Effects of Bi(x) additives on microstructure and superconductivity in $YBa_{2-x}Bi_xCu_3O_{7-\delta}$

Shanker Ram*
Department of Materials Science and Engineering, McMaster University, Hamilton, Ontario, Canada L8S 4L7 Canada

K. A. Narayan
Department of Chemical Engineering, Indian Institute of Technology, Kanpur-208 016, India
(Received 25 July 1989; revised manuscript received 9 July 1990)

New compositions of the high-T_c superconductor $YBa_{2-x}Bi_xCu_3O_{7-\delta}$, with $x \leq 0.5$, have been prepared by the usual ceramic process. The presence of bismuth ($x < 0.3$) in these compositions activates crystallization of the superconductor phase (which gives an improved $T_c \sim 97$ K), processed at 930 °C/12 h in an O_2 atmosphere. The crystallites exhibit very small sizes and sharp distribution.

I. INTRODUCTION

High-T_c superconductors based on a $Bi^{3+} \rightarrow Y^{3+}$ substituted $YBa_2Cu_3O_{7-\delta}$ composition[1] or the bismuth-containing compositions $Bi_2Sr_{3-x}Ca_xCu_2O_8$ (with $x \neq 0$)[2] have shown better thermal stability and superior superconductivity properties, compared to the pure $YBa_2Cu_3O_{7-\delta}$ superconductor. The growth of the superconductor phase and the superconductivity properties strongly depend on experimental parameters such as sintering temperature, period for the sintering, and the atmosphere in which the sample is processed. Processing for a longer period and at high temperature ruins the superconductivity. An advantage of processing these compositions with bismuth is that Bi_2O_3 appears to function as an internal catalyst and favors growth of the superconductor phase, moderately reducing the sintering temperature and period of the reaction. Bismuth oxide also has been used earlier as a "nucleation catalyst" in the processing of ceramics.[3]

In this Brief Report we report a rather new ceramic superconductor, $YBa_{2-x}Bi_xCu_3O_{7-\delta}$ (with $x \leq 0.5$). The effects of $Bi_2O_3(x)$ additions on the growth of the superconductor phase, superconductivity properties, and microstructure are examined.

II. EXPERIMENTAL DETAILS

The samples $YBa_{2-x}Bi_xCu_3O_{7-\delta}$, with $x \leq 0.5$, were prepared by the solid-state reaction of Y_2O_3, $BaCO_3$, Bi_2O_3, and CuO mixed in the stoichiometric composition. The mixed powder was calcined at 950 °C in air for 12 h, powdered and pressed in pellet form, and finally sintered at 930 °C (at 950 °C for those containing no Bi_2O_3) for 12 h followed by 600 °C/2 h in an oxygen gas flow (~ 250 cm^3/min). The crystallization of the $YBa_{2-x}Bi_xCu_3O_{7-\delta}$ phase was analyzed by using x-ray diffractometry and optical microscopy.

III. RESULTS AND DISCUSSION

The bismuth in the composition series $YBa_{2-x}Bi_xCu_3O_{7-\delta}$, $x < 0.3$, behaves as an "internal nucleation catalyst" and favors the crystallization of pure superconductor phase. The x-ray diffractograms (Fig. 1) reveal the peaks characteristic of a single-crystalline phase for a sintering at 930 °C for 12 h. The samples processed without Bi_2O_3 additives contain impurities due to the reactants and/or the so-called green phase (Y_2BaCuO_5). Several repeated cycles of processing were needed to eliminate the impurity phases,[4,5] but that introduces distortion and several other growth defects.

