

Effects of bismuth replacement for copper on the microstructure and superconductivity of $\text{YBa}_2\text{Cu}_3\text{O}_y$

N. YANG, R. S. LIU, W. N. WANG, P. T. WU

Materials Research Laboratory, Industrial Technology Research Institute, 195-5, Chung Hsing Road, Section 4, Chutung, Hsinchu 31015, Taiwan

The partial replacement of copper with bismuth in $\text{YBa}_2\text{Cu}_3\text{O}_y$ had led to a new phase instead of crystal site substitution. The resulting YBa_2BiO_6 could also be found whenever $\text{YBa}_2\text{Cu}_3\text{O}_y$ reacted with Bi_2O_3 . The YBa_2BiO_6 was formed either at the expense of $\text{YBa}_2\text{Cu}_3\text{O}_y$ or by decomposing it, together with the liberation of copper oxide. Electrical measurements revealed the trend toward increased semiconducting normal state resistivity for bismuth-replaced samples. The insulating YBa_2BiO_6 phase was responsible for the deterioration of both superconductivity and mechanical strength.

1. Introduction

Since the discovery of superconductivity in La-Ba-Cu-O by Bednorz and Muller [1], elemental substitution based on the perovskite structure has produced several new families of superconducting materials with improved T_c such as the 90 K Y-Ba-Cu-O [2], 110 K Bi-Sr-Ca-Cu-O [3] and 125 K Tl-Ba-Ca-Cu-O [4]. Further substitutions were carried out in an attempt to modify the existing compound and to interpret the superconducting mechanism.

Bismuth has been introduced into the $\text{YBa}_2\text{Cu}_3\text{O}_y$ (1-2-3) system to replace yttrium partially [5] and is reported to have improved the grain contact by forming flux during sintering. It was also used as an oxide additive in the 1-2-3 system [6] which possibly resulted in liquid-phase sintering. However, the mechanism and its effect were not clear. Jung *et al.* [7] have tried yttrium substitution with bismuth at higher contents and claimed $\text{BiBa}_2\text{Cu}_3\text{O}_y$ formation and concluded that there was no solubility of bismuth in the yttrium-based lattice. Blower and Greaves [8] identified the YBa_2BiO_6 structure during the same replacement, and confirmed the resistivity behaviour, which apparently disagreed with previous results.

Most of the experiments attempted the partial substitution of yttrium by bismuth but gave no evidence of the yttrium site occupancy. In addition, the densification phenomenon and the reaction sequence resulting from elemental exchange remains to be substantiated. We have examined the replacement of copper by bismuth in 1-2-3 and investigated the reaction between 1-2-3 and Bi_2O_3 in order to clarify some of the anomaly.

2. Experimental procedure

The materials were prepared by the solid state method using 99% purity Y_2O_3 (Merck), BaCO_3 , CuO

(Riedel-de-Haen) and Bi_2O_3 (Merck) powders according to the molar ratio expressed in $\text{YBa}_2\text{Cu}_{3-x}\text{Bi}_x\text{O}_y$, with $x = 1$ being the maximum. The mixtures were homogenized with ethanol in a micronizer. After drying, the mixtures were calcined at 925°C for 4 h then reground and pressed into pellet. Sintering was carried out in air at 925 and 950°C for 4 to 12 h. The heating rate was controlled at 5°C min^{-1} as in calcination. After sintering, all the specimens were furnace cooled. In order to understand the mechanism of solid state reactions, 1-2-3 powder was prereacted at 950°C and then mixed with Bi_2O_3 in appropriate ratios.

After pressing into discs, heat treatment was performed at constant temperatures. Stoichiometric YBa_2BiO_6 was also prepared in the same way to compare its formation in the presence of CuO . The reactions during calcination were scanned by differential thermal analysis (DTA) and thermogravimetric analysis (TGA) at a heating rate of $10^\circ\text{C min}^{-1}$. Microstructure was examined by optical and scanning electron microscopy (SEM). Superconducting behaviour was characterized through resistivity measurement using a standard four-point method. X-ray diffraction (XRD) analysis on sintered or reacted specimens using $\text{CuK}\alpha$ radiation was performed with a Philips PW 1710 diffractometer.

