) (b) (c) (d)

Fig. 3. Transmission electron micrographs showing regions containing the $BaCuO_2$ phase. Diffraction patterns from $BaCuO_2$ are shown as insets in (a) zone axis ⟨100⟩ and (b) zone axis ⟨111⟩.

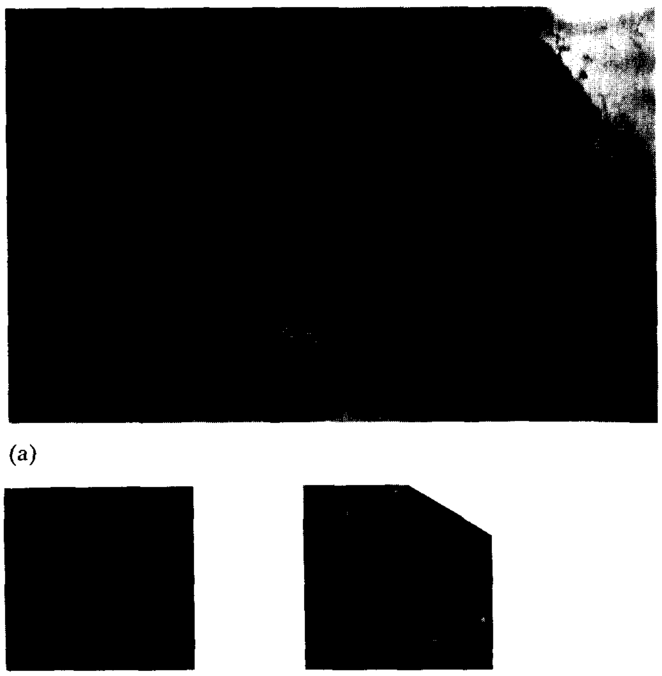


Fig. 4. Transmission electron micrograph showing a $BaCuO_2$ particle embedded in a CuO grain (a), and corresponding diffraction patterns from $BaCuO_2$ (zone axis $\langle 3\bar{4}1 \rangle$) (b) and CuO (c). The diffraction patterns were printed with a different magnification than that used in Fig. 3.

$YBa_2Cu_3O_{7-x}$ superconductors [7]. Both of the starting materials were used in the synthesis of the bulk $YBa_2Cu_3O_{7-x}$ superconductor studied in this experiment. As shown above, there is excess CuO during the reaction process and it is likely that CuO and $BaCO_3$ react to form the $BaCuO_2$ phase present in the final product. It is interesting to note that many of the residual $BaCuO_2$ particles exist at triple grain junctions. More interestingly, but reasonably, the CuO grain with a $BaCuO_2$ particle embedded is free from Ba, while the other two analyses show that CuO without adjacent $BaCuO_2$ does contain a small amount of Ba. It may be noted that the initial powder size is of the order of 0.2 μm [4]. However, this $BaCuO_2$ phase is present with only a very small volume fraction, estimated to be much less than 1%.

The correlation between the existence of these two kinds of residual phases and product superconducting properties is not clear at present.

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