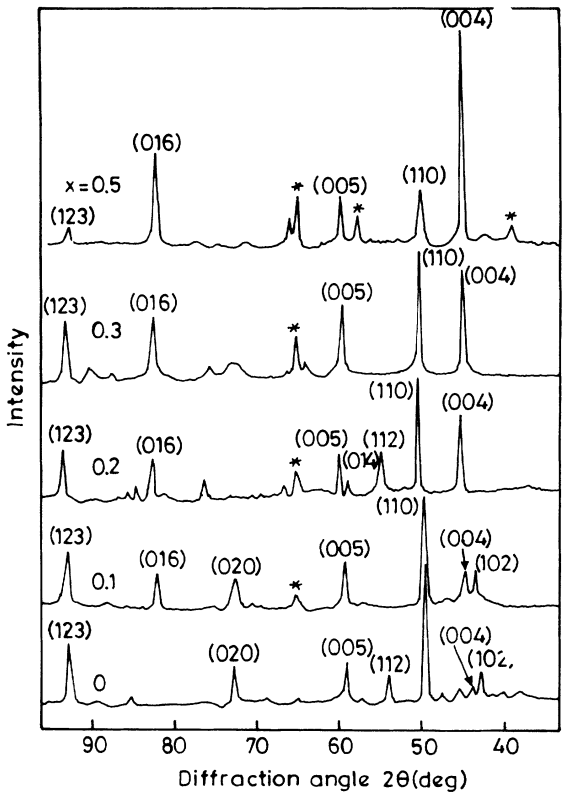

FIG. 1. X-ray diffractograms of $YBa_{2-x}Bi_xCu_3O_{7-\delta}$ (recorded using Cr $K\alpha$ radiation). (*) These peaks are not assigned firmly.

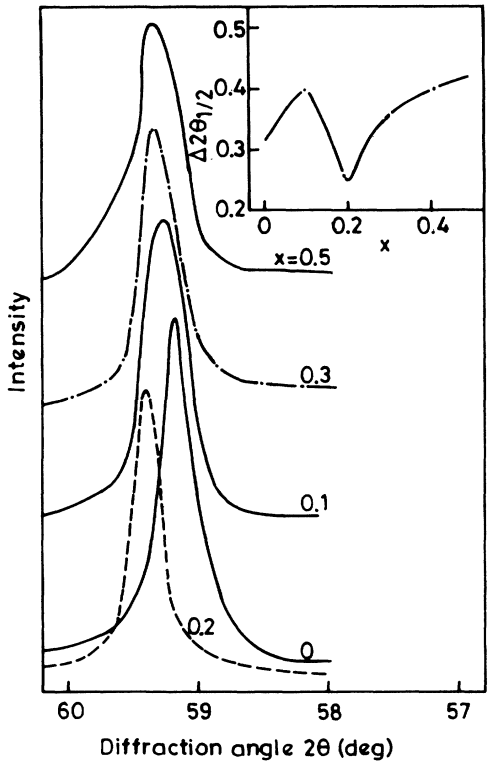

FIG. 2. Effect of bismuth (x) addition on (005) diffraction peak of $YBa_{2-x}Bi_xCu_3O_{7-\delta}$ (orthorhombic crystal structure), variation of half-bandwidth ($\Delta 2\theta_{1/2}$) shown in the inset.

The compositions processed with Bi_2O_3, especially those with $x=0.2$ and 0.3, exhibit characteristically sharp and symmetric diffraction lines. For example, Fig. 2 shows the diffractograms for the (005) peak record on an expanded scale. The figure in the inset gives a plot for the half-bandwidth ($\Delta 2\theta_{1/2}$) of this peak measured as a function of x. A minimum value of $\Delta 2\theta_{1/2}$ occurs for $x \sim 0.2$. It appears that the Bi^{3+} substitutes in $YBa_{2-x}Bi_xCu_3O_{7-\delta}$ crystals and activates the reaction, leading to eventually homogeneous and sharp size distribution of the crystallites, which contain reduced distortion or strain growth defects. The defects due to all these

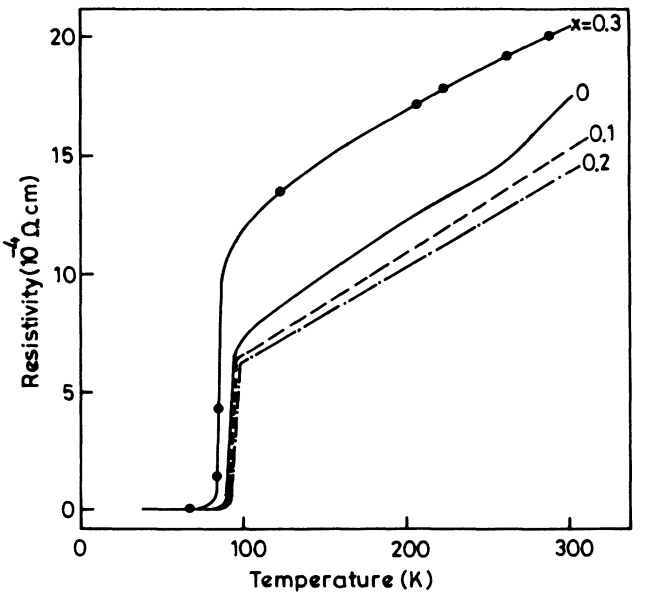

FIG. 3. Electrical resistivity plotted vs temperature for $YBa_{2-x}Bi_xCu_3O_{7-\delta}$.