3. Results and discussion

3.1. Resistivity measurement

The calcined powders displayed colour variations ranging from black to brown as bismuth replacement proceeded. The sintered pellet also showed less shrinkage and lower bonding strength as more bismuth was introduced. Fig. 1 illustrates the superconducting transition behaviour of $\text{YBa}_2\text{Cu}_{3-x}\text{Bi}_x\text{O}_y$ samples. The $x = 1$ specimen is not recorded because its room-temperature resistivity went beyond $200\ \Omega\text{cm}$ which is the limit of the measuring equipment. It is evident that

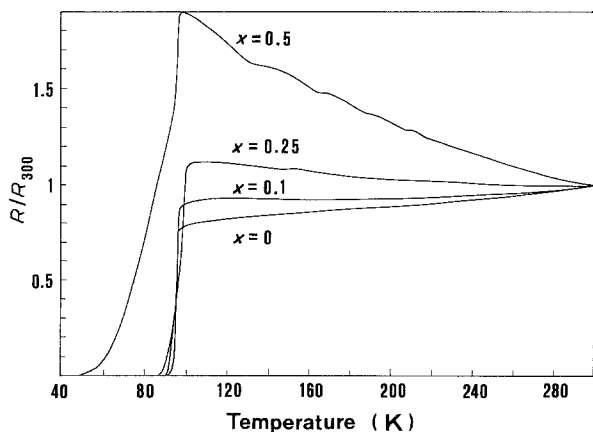


Figure 1 Normalized electrical resistivity as a function of temperature for bismuth-replaced 1-2-3.

as copper was gradually replaced by bismuth, the normal state resistivity became semiconducting and the tailing became more obvious. Because the onset temperature remains the same, the material that is responsible for superconductivity should be the 1-2-3. The tailing extending to low temperatures is indicative of the formation of a non-superconducting phase which accumulates in the 1-2-3 matrix and finally isolates it. The non-superconducting phase was also considered to impede densification and resulted in weak bonding of the sintered pellet.

3.2. Phase identification and reaction analysis

The XRD profiles of sintered specimens are given in Fig. 2. The $x = 0$ compound showed non-

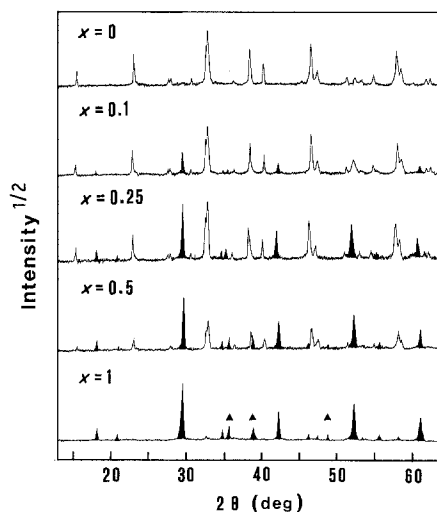


Figure 2 XRD profile indicating gradually emerging YBa_2BiO_6 and CuO (both marked black) coexisting with diminishing 1-2-3 phase as a result of bismuth introduction. The main peaks of CuO are labelled with triangles.

preferentially oriented 1-2-3. As x increases, another group of peaks emerged with increased intensity which was identified to be YBa_2BiO_6 and CuO . No impurity peaks other than these three could be found in the spectrum. The YBa_2BiO_6 phase coexists with 1-2-3 and CuO and varies only in relative intensity over the composition range in this experiment. When $x = 1$, the pattern mainly consists of YBa_2BiO_6 and CuO with 1-2-3 peaks hardly discernible. From the XRD analysis it can be concluded that when bismuth replaces part of the copper in 1-2-3 composition, a proportion of the yttrium and barium sites were taken

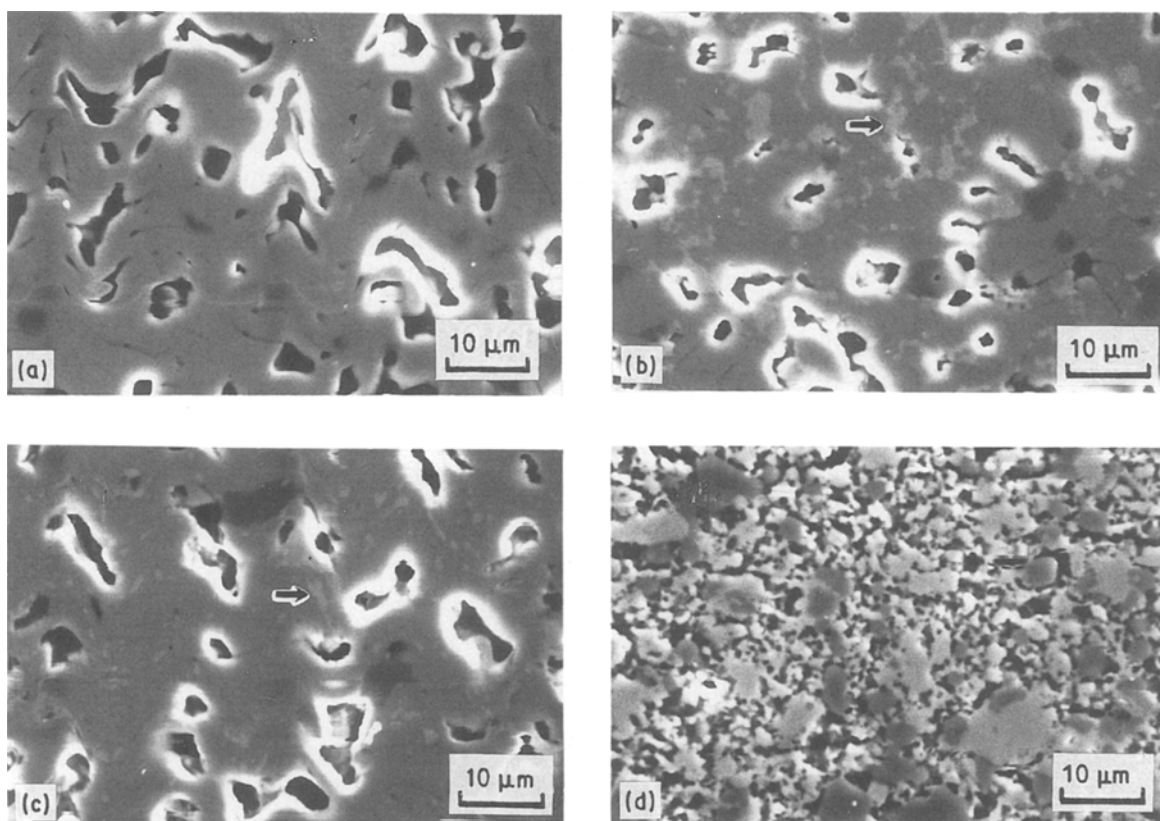
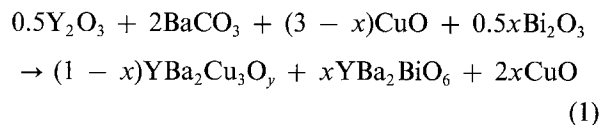
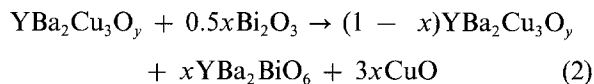


Figure 3 SEM microstructure associated with the replacement. $x =$ (a) 0, (b) 0.1, (c) 0.25, (d) 1. Formation of globular CuO and granular YBa_2BiO_6 (indicated by arrows) became evident when 0.1 mol Cu was replaced by bismuth. As the volume fraction of YBa_2BiO_6 increases, the sintering of 1-2-3 phase become hindered.

by bismuth to form YBa_2BiO_6 , the remainder forming 1-2-3 with surplus copper squeezed out. The reactions are represented by the sequence



When prereacted 1-2-3 powers were heated in the presence of Bi_2O_3 , XRD indicates YBa_2BiO_6 and CuO formation even at 800°C . The reaction seems to follow



According to Reaction 2, the 1-2-3 compound was decomposed by Bi_2O_3 at high temperatures. Binary or tertiary liquid from bismuth, barium and copper might play important roles in the process because the reactions occurred at temperatures below the melting point of Bi_2O_3 where solid state diffusion is not usually dominating.

3.3. Microstructure

Fig. 3 demonstrates the SEM microstructure as bismuth was gradually introduced. The 1-2-3 specimen mainly consists of equiaxed grains and pores, both are several micrometres in size. Impurity phase can be occasionally found gathered along grain boundaries and had been identified as Ba-Cu-O by SEM. The morphology suggests a liquid origin at high temperature and can be traced back to a local fluctuation of composition. The $x = 0.1$ sample contains globular CuO and granular YBa_2BiO_6 dispersed in the matrix but the Ba-Cu-O grain boundary phase can no longer be observed. Further bismuth replacement resulted in higher YBa_2BiO_6 which tended to form a network and the sintering of 1-2-3 particles becomes hindered.