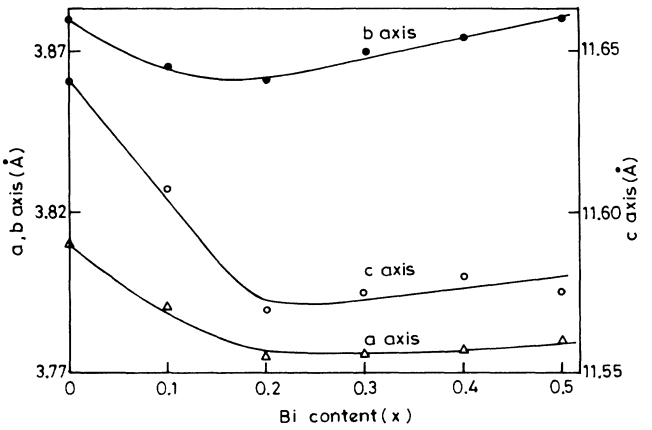

FIG. 4. Variation of the crystal lattice (orthorhombic) axes a, b, and c for $YBa_{2-x}Bi_xCu_3O_{7-\delta}$ with x.

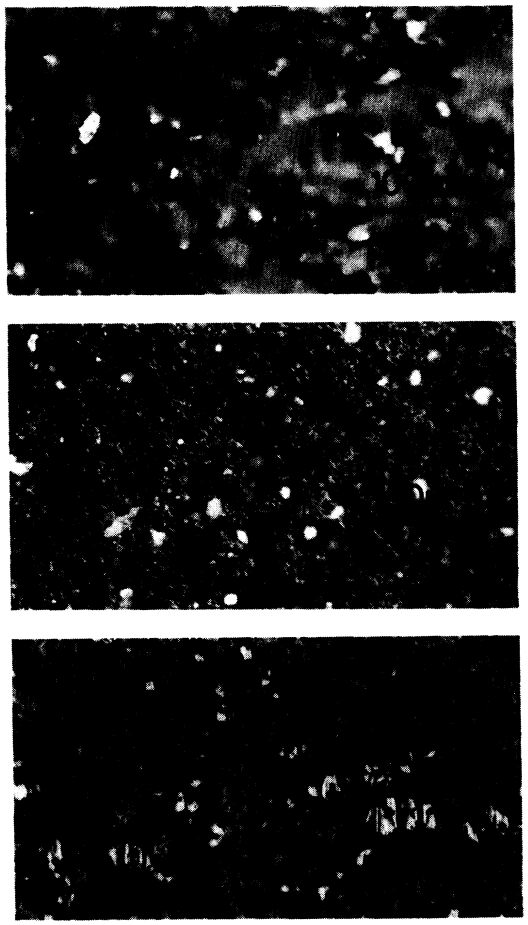

FIG. 5. Microstructures of $YBa_{2-x}Bi_xCu_3O_{7-\delta}$ samples (a) $x=0$, (b) 0.1, and (c) 0.2.

factors cause broadening in diffraction peaks. An asymmetry in the (005) peak observed for samples with $x=0$ or 0.5 reflects large variation in the grain size consistent with the microstructure. The results of resistivity are summarized in Fig. 3. The samples with $x \leq 0.2$ reveal an improved onset temperature around 100 K and the resistivity vanishes at ~ 94 K. A $T_c \sim 97$ K is obtained as the mean value of the temperatures at these points for a sample of $x \sim 0.2$. $YBa_2Cu_3O_{7-\delta}$ ($x=0$) prepared under the same condition gives a somewhat lower $T_c \sim 91$ K.[1,6]

Growth of comparatively pure and perfect crystallites of $YBa_{2-x}Bi_xCu_3O_{7-\delta}$ seems a reasonable cause for the improved T_c. The crystal structure (orthorhombic[4]) is not modified much by the addition of bismuth; however, the crystal axes decrease (Fig. 4) considerably, showing the optimum effects for $x \leq 0.2$. It is likely due to the smaller ionic size of Bi^{3+} (0.96 Å) substituting for the Ba^{2+} (1.34 Å).