From the disappearance of Ba-Cu-O, it was considered that controlled Bi_2O_3 doping might act as a scavenger in removing grain-boundary film segregation in 1-2-3 material. Because the reaction products YBa_2BiO_6 and CuO are both non-spreading, it may not impair the passage of current as much as does the solidified Ba-Cu-O liquid film.

3.4. YBa_2BiO_6 preparation

Stoichiometric YBa_2BiO_6 preparation indicates that BaBiO_3 formation started at 650°C , which reacts with yttrium later to form YBa_2BiO_6 . Single-phase material was not obtained after treatment at 940°C for 12 h. The pellet showed no shrinkage and was readily fractured indicating no significant sintering at these temperatures. When CuO was introduced, it gave better crystallinity in XRD patterns along with the CuO peaks. The reaction to form YBa_2BiO_6 was possibly catalysed by a transient liquid phase because the specimens shrank appreciably compared to the non-added one.

3.5. Differential thermal analysis

The DTA and TGA tracings in Fig. 5 clearly indicate

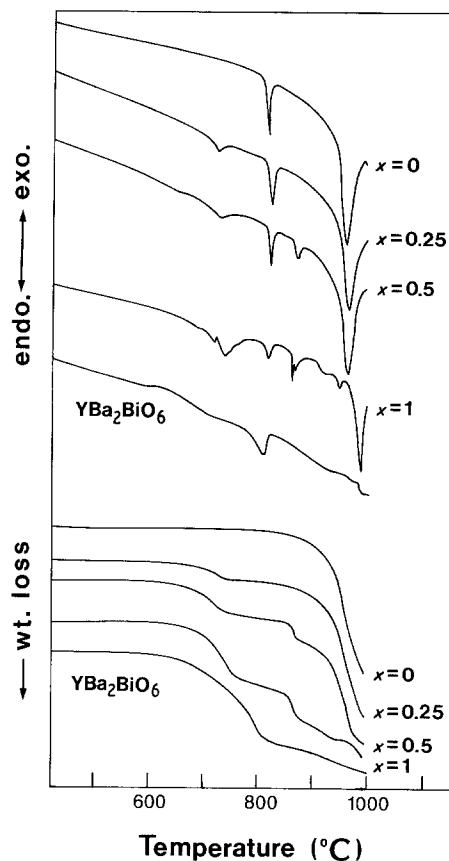


Figure 4 DTA and TGA curves showing BaBiO_3 formation below 700°C in bismuth-replaced compositions. The peak at 860°C corresponds to abrupt weight loss in $x = 0.25$ and $x = 0.5$ samples, considered to be associated with liquid-phase formation.

endothermic events and weight loss below 700°C as bismuth was introduced. The XRD results confirmed the formation of BaBiO_3 in the same temperature range. Another endothermic peak appeared around 860°C for $x = 0.25$ and $x = 0.5$ specimens. The corresponding weight loss inflection suggests accelerated decomposition of BaCO_3 possibly resulting from transient liquid phase formation. The CuO -free YBa_2BiO_6 gives a comparatively simple profile which also manifests incompleteness of the reaction below 1000°C .

4. Conclusions

The effects of bismuth substitution on $\text{YBa}_2\text{Cu}_3\text{O}_y$ have been studied by partial replacement of copper and by reacting $\text{YBa}_2\text{Cu}_3\text{O}_y$ with Bi_2O_3 at high temperatures. Both led to YBa_2BiO_6 and CuO . In the former case, preferential formation of YBa_2BiO_6 consumed part of the raw material, the remainder forming $\text{YBa}_2\text{Cu}_3\text{O}_y$, leaving free CuO . The prereacted $\text{YBa}_2\text{Cu}_3\text{O}_y$ was decomposed in the presence Bi_2O_3 which also resulted in the appearance of YBa_2BiO_6 and CuO . The formation of YBa_2BiO_6 was catalysed by CuO through liquid-phase reactions. The insulating YBa_2BiO_6 accounted for the degradation of both superconducting and mechanical properties.

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