More convincing and direct effects of the Bi_2O_3 addition are demonstrated by the microstructure shown in Fig. 5. The distinct and well-separated crystals of $YBa_{2-x}Bi_xCu_3O_{7-\delta}$ with effectively small sizes (cf. Table I) and a very much sharper distribution were obtained after the use of the additives. Moreover, the samples with $x \leq 0.1$ contain a considerable amount of impurities (probably copper oxide[5]), showing characteristically intense reflected light in the micrographs, which are eliminated [cf. Fig. 5(c)] by adding $x \sim 0.2$ Bi_2O_3.

TABLE I. Grain size and T_c results for the $YBa_{2-x}Bi_xCu_3O_{7-\delta}$ superconductors.

Sample	Grain size[a] (μm)	T_c (K)
$x=0$	15	91
0.1	5	94
0.2	5	97
0.3	5	85
0.4 (or 0.5)	20	<77

[a]Grain size is reported for the average size.

ACKNOWLEDGMENTS

S. Ram is thankful to Professor G. P. Johari (at Canada) and Professor J. C. Joubert (at Grenoble, France) for personal discussions and allowing us to utilize their laboratory facilities.

*Present address: LMGP, UA 1109, ENSPG, Domaine Universitaire, BP 46, 38402, Saint Martin d'Hères, Grenoble, France.

[1]J. Jung, J. P. Franck, W. A. Miner, and M. A. K. Mohamed, Phys. Rev. B **37**, 7510 (1988).

[2]Z. Iqbal, H. Eckhard, F. Reidinger, A. Bose, J. C. Barry, and B. L. Ramakrishna, Phys. Rev. B **38**, 859 (1988).

[3]S. Ram, J. Magn. Magn. Mater. **80**, 241 (1989); **82**, 129 (1989).

[4]E. T. Muromachi, Y. Uchida, Y. Matsui, and K. Kato, Jpn. J. Appl. Phys. **26**, L476 (1987); **26**, 619 (1987).

[5]B. Kumar, R. S. Hamer, T. N. Wittberg, and S. K. Cordonnie, J. Mater. Sci. **23**, 3879 (1988).

[6]R. Bartucci, E. Colavita, L. Sportelli, G. Balestrino, and S. Barbanera, Phys. Rev. B **37**, 2313 (1988).

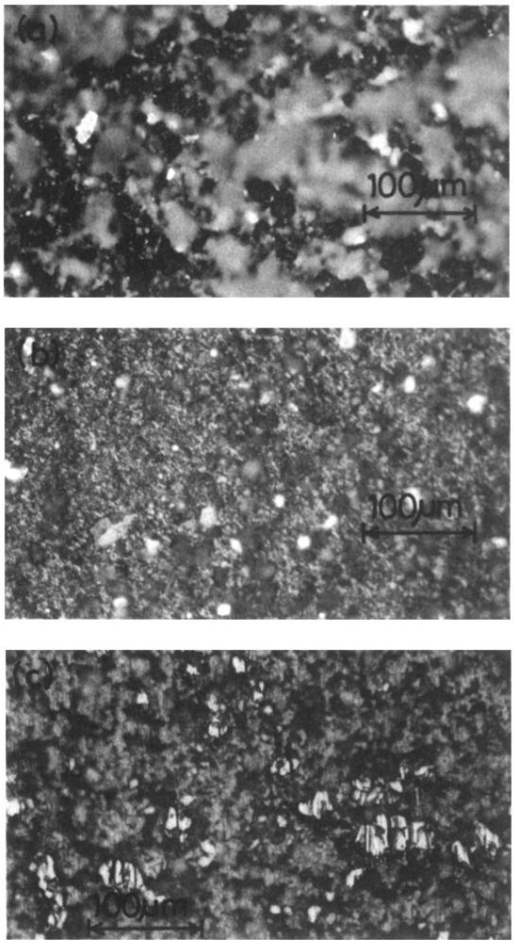

FIG. 5. Microstructures of $YBa_{2-x}Bi_xCu_3O_{7-\delta}$ samples (a) $x=0$, (b) 0.1, and (c) 0.